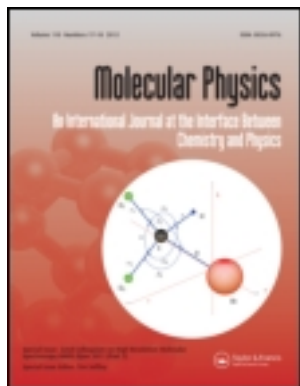


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INVITED ARTICLE

Deformation of the benzene ring upon fluorination: equilibrium structures of all fluorobenzenes

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Born–Oppenheimer equilibrium structure (r_e^{BO}) estimates are reported for benzene and all 12 possible fluorobenzenes, based on geometry optimizations performed at the coupled cluster level of electronic structure theory including single and double excitations augmented by a perturbational estimate of the effects of connected triple excitations [CCSD(T)] and Gaussian basis sets of at least triple zeta quality. Furthermore, accurate semiexperimental equilibrium (r_e^{SE}) structures are determined for C_6H_6 , $\text{C}_6\text{H}_5\text{F}$, and 1,2- and 1,3-difluorobenzene. They are obtained through a least-squares structural refinement procedure based on equilibrium rotational constants of as many isotopologues as feasible, determined by correcting experimental vibrationally averaged ground-state rotational constants with computed *ab initio* vibration–rotation interaction constants and electronic g -factors, and using a few structural constraints based on the best r_e^{BO} estimates. The r_e^{BO} and r_e^{SE} equilibrium structures are in excellent agreement with each other for the four semirigid molecules but in almost all cases they differ significantly from previously determined equilibrium structure estimates based on rotational spectroscopy or gas electron diffraction. The nature of deformations of the benzene ring induced by a single fluorine substitution can be characterized as follows: (a) the strongest effect is the pushing of the ipso carbon atom toward the ring center resulting in a deformation at the ipso [by $+2.7(1)^\circ$] and ortho [$-1.7(1)^\circ$] CCC angles, (b) a simultaneous decrease in the ortho CC bond length of the benzene ring by 0.009 \AA and (c) a decrease of all the CH bond lengths. Additivity relations concerning the F substitution effects are obtained based on the equilibrium structures of all possible fluorobenzenes.

Keywords: *ab initio*; fluorobenzene; equilibrium structures; semiexperimental structure; ring distortions; spectroscopic constants; structural refinement

1. Introduction

One of the unique concepts of chemistry is the assumed existence of functional groups and their subsequent use in the prediction and interpretation of molecular properties. It is also widely appreciated that structure determines function and thus determination of the structure of compounds in all three phases occupies a central role in our understanding of molecular phenomena. Substituents are special among functional groups and thus understanding substituent effects on chemical and physical properties, including the (equilibrium) structures of molecules, has a wide appeal. The structural distortions caused by substituents are usually relatively small and thus their experimental and/or theoretical determination is not without difficulty. These studies also require a suitable reference compound for which accurate reference structural parameters are available. For this and for other reasons as well, substituent effects in the gas phase have been studied extensively, both experimentally and theoretically [1–20], during the last almost half of a century using the highly symmetric and relatively rigid benzene molecule as a reference. Several book chapters have been written on this topic [21]. The fluorobenzene

derivatives considered in this study are formed by replacing H atoms of the benzene ring with F atoms. Among the substituent effects of most practical interest are deformations of the benzene ring. Such ring distortions have first been revealed for phenylsilane [1], $\text{C}_6\text{H}_5\text{—SiH}_3$, where, for example, the distortion of the ipso CCC_i bond angle, also called α (see Figure 1) was as much as 2.6° .

The angular changes in the geometry of the benzene ring are efficient indicators for the interaction between the substituents (an atom or a group) and the benzene ring. The changes caused by the substitution can be evaluated either at the level of rovibrationally averaged structural parameters or at the level of equilibrium parameters. Since these changes are quite small, it is clearly preferable to determine the extent of distortions using equilibrium structural information, devoid of averaging and temperature effects. Among the structural parameters the most representative values are the variations of the ipso (CCC_i) and ortho (CCC_o = β) CCC angles, and the lengths of the CC, CH and CF bonds (abbreviated as o = ortho, m = meta and p = para in Figure 1). The CCC_i angle may vary in a relatively large interval and, similarly to other parameters, its value depends

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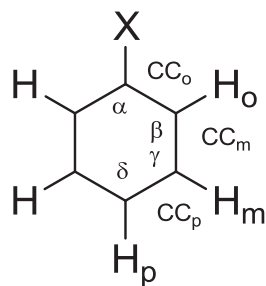


Figure 1. Labeling of CCC bond angles and CC and CH bonds in fluorobenzene, C_6H_5F , and in other fluorinated benzenes investigated. $\alpha \equiv CCC_i$, $\beta \equiv CCC_o$, $\gamma \equiv CCC_m$, $\delta \equiv CCC_p$ (i = ipso, o = ortho, m = meta, and p = para).

mainly on the electronegativity (EN) of the substituent and on inductive, resonance, and steric interactions between the substituent and the ring.

The high accuracy needed during the determination of the equilibrium structures of substituted benzenes requires a very careful analysis of the different factors governing the accuracy of the r_e^{SE} and r_e^{BO} structure determinations. As to the joint experimental and theoretical r_e^{SE} structures, the following factors are investigated carefully during the present study: (a) the true uncertainties of the experimental ground-state rotational constants, as even small inconsistencies affect the structures derived considerably; (b) the contribution of electronic g -factors to the derived equilibrium rotational constants, as these small contributions are often neglected while they could be important; (c) the effect the accuracy of the computed anharmonic force field [22] plays during deduction of equilibrium rotational constants and (d) weighting and conditioning and the use of predicate observations during the least-squares structural refinement procedure. As to the r_e^{BO} structures, we performed geometry optimization at the highest feasible level of electron correlation treatment, CCSD(T) [23] using the cc-pCVTZ atom-centered, fixed-exponent, correlation-consistent Gaussian basis set [24] and investigated problems associated with use of finite basis sets. As far as we know, apart from the small molecule H_2O [25], such detailed investigation of all these factors simultaneously has only been performed before during the determination of the equilibrium structures of the lowest-energy conformers of α -alanine [26]. Apart from somewhat extreme cases [27,28], the single-reference CCSD(T) technique with basis sets starting at the triple-zeta level provides accurate estimates of r_e^{BO} structures as shown, for example, by the extensive studies of Helgaker and co-workers [29–32].

2. Computational details

Three distinct levels of electronic structure theory have been used in this study: second-order Møller–Plesset perturbation theory (MP2) [33], coupled cluster theory in-

cluding single and double excitations (CCSD) [34] augmented with a perturbational estimate of the effects of connected triple excitations, CCSD(T) [23], and Kohn–Sham density functional theory (DFT) [35] using Becke’s three-parameter hybrid exchange functional [36] and the Lee–Yang–Parr correlation functional [37], together denoted as B3LYP. The *ab initio* and DFT geometry optimizations performed at the levels described yield estimates of r_e^{BO} .

For the CCSD(T) and MP2 electronic structure computations several basis sets were employed: (a) the correlation-consistent polarized double-zeta, triple-zeta, and quadruple-zeta basis sets cc-pVDZ, cc-pVTZ and cc-pVQZ [38] which are abbreviated as VDZ, VTZ and VQZ, respectively, throughout this paper; (b) the core-valence cc-pCVTZ basis, denoted here as CVTZ; (c) the correlation-consistent polarized weighted core-valence triple zeta and quadruple zeta basis sets (abbreviated here as wCVTZ and wCVQZ, respectively) [24,39] which are used to improve the computed structure by the inclusion of core correlation effects [40] and (d) a version of the VQZ set augmented with diffuse functions (aug-cc-pVQZ, AVQZ in short) [41]. B3LYP computations were also performed with the split-valence basis sets 6-31G and 6-311G including appropriate diffuse and polarization functions, as implemented in Gaussian03 [42].

The CCSD(T) computations, including geometry optimizations employing analytic first derivatives [43], were performed with the CFOUR [44] electronic structure program package, while the lower-level B3LYP and MP2 computations utilized the Gaussian03 program suite [42]. The frozen-core approximation (hereafter denoted as FC), i.e. keeping the 1s orbitals of the second-row atoms doubly occupied during correlated-level calculations, was used at the MP2 and CCSD(T) levels, and all-electron (AE) wCVTZ MP2 and CCSD(T) as well as wCVQZ MP2 computations were also performed to gauge the effect of core correlation on the structural parameters.

To correct the effective experimental rotational constants for each isotopologue and to obtain their equilibrium counterparts, quartic force field computations were performed at the optimized structures at the following levels: 6-31G* B3LYP, 6-311G(2d,2p) B3LYP, 6-311 + G(3df,2pd) B3LYP, 6-31G* MP2(FC) and VTZ MP2(FC) using the appropriate features of the electronic structure program package Gaussian03 [42].

3. The least-squares method of structure refinement

The linear least-squares method is well known and presented in many textbooks [45,46]. There are, however, a few important details, which are worth discussing here in order to understand the true accuracy of the r_e^{SE} structures determined via least-squares refinements.

3.1. Weighting

When the equilibrium values of internal coordinates are calculated from the moments of inertia by the least-squares method, a non-weighted fit is often performed. This is not correct because the accuracy of the different rotational constants is rarely the same. In particular, the A constants have usually a considerably larger uncertainty than the others. Another common practice is to use the inverse of the square of the experimental uncertainty of the ground-state constants as weights. This is again not fully correct. There is indeed no direct relationship between the errors of the ground-state constants and those of the equilibrium ones. Furthermore, it often happens that the constants of the parent species are determined with a much higher precision. The consequence is that these constants are ‘leverage points’, the fit becomes unbalanced, and the leverage points have the potential of strongly affecting the structural results.

One way to circumvent these difficulties is to use the iteratively reweighted least squares (IRLS) method, whereby data with large residuals are weighted down. Two different weighting schemes are used in the present work. They both make use of the mean absolute deviation (MAD) of the residuals $e_i = I_i(\text{exp}) - I_i(\text{calc})$, where I_i is the i th moment of inertia and

$$\text{MAD}(e_i) = \text{median}|e_i - \text{median}(e_i)|. \quad (1)$$

From the MAD, a robust estimation of the standard deviation may be derived,

$$s = \text{MAD}/0.6745. \quad (2)$$

In Huber’s weighting scheme, the weight w_i is given by

$$\begin{aligned} |e_i| < 2\text{MAD} & \quad w_i = 1 \\ |e_i| \geq 2\text{MAD} & \quad w_i = 1.345/(|e_i|/s). \end{aligned} \quad (3)$$

In the biweight weighting,

$$\begin{aligned} |e_i|/s \leq 4.685 & \quad w_i = [1 - [(e_i/s)/4.685]^2]^2 \\ |e_i|/s > 4.685 & \quad w_i = 0. \end{aligned} \quad (4)$$

Of course, after an IRLS fit, it is advisable to check that the final weights are compatible with the estimated uncertainties of the input data. In particular, the uncertainty of the equilibrium constants cannot be smaller than the uncertainty of the ground-state constants.

3.2. Conditioning

During a structure determination by the least-squares method, it is common to encounter the problem of ill-conditioning, whereby some parameters are very sensitive to small perturbations of the data. This is due to the fact that the number or the variety of the data is not large enough.

Conditioning becomes particularly important during determination of an r_e^{SE} structure when some isotopologues are not available or when some atoms are close to a principal axis. Furthermore, isotopic substitution generally leads to a very small change of the moments of inertia, which is not favorable for an accurate structure determination. Therefore, it is useful to have a reliable diagnostic allowing the determination of parameters affected the most by ill-conditioning.

Belsley [47] advocated the use of the variance-decomposition proportions (VDP) for this purpose. The VDPs are numbers between zero and one. When the least-squares system of normal equations is solved by means of the singular value decomposition (SVD) of the design matrix, the variance of any parameter is found to be a sum of p components (p is the number of parameters) with the squared singular values μ_j^2 as denominators. The component associated with the smallest singular value μ_j (or largest condition index μ_{max}/μ_j , also called condition number) will hence account for the largest proportion of the variance. High variance proportions for two (or more) parameters provide evidence that these two (or more) parameters are involved in a near dependency. Belsley suggested that a degrading collinearity is present when for a condition index larger than 30 the associated VDP for two or more structure variables is larger than 0.5. When a near-dependency between two variables is so high as to leading to unreliable values, the only solution is to keep these variables fixed at a reasonable value or, better, to import the value of these variables from another source. This may be done by using the mixed estimation method, where auxiliary information is added directly to the data matrix during the least-squares fit [48]. This auxiliary information, usually called predicate observations, consists of carefully chosen values for the internal coordinates, together with their corresponding uncertainties.

4. Equilibrium structures of benzene, C_6H_6

The structure of the benzene molecule in its ground electronic state provides the reference CC and CH bond lengths for the investigation of the substituent effects of F; thus, these parameters should be known as reliably as possible.

Benzene has been investigated by many experimental and theoretical techniques confirming that benzene is a symmetric-top molecule and its equilibrium structure has D_{6h} point-group symmetry. Note that certain Gaussian basis sets yield lower-symmetry structures [49] but this is just an artifact and should not be considered here further. Somewhat surprisingly, very few papers are devoted to an accurate determination of the equilibrium structure of benzene. In 1991, Plíva *et al.* [50] estimated a structure from the B_0 ground-state rotational constants of the symmetric isotopologues $^{12}\text{C}_6\text{H}_6$, $^{13}\text{C}_6\text{H}_6$, $^{12}\text{C}_6\text{D}_6$, $^{13}\text{C}_6\text{D}_6$ and $^{12}\text{C}_6\text{H}_3\text{D}_3$. Using approximate corrections for the

rovibrational contribution, they found $r_e(\text{CC}) = 1.3902(2)$ and $r_e(\text{CH}) = 1.0862(15)$ Å. In 1997, Martin *et al.* [51] performed frozen-core VTZ CCSD(T) computations and, after a small empirical correction, found $r_e^{\text{BO}}(\text{CC}) = 1.3918(20)$ and $r_e^{\text{BO}}(\text{CH}) = 1.0813(10)$ Å. In 2000, Gauss and Stanton [52] determined an r_e^{SE} structure for benzene using the ground-state rotational constants of the same four D_{6h} -symmetry isotopologues as employed by Pliva *et al.* [50] and an *ab initio* cubic force field computed at the frozen-core VTZ MP4(SDQ) level, with $r_e^{\text{SE}}(\text{CC}) = 1.3914(10)$ and $r_e^{\text{SE}}(\text{CH}) = 1.0802(20)$ Å. In this structure determination, the electronic g -factor correction was neglected. It is indeed often assumed that this effect on equilibrium structures is negligible. However, this assumption is not always correct. For example, the correction is as large as 37 MHz for the A rotational constant of ozone [53]. Furthermore, in the case of the SiC_3 cyclic isomers the rather large residual equilibrium inertial defect was found to be reduced significantly by inclusion of the electronic contribution [54], while for the diatomics BH and CH^+ inclusion of this correction led to changes in the bond distances of about 0.002 Å [55]. The assumption of Gauss and Stanton [52] has to be checked in the present case as for aromatic molecules ring currents may lead to a non-negligible correction [56]. The g -factor was computed at the 6-311 + G(3df,2pd) B3LYP level of theory with the help of the G03 program using London orbitals. The result is $g_{bb} = 0.0843$ [compare this with the experimental value of Ref. [57], $g_{aa} = 0.068(25)$]. With this value, the electronic correction [58] is only 0.26 MHz for the parent species, $^{12}\text{C}_6\text{H}_6$. This additional correction diminishes the residuals of the structural fit redone by us but does not significantly affect the structure determined, providing independent confirmation of the r_e^{SE} CC and CH bond lengths obtained by Gauss and Stanton. Gauss and Stanton also optimized the structure of benzene at the all-electron VQZ CCSD(T) level which is known to provide distances accurate to better than 0.003 Å [29]. All these results are reported in Table 1.

We recomputed the Born–Oppenheimer equilibrium structure (r_e^{BO}) of benzene at the all-electron CVTZ CCSD(T) level of electronic structure theory and the effect of further basis set enlargement, CVTZ \rightarrow wCVQZ, was estimated at the MP2 level. In other words, the r_e^{BO} parameters are obtained using the following equation:

$$r_e^{\text{BO}}(\text{I}) = \text{CVTZ CCSD(T)}_{\text{AE}} + \text{wCVQZ MP2(AE)} - \text{CVTZ MP2(AE)}. \quad (5)$$

It is worth noting that the correction due to basis set enlargement is rather small, the CC bond length decreases by about 0.003 Å, while the CH bond length decreases by 0.001 Å. These small corrections give us confidence in the accuracy of the $r_e^{\text{BO}}(\text{I})$ structure. As a further check, the structure was also computed at the wCVQZ CCSD(T)_{AE}

Table 1. Born–Oppenheimer equilibrium structures, r_e^{BO} , of benzene (all bond lengths in Å), all electronic structure computations reported, unless noted otherwise, correlated all the electrons explicitly.

Method	Basis set	$r(\text{CC})$	$r(\text{CH})$
r_e^{SE} ^a		1.3914(10)	1.0802(20)
CCSD(T) ^a	VTZ	1.3917	1.0778
CCSD(T)	CVTZ	1.3944	1.0821
CCSD(T) ^b	VQZ	1.3911	1.0800
CCSD(T) ^c	wCVQZ	1.3916	1.0811
MP2	VTZ	1.3880	1.0766
MP2	CVTZ	1.3903	1.0803
MP2	wCVQZ	1.3876	1.0792
$r_e^{\text{BO}}(\text{I})$ ^d		1.3918	1.0810
$r_e^{\text{BO}}(\text{II})$ ^e		1.3913	1.0804
B3LYP	6-311 + G (3df,2pd)	1.3909	1.0818

^aThe corresponding frozen-core VTZ CCSD(T) results are $r(\text{CC}) = 1.3975$ and $r(\text{CH}) = 1.0831$ Å.

^bRef. [52], confirmed during this study using analytic gradients.

^cThe all-electron cc-pCVQZ CCSD(T) optimized parameters are $r(\text{CC}) = 1.3918$ and $r(\text{CH}) = 1.0811$ Å.

^dSee Equation (5).

^eSee Equation (6).

level of theory, see Table 1. The results are in pleasing agreement with those of Equation (5).

Then, the r_e^{BO} structure was computed at the all-electron VTZ CCSD(T) level and the effect of further basis set enlargement VTZ \rightarrow wCVQZ was estimated at the MP2 level. This gives another estimate of the equilibrium structure, $r_e^{\text{BO}}(\text{II})$,

$$r_e^{\text{BO}}(\text{II}) = \text{VTZ CCSD(T)}_{\text{AE}} + \text{wCVQZ MP2(AE)} - \text{VTZ MP2(AE)}. \quad (6)$$

Here, the correction due to basis set enlargement is quite small, being noticeable only for the CH bond length, which is increased by about 0.003 Å and thus approaches the best r_e^{BO} estimate. The results obtained and shown in Table 1 are in perfect agreement with the r_e^{BO} and r_e^{SE} structures of Gauss and Stanton [52].

Finally, r_e^{BO} was also estimated at the 6-311 + G(3df,2pd) B3LYP level of theory. The results are given in Table 1. The CC bond length is well reproduced but the CH bond length is too long by 0.0015 Å.

The structure of benzene is completely defined by only two parameters, for example the CC and CH bond lengths, whereas ground-state rotational constants are available for nine isotopologues. It is an almost ideal case to check the accuracy of the empirical structures, particularly the mass-dependent ones [59]. The results are given in Table 2. In this particular case, the $r_m^{(2)}$ structure, with $r(\text{CC}) = 1.3911(5)$ and $r(\text{CH}) = 1.0813(1)$ Å, is extremely close to the best r_e^{BO} structure given in Table 1. On the other hand, the purely empirical structures, the effective r_0 and the substitution

Table 2. Empirical structures of benzene (all bond lengths in Å).

	$r(\text{CC})$	$r(\text{CH})$	σ^a
r_0	1.3970(1)	1.0818(10)	179
r_s	1.3938(9)	1.0833(9)	19.6
$r_m^{(1)}$	1.3918(7)	1.0812(2)	10.2
$r_m^{(2)}$	1.3913(7)	1.0813(1)	8.40

^aStandard deviation of the weighted fit, $\sigma = \frac{1}{n-p} \sum_i \frac{r_i^2}{s_i^2}$, where r_i is the residual of the i th data, s_i is its uncertainty, n is the number of data and p the number of parameters (for a perfect fit, $\sigma = 1$).

r_s , are poor approximations of the equilibrium structure of benzene, although the standard deviations of the fitted parameters are unreasonably small.

In summary, highly dependable r_e^{BO} and r_e^{SE} $r_e(\text{CC})$ and $r_e(\text{CH})$ equilibrium structural parameters are available for benzene, anchoring firmly the reference values for the present study.

5. Equilibrium structures of fluorobenzene, $\text{C}_6\text{H}_5\text{F}$

Fluorobenzene (PhF) is a singly substituted benzene whose equilibrium structure is of point-group symmetry C_{2v} . Among the seven distance- and angle-type internal coordinates presented in Figure 1 for the ring there exist two geometric constraints: $\alpha/2 + \beta + \gamma + \delta/2 - 2\pi = 0$ and $\text{CC}_o \sin(\alpha/2) + \text{CC}_m \sin(\beta + \alpha/2 - \pi) - \text{CC}_p \sin(\delta/2) = 0$. Thus, five independent parameters are required to describe the structure of the ring and the complete equilibrium structure of PhF is defined by eleven independent structural variables.

The microwave (MW) spectrum of PhF has been investigated repeatedly [2,16,60–62], the first study being almost 60 years old. The rotational spectra of many dimers involving PhF have also been measured [63]. A complete substitution (r_s) structure of PhF was determined in 1968 [2]. Quite recently, an empirical, effective r_0 structure was also determined [16]. In the same work, a mass-dependent $r_m^{(1)}$ structure was calculated. In this structure determination technique, using only ground-state rotational constants, the variation of the rovibrational contribution is approximately taken into account by three extra parameters [59,64]. It is interesting to note that the r_0 structure, which is often assumed to be a good approximation of the equilibrium structure, provides an *ipso* CCC angle, $\alpha \equiv \text{CCC}_i$, of $123.12(18)^\circ$. The structural refinement within a gas-phase electron diffraction (GED) study [65] of PhF was performed in a way allowing an approximate determination of all the inner-ring angles. These angles were also obtained via a nuclear magnetic resonance (NMR) study in a nematic phase [66]. The structural distortions observed during the GED and NMR studies are in good agreement with the r_s structure and point out a significant angular distortion of the benzene ring caused by the F atom. In particular, the CCC_i

angle was found to be $123.4(2)^\circ$. It is also worth mentioning that the geometrical structure of PhF was investigated a long time ago by introductory *ab initio* electronic structure computations [13,67], indicating considerably smaller distortions of the benzene ring (see, for example, table 4 of Ref. [13]). As it turns out the introductory computational results provide a more accurate representation of the angular and bond length distortions of the ring in PhF than the previous interpretations of the MW, GED and NMR experimental results.

5.1. *Ab initio Born–Oppenheimer equilibrium structure, r_e^{BO}*

Estimates to the r_e^{BO} structure of PhF were computed as for benzene, using Equations (5) and (6). As to the $r_e^{\text{BO}}(\text{I})$ structure of PhF, it is worth noting that the corrections due to basis set enlargement are rather small and, as for benzene, the CC bond lengths decrease by about 0.003 Å, the CH bond lengths decrease by 0.001 Å, while the CF bond length remains almost unchanged. Only CCC_i is affected slightly by this correction, its value is increased by 0.14° . These small corrections give us confidence in the accuracy of the $r_e^{\text{BO}}(\text{I})$ structure. As to the $r_e^{\text{BO}}(\text{II})$ structure, the corrections due to basis set enlargement are quite small, being noticeable only for the CH bond lengths, which are increased by about 0.003 Å. The r_e^{BO} of PhF was also estimated at the much more approximate 6-311 + G(3df,2pd) B3LYP level of theory. The results of all these optimizations are given in Table 3. The $r_e^{\text{BO}}(\text{I})$ and $r_e^{\text{BO}}(\text{II})$ structures are almost identical, the largest difference is only 0.0006 Å for the $r(\text{CH}_o)$ bond length. The agreement between $r_e^{\text{BO}}(\text{I})$ and VTZ CCSD(T)_AE is also quite good with the exception of the CH bond lengths, which are shorter by about 0.0033 Å at the VTZ CCSD(T)_AE level. Finally, the 6-311 + G(3df,2pd) B3LYP structure is in good agreement with $r_e^{\text{BO}}(\text{I})$, except for the $r(\text{CF})$ bond length, which is longer at the B3LYP level by a significant 0.0066 Å.

Because the F atom has high EN, the effect of adding diffuse functions to the basis set must also be investigated. For this purpose, the MP2 method was used together with the AVQZ basis set. The results are given in Table S1 of the Supplementary Material. As expected, the largest change is found for the $r_e(\text{CF})$ bond length, which increases by 0.00016 Å when going from VQZ to AVQZ. The *ipso* CCC angle is decreased by 0.11° . These small changes are of the same order of magnitude as the expected accuracy of the r_e^{BO} structure estimates. Furthermore, the small effect of further basis set enlargement, VQZ \rightarrow V5Z, acts in the opposite direction, as it is generally observed when the variation with the size of the basis set is monotonous and in agreement with the effect of the VTZ \rightarrow VQZ enlargement. In conclusion, these corrections may be neglected even at the level of accuracy sought in this study.

Table 3. *Ab initio* estimates of the r_e^{BO} structure of fluorobenzene (distances, r , in Å, angles, \angle , in degrees).^a

Parameter	CCSD(T)_AE	MP2(AE)	CCSD(T)_AE	MP2(AE)	MP2(AE)	B3LYP	$r_e^{\text{BO}}(\text{I})^b$	$r_e^{\text{BO}}(\text{II})^c$
	VTZ	VTZ	CVTZ	CVTZ	wCVQZ	6-311 + G(3df,2pd)		
$r(\text{C}_1\text{-C}_2)\equiv\text{CC}_o$	1.3835	1.3802	1.3861	1.3829	1.3800	1.3833	1.3832	1.3832
$r(\text{C}_2\text{-C}_3)\equiv\text{CC}_m$	1.3910	1.3873	1.3940	1.3897	1.3872	1.3906	1.3915	1.3910
$r(\text{C}_3\text{-C}_4)\equiv\text{CC}_p$	1.3916	1.3880	1.3942	1.3901	1.3874	1.3908	1.3916	1.3911
$r(\text{C}_2\text{-H})\equiv\text{CH}_o$	1.0759	1.0749	1.0807	1.0791	1.0780	1.0804	1.0796	1.0790
$r(\text{C}_3\text{-H})\equiv\text{CH}_m$	1.0774	1.0761	1.0817	1.0799	1.0788	1.0815	1.0805	1.0800
$r(\text{C}_4\text{-H})\equiv\text{CH}_p$	1.0768	1.0756	1.0812	1.0794	1.0783	1.0808	1.0801	1.0796
$r(\text{C-F})$	1.3433	1.3427	1.3439	1.3431	1.3428	1.3502	1.3436	1.3435
$\angle(\text{C}_2\text{C}_1\text{C}_6)\equiv\text{CCC}_i$	122.37	122.25	122.34	122.22	122.37	122.54	122.48	122.49
$\angle(\text{C}_1\text{C}_2\text{C}_3)\equiv\text{CCC}_o$	118.48	118.56	118.48	118.56	118.47	118.30	118.39	118.39
$\angle(\text{C}_2\text{C}_3\text{C}_4)\equiv\text{CCC}_m$	120.43	120.40	120.45	120.41	120.41	120.57	120.45	120.45
$\angle(\text{C}_3\text{C}_4\text{C}_5)\equiv\text{CCC}_p$	119.81	119.84	119.81	119.83	119.87	119.72	119.84	119.84
$\angle(\text{C}_1\text{C}_2\text{H}_2)$	119.59	119.52	119.65	119.57	119.62	119.82	119.69	119.69
$\angle(\text{C}_4\text{C}_3\text{H}_3)$	120.11	120.15	120.12	120.16	120.15	120.06	120.11	120.11

^ai = ipso, o = ortho, m = meta, and p = para. See also Figure 1.

^b $r_e^{\text{BO}}(\text{I}) = \text{CVTZ CCSD(T_AE)} + \text{wCVQZ MP2(AE)} - \text{CVTZ MP2(AE)}$.

^c $r_e^{\text{BO}}(\text{II}) = \text{VTZ CCSD(T_AE)} + \text{wCVQZ MP2(AE)} - \text{VTZ MP2(AE)}$.

5.2. Anharmonic force field

To check the reliability of the *ab initio* anharmonic force fields employed for the structure analysis, the quartic force field of the parent species was computed at the B3LYP level with three different basis sets, 6-31G*, 6-311(2d,2p) and 6-311 + G(3df,2pd), and at the MP2 level with the 6-31G* and VTZ basis sets. The B3LYP functional of DFT theory was chosen since it is now well established that for simple semirigid molecules this semiempirical level of electronic structure theory gives results comparable or even superior to the MP2 method at a much lower cost [68,69] (a notable exception is when dispersion forces are not negligible as, for instance, in van der Waals complexes). All B3LYP computations were made with an ‘ultrafine’ grid (pruned (99,590) grid). As a check, the 6-311 + G(3df,2pd) B3LYP computation was repeated with a ‘fine’ grid (pruned (75,302) grid). No significant differences were found. Parameters of the optimized structures obtained at the B3LYP and MP2 levels are reported in Table S2 of the Supplementary Material. Compared to the $r_e^{\text{BO}}(\text{I})$ structure, the structures computed with the 6-31G* basis set are of poor quality, the 6-311G(2d,2p) B3LYP structure is reasonable for the bond lengths, whereas the VTZ MP2(FC) structure gives accurate bond angles. However, the most accurate structure seems to be the 6-311 + G(3df,2pd) B3LYP structure, which is quite close to the $r_e^{\text{BO}}(\text{I})$ one, except for the $r(\text{CF})$ bond length which is too long by a substantial 0.007 Å.

The theoretical lowest-order vibration–rotation interaction constants (the so-called α -constants) deduced from the *ab initio* cubic force fields were combined with the known experimental ground-state rotational constants to yield, within second-order vibration–rotation perturbation theory (VPT2) [70,71], semiexperimental equilibrium rotational constants, which were also corrected for the electronic contribution [72]. The g constants needed to deter-

Table 4. Equilibrium inertial defect, Δ_e ($\text{u}\text{\AA}^2$), of fluorobenzene calculated with various force fields.

Method	Basis set	Δ_e^a	$\Delta_e(\text{corr})^b$
B3LYP	6-31G*	−0.0116	+0.0002
B3LYP	6-311 + G(3df,2pd) ^c	−0.0124	−0.0006
B3LYP	6-311 + G(3df,2pd) ^d	−0.0125	−0.0007
B3LYP	6-311G(2d,2p)	−0.0141	−0.0023
MP2	6-31G*	0.0160	+0.0278
MP2	VTZ	−0.0107	+0.0011

^aWithout electronic correction.

^bWith electronic correction.

^cUltrafine grid.

^dFine grid.

mine this effect are known for PhF experimentally [73]. The corrected rotational constants were used to calculate the equilibrium inertial defect,

$$\Delta_e = I_c^e - I_a^e - I_b^e, \quad (7)$$

which should be zero for a planar molecule such as fluorobenzene. The values obtained for the equilibrium inertial defect are reported in Table 4. As anticipated, the electronic correction is not negligible. The experimental ground-state inertial defect is $\Delta_0 = +0.0352 \text{ u}\text{\AA}^2$ for the parent species. After adding the rovibrational correction, computed at the 6-31G* B3LYP level, it becomes $-0.0116 \text{ u}\text{\AA}^2$, and after the electronic correction it is $\Delta_e = -0.0002 \text{ u}\text{\AA}^2$, *i.e.*, practically zero. Similar values are obtained for all isotopologues of PhF for which measured rotational constants are available. This observation confirms that the rovibrational correction is likely to be accurate and that the electronic correction, although small, is definitely not negligible in this case. Surprisingly, the seemingly best results are obtained at the 6-31G* B3LYP level of theory, the 6-311 + G(3df,2pd)

B3LYP results are slightly worse. The VTZ MP2(FC) result is actually even worse and the 6-31G* MP2(FC) results appear to be extremely inaccurate.

The experimental ground state and the computed equilibrium quartic centrifugal distortion constants are compared for the best three force fields in Table S3 of the Supplementary Material. Taking into account the fact that the difference between the ground-state and the equilibrium constants is expected to be a few percent, the agreement is satisfactory for the different levels of computation, although the 6-31G* B3LYP results seem to be slightly less accurate.

Table S4 of the Supplementary Material reports the computed vibration–rotation interaction constants α_i^X ($X = A, B, C$) for the lowest vibrational states of fluorobenzene and compares them with the available experimental data. The ν_{11} state at 248.6 cm^{-1} is the lowest-energy vibrational state of the semirigid PhF molecule and this normal mode is well isolated from the others. The agreement between the experimental and calculated constants is quite good for the different force fields. With the exception of the α_{16b}^A and α_{6a}^A constants, which are affected by a Coriolis interaction, the agreement is also good for the other states. However, it seems that the VTZ MP2(FC) constants are slightly less accurate.

A comparison between the computed and experimental vibrational fundamentals is difficult, as the vibrational spectrum is perturbed by many anharmonic resonances. However, the lowest fundamental wavenumbers below 1000 cm^{-1} can be safely compared. Table S5 of the Supplementary Material shows this comparison. These data were obtained from the computed harmonic wavenumbers ω_i and the corresponding anharmonicity corrections $\omega_i - \nu_i$ computed using the anharmonicity constants x_{ij} derived from the theoretical quartic force fields. Again, the VTZ MP2(FC) level yields the worst results and the 6-31G* B3LYP results are even better than the usually more reliable 6-311 + G(3df,2pd) B3LYP ones.

In conclusion, in the particular case of PhF, the 6-31G* B3LYP and the 6-311 + G(3df,2pd) B3LYP levels of electronic structure theory give the best results for the calculation of the force field up to quartic terms. In this particular case, the inertial defect is a good indicator of the quality of the harmonic part of the force field.

5.3. Semiexperimental equilibrium structure, r_e^{SE}

Ground-state rotational constants have been measured for nine isotopologues of PhF. The accurate constants of the parent species are taken from the millimeterwave investigation of the rotational spectrum [16], those of the monodeuterated species are from an accurate Fourier transform microwave (FTMW) spectroscopic work [62], the constants of the $^{13}\text{C}_p$ isotopologue are from another FTMW work [16], while the constants of the other ^{13}C species and the

trideuterated species are from an older microwave investigation [2]. These latter constants are the least accurate ones.

The anharmonic force fields of the nine isotopologues were computed at the 6-31G* B3LYP level (see Section 5.2 for a justification) and the corresponding semiexperimental equilibrium rotational constants are given in Table 5. From the values of the equilibrium inertial defects it appears that the rotational constant $A(^{13}\text{C}_i)$ is inaccurate.

The semiexperimental equilibrium structure, r_e^{SE} , was first calculated with the help of Kraitchman's equations [74]. The results are given in Table 6. Then, r_e^{SE} of PhF was determined using the least-squares method, first without weighting, then using the estimated weights, and, finally, using the IRLS method with Huber weighting and biweight weighting. The results are also given in Table 6. The residual of the $A(^{13}\text{C}_i)$ constant in the unweighted fit is quite large, indicating that this constant is probably determined inaccurately experimentally. This is in agreement with the large value of the inertial defect and it is confirmed by the IRLS fits, whereby both procedures weight this constant down, see the residuals in Table 5. The fits were repeated without the constants of the D_3 species, which are redundant, at least in theory, and which are, furthermore, less accurate than the constants of the D_1 species. As shown in Table 6, where only the results with Huber weighting is given, this omission significantly worsens the accuracy of the parameters. Indeed, the omission of the D_3 species increases the condition number from 1166 to 2339, indicating a problem of ill-conditioning. The results from Kraitchman's equations and from the least-squares fits are in good agreement and the standard deviation of the parameters is satisfactory. These results are also in excellent agreement with the best r_e^{BO} structure (Table 3).

Finally, it has to be noted that the $r_e^{\text{SE}}(\text{CF})$ and $r_e^{\text{SE}}(\text{CC}_m)$ bond lengths are less accurate. In the case of the CF bond length, it is due to the fact that there is no isotopic substitution available for the fluorine atom. The problem of the CC_m bond length is different, it is due to the fact that one of the Cartesian coordinates of the C_o atom is quite small, $a(\text{C}_o) = -0.1912(9) \text{ \AA}$, and therefore less accurate, see Table S6 of the Supplementary Material for a complete set of Cartesian coordinates. These two problems are at the origin of the relatively poor conditioning, as indicated by the rather large condition number, 1166, even when all isotopic species are included.

Next, the same procedure was repeated with an anharmonic force field calculated at the 6-311 + G(3df,2pd) B3LYP level of electronic structure theory. The semiexperimental equilibrium rotational constants are given in Table 5. These constants are significantly larger than the previous ones: by about 5.3 MHz for A , 1.4 MHz for B , and 1.2 MHz for C . Looking at the inertial defects, there is not much difference compared to the 6-31G* B3LYP force field results. For the parent species, after the rovibrational correction, the inertial defect is -0.0124 u\AA^2 , and after

Table 5. Ground-state and semiexperimental equilibrium rotational constants of fluorobenzene (MHz).

	N	$^{13}\text{C}_i$	$^{13}\text{C}_o$	$^{13}\text{C}_m$	$^{13}\text{C}_p$	2-D	3-D	4-D	2,4,6- D_3	
	A_0	5663.714	5663.780	5572.000	5574.690	5663.916	5390.623	5394.425	5663.552	5134.750
	B_0	2570.653	2561.281	2570.243	2551.758	2524.489	2562.815	2530.044	2459.775	2445.022
	C_0	1767.914	1763.517	1758.674	1750.245	1745.977	1736.805	1722.077	1714.770	1656.192
Ref. ^a	[16]	[2]	[2]	[2]	[16]	[62]	[62]	[62]	[62]	[16]
FF1 ^b	A_e	5705.684	5705.477	5613.101	5615.790	5706.420	5429.615	5433.556	5705.799	5171.226
	B_e	2584.324	2574.763	2583.845	2565.266	2537.898	2576.527	2543.501	2472.627	2457.980
	C_e	1778.686	1774.167	1769.356	1760.872	1756.544	1747.352	1732.500	1725.064	1666.079
	Δ_e^c	0.0002	-0.0053	0.0013	0.0040	0.0001	0.0000	0.0000	0.0000	-0.0021
^d	ΔA	-0.047	-0.254	0.054	0.121	-0.045	0.023	0.004	0.068	-0.047
	ΔB	-0.002	-0.009	0.005	0.013	0.004	0.005	0.000	-0.002	-0.011
	ΔC	-0.008	0.005	-0.001	-0.007	-0.002	0.005	0.000	0.005	0.002
FF2 ^c	A_e	5711.014	5710.802	5617.975	5621.368	5710.964	5433.874	5438.870	5710.979	5174.538
	B_e	2585.727	2576.186	2585.229	2566.708	2539.102	2577.870	2544.985	2473.777	2459.038
	C_e	1779.874	1775.361	1770.494	1762.103	1757.654	1748.415	1733.733	1726.101	1666.914
	Δ_e^c	-0.0006	-0.0059	0.0006	0.0035	-0.0008	-0.0007	-0.0007	-0.0007	-0.0030
^d	ΔA	-0.016	-0.228	0.059	0.105	-0.066	0.028	-0.010	-0.051	-0.072
	ΔB	-0.002	-0.016	-0.007	0.013	0.002	-0.005	-0.003	0.003	-0.011
	ΔC	0.001	0.007	-0.001	-0.005	0.000	0.005	0.001	0.000	0.004

^aReference for the ground state constants.

^bFrom the 6-31G* B3LYP cubic force field.

^cEquilibrium inertial defect.

^dResiduals (obs - calc) of the least-squares fit, Huber weighting.

^eFrom the 6-311 + G(3df,2pd) B3LYP cubic force field.

the electronic correction it becomes $\Delta_e = -0.0006 \text{ u}\text{\AA}^2$. The results of the fits are also given in Table 6. Again, the different weighting schemes give almost identical results. For the bond lengths, the two force fields give compatible results, those of the 6-311 + G(3df,2pd) B3LYP force field being slightly more accurate. On the other hand, there are significant differences for the bond angles, up to almost 0.5° for $\angle\text{CCC}_m$ and $\angle\text{CCC}_p$. It is important to determine which set of constants is more accurate. With the 6-311 + G(3df,2pd) B3LYP force field, the residuals of the fits are slightly smaller, as well as the standard deviations of the fitted parameters. Furthermore, the 6-311 + G(3df,2pd) B3LYP structure is closer to the r_e^{BO} structures, see Table 3. Thus, it seems that the r_e^{SE} structure derived from the 6-311 + G(3df,2pd) B3LYP force field should be more accurate. However, when comparing the r_e^{SE} structures of Tables 6 and 7 with the r_e^{BO} structure from Table 3, one arrives at the opposite conclusion. Furthermore, with the 6-311 + G(3df,2pd) B3LYP force field the angles γ and δ deviate too much from 120° , γ being too large and δ too small.

The condition number of the system of normal equations is rather large, indicating that the system is not well conditioned. It is useful to check whether the ill-conditioning is mainly responsible for the discrepancies of the bond angles. An inspection of the variance-decomposition proportions associated with the condition number indicates that two of them are potentially harmful, corresponding to the fitted parameters $r(\text{CC}_p)$ and $r(\text{CF})$, see Table S7 of the Supplementary Material. An easy way to

improve the conditioning is to use the method of predicate observations. First, the r_e^{BO} value of the CF bond length is added as predicate observation with a reasonable uncertainty of 0.002 \AA . This indeed decreases the condition number by a factor of two but does not significantly affect the values of the parameters, see Table S8 of the Supplementary Material. Increasing the weight of the predicate value (up to $\sigma = 0.0001 \text{ \AA}$) does not improve the situation. The same procedure was repeated by adding the r_e^{BO} value of the non-bonded C_1C_4 distance as a predicate observation, $r_e(\text{C}_1\text{C}_4) = 2.7544(20) \text{ \AA}$. Again, it does not significantly affect the values of the structural parameters. The conclusion is that the relatively poor conditioning does not explain the discrepancy of the bond angles and that the origin very likely lies in an inner incompatibility of the two force fields.

The standard deviations of the residuals of the fit are quite small: 76 kHz for A , 7 kHz for B and 7 kHz for C (Huber weighting, biweight gives slightly smaller values). Because of the small values of the residuals, the standard deviation of the parameters is also quite small. However, the error on the rotational constants is much larger than indicated by the standard deviations of the residuals. A statistical analysis of many results leads to the conclusion that the accuracy of the semiexperimental equilibrium rotational constants is a few percent (from 2% up to about 10%) of the rovibrational contributions [75]. Furthermore, comparing the two sets of semiexperimental constants, one may estimate that the error on A is a few MHz, and the errors on B and C are about one MHz. These errors, which are

Table 6. Semiexperimental structures of fluorobenzene (distances in Å, angles in degrees).

Method ^a	Kraitchman	Unweighted	Weighted	Huber	Biweight	Range	Without D ₃ ^b
6-31G* B3LYP force field							
$r(C_1-C_2) \equiv CC_0$	1.3840	1.3834(5)	1.3836(3)	1.38341(46)	1.38340(45)	0.0002	1.3826(19)
$r(C_2-C_3) \equiv CC_m$	1.3914	1.392(2)	1.3922(7)	1.3933(13)	1.3932(12)	0.0011	1.3943(40)
$r(C_3-C_4) \equiv CC_p$	1.3915	1.3910(4)	1.3913(2)	1.39096(36)	1.39099(35)	0.0004	1.39040(67)
$r(C_2-H) \equiv CH_0$	1.0784	1.0780(6)	1.0786(3)	1.07800(55)	1.07802(54)	0.0006	1.0779(17)
$r(C_3-H) \equiv CH_m$	1.0795	1.0798(4)	1.0797(2)	1.07986(31)	1.07984(30)	0.0002	1.087(13)
$r(C_4-H) \equiv CH_p$	1.0803	1.0801(3)	1.0802(1)	1.08011(27)	1.08011(26)	0.0001	1.08012(33)
$r(C-F)$	1.3441	1.3435(12)	1.3437(6)	1.3435(10)	1.3435(10)	0.0003	1.3431(28)
$\angle(C_2C_1C_6) \equiv CCC_i$	122.53	122.67(8)	122.60(4)	122.666(70)	122.664(68)	0.07	122.71(25)
$\angle(C_1C_2C_3) \equiv CCC_0$	118.36	118.27(5)	118.33(3)	118.269(46)	118.272(45)	0.06	118.24(12)
$\angle(C_2C_3C_4) \equiv CCC_m$	120.41	120.44(3)	120.42(2)	120.435(27)	120.433(26)	0.02	120.439(35)
$\angle(C_3C_4C_5) \equiv CCC_p$	119.93	119.93(4)	119.92(1)	119.927(30)	119.927(29)	0.01	119.924(37)
$\angle(C_1C_2H_2)$	119.69	119.81(8)	119.74(4)	119.808(69)	119.807(67)	0.07	119.87(29)
$\angle(C_4C_3H_3)$	120.16	120.19(4)	120.16(2)	120.195(36)	120.194(36)	0.03	120.27(96)
6-311 + G(3df,2pd) B3LYP force field							
$r(C_1-C_2) \equiv CC_0$		1.3836(5)	1.3835(5)	1.38355(44)	1.38352(38)	0.0000	
$r(C_2-C_3) \equiv CC_m$		1.3926(14)	1.3923(13)	1.3926(12)	1.3926(10)	0.0003	
$r(C_3-C_4) \equiv CC_p$		1.3907(4)	1.3908(4)	1.39064(34)	1.39067(29)	0.0001	
$r(C_2-H) \equiv CH_0$		1.0788(6)	1.0790(5)	1.07884(53)	1.07887(45)	0.0001	
$r(C_3-H) \equiv CH_m$		1.0802(3)	1.0802(3)	1.08023(30)	1.08022(25)	0.0001	
$r(C_4-H) \equiv CH_p$		1.0791(3)	1.0791(3)	1.07909(26)	1.07909(21)	0.0000	
$r(C-F)$		1.3439(11)	1.3441(10)	1.3439(10)	1.34392(86)	0.0002	
$\angle(C_2C_1C_6) \equiv CCC_i$		122.94(8)	122.93(7)	122.942(67)	122.942(58)	0.01	
$\angle(C_1C_2C_3) \equiv CCC_0$		117.93(5)	117.94(4)	117.930(44)	117.933(38)	0.01	
$\angle(C_2C_3C_4) \equiv CCC_m$		120.87(3)	120.87(3)	120.872(26)	120.869(22)	0.01	
$\angle(C_3C_4C_5) \equiv CCC_p$		119.45(3)	119.45(3)	119.453(29)	119.454(24)	0.00	
$\angle(C_1C_2H_2)$		119.92(8)	119.91(7)	119.926(66)	119.926(56)	0.01	
$\angle(C_4C_3H_3)$		120.02(4)	120.01(4)	120.021(35)	120.022(30)	0.01	

^a See text.^b D₃ isotopologue excluded, Huber weighting.

Table 7. Internal angles of the ring of fluorobenzene (in degrees).

	GED ^a	MW	NMR ^b	$r_e^{\text{BO}}(\text{I})^c$	$r_e^{\text{SE}}(\text{I})^d$	$r_e^{\text{SE}}(\text{II})^e$
$\alpha = \angle(\text{C}_2\text{C}_1\text{C}_6)$	123.4(2)	123.4	123.14(15)	122.48	122.67(7)	122.94(7)
$\beta = \angle(\text{C}_1\text{C}_2\text{C}_3)$	118.0(2)	117.9	118.10(12)	118.39	118.27(5)	117.93(4)
$\gamma = \angle(\text{C}_2\text{C}_3\text{C}_4)$	120.2(3)	120.5	120.34(4)	120.45	120.43(3)	120.87(3)
$\delta = \angle(\text{C}_3\text{C}_4\text{C}_5)$	120.2(4)	119.8	119.98(20)	119.84	119.93(3)	119.45(3)

^aGas electron diffraction (GED) study [65].

^bNMR study in a nematic phase [66].

^cBest r_e^{BO} structure, see Table 3.

^d r_e^{SE} structure calculated with the 6-31G* B3LYP force field, see Table 4.

^e r_e^{SE} structure calculated with the 6-311 + G(3df,2pd) B3LYP force field, see Table 4.

mainly systematic, are not taken into account in the standard deviations. In conclusion, the standard deviation of the parameters is not a reliable indicator of their accuracy.

Table 8 compares the different determinations of the equilibrium structure of PhF. The r_e^{BO} and r_e^{SE} structures are in extremely good agreement. Furthermore, they appear to be significantly more accurate than the previous determinations. The present work provides substantially improved structural parameters for PhF. Comparing them to those of the other structures, it appears that the different empirical structures, r_0 , r_s and even r_m are not reliable. However, it may be noted that the effective bond angles \angle_0 are rather close to the equilibrium values. This strengthens the conclusion of Domenicano that the \angle_0 bond angles are often more accurate than the r_0 bond lengths [21].

6. Equilibrium structures of difluorobenzenes

Stiefvater measured the microwave spectra of the parent species as well as of ten isotopologues of 1,2-difluorobenzene [76]. The rotational constants derived permitted the determination of two independent r_s structures using the normal and the 4,5- d_2 species as parent molecules. For both structures the first moment condition was used to determine the fluorine positions. The two structures are highly consistent.

In a subsequent paper, Stiefvater performed a similar study on 1,3-difluorobenzene [77]. In this case, twelve different isotopologues were investigated and the normal and 2,4,6- d_3 species were used to determine two highly consistent r_s structures. The structures of 1,2- and 1,3-difluorobenzene were also determined by a combined analysis of GED, rotational spectroscopy, and liquid-crystal NMR data [78]. The derived structure is a vibrationally averaged structure and only the angles are directly comparable to the equilibrium values.

No rotational constants are available for 1,4-difluorobenzene because the molecule has no dipole moment. On the other hand, it is better suited for an electron diffraction analysis than the other difluorobenzene isomers as many atom–atom interactions double in the electron scattering. A GED analysis indeed permitted to obtain the r_g

value of the $\text{C}_1\cdots\text{C}_4$ non-bonded distance as well as the bond angle $\angle(\text{C}_2\text{C}_1\text{C}_6)$, determined to be $123.5(1)^\circ$ [79]. More recently, a combined analysis of GED and liquid-crystal NMR data permitted to obtain a considerably more accurate structure [80].

In this study, the r_e^{BO} structures of the three-difluorobenzene isomers were computed in a way similar to that used for fluorobenzene and employing Equation (5). The results are given in Tables 9–11 for 1,2-difluorobenzene, 1,3-difluorobenzene, and 1,4-difluorobenzene, respectively. Just like for PhF, the corrections due to basis set enlargement are small, the CC bond lengths decrease by about 0.003 Å and the CH bond lengths decrease by 0.001 Å. For 1,2-difluorobenzene, the changes of the bond angles are negligible. For 1,3-difluorobenzene, the $\angle(\text{C}_1\text{C}_2\text{C}_3)$ angle decreases by 0.16° , whereas the $\angle(\text{C}_2\text{C}_3\text{C}_4)$ angle increases by 0.12° . For 1,4-difluorobenzene, the $\angle(\text{C}_2\text{C}_1\text{C}_6)$ increases by 0.16° . The structure of 1,4-difluorobenzene was also optimized at the VQZ CCSD(T)_FC level of theory. The bond angles were found to be almost identical to the r_e^{BO} values, confirming that the latter are accurate.

For 1,2- and 1,3-difluorobenzenes, the anharmonic force fields were computed at the B3LYP level with the 6-31G* and the 6-311 + G(3df,2pd) basis sets. The r_e^{SE} structures were calculated in the same way as for PhF. The rotational constants are given in Tables S9 and S10 of the Supplementary Material for 1,2-difluorobenzene and 1,3-difluorobenzene, respectively. For the normal species of 1,2-difluorobenzene, the ground-state inertial defect is $\Delta_0 = 0.049 \text{ u}\text{\AA}^2$. After adding the rovibrational correction, calculated with the help of the 6-31G* B3LYP force field, the equilibrium inertial defect becomes $\Delta_e = -0.014 \text{ u}\text{\AA}^2$, and once the electronic correction is taken into account, it is $\Delta_e = -0.0016 \text{ u}\text{\AA}^2$. If the 6-311 + G(3df,2pd) B3LYP force field is used instead, the equilibrium inertial defect, after the electronic correction, is significantly farther away from zero at $\Delta_e = -0.0035 \text{ u}\text{\AA}^2$, indicating that the 6-31G* B3LYP force field is more accurate, as it is confirmed below. For the normal species of 1,3-difluorobenzene, the ground-state inertial defect is $\Delta_0 = 0.047 \text{ u}\text{\AA}^2$, after the rovibrational correction calculated with the 6-31G* B3LYP force field the

Table 8. Comparison of different structures of fluorobenzene (distances in Å, angles in degrees)

Method Ref.	GED ^{a,b} [65]	NMR ^b [66]	r_s [16]	r_0 [17]	$r_m^{(IL)}$ [17]	$r_e^{BO(I)}$ ^c This work	$r_e^{SE(I)}$ ^d This work
$r(C-C_o)$			1.383	1.3864(11)	1.3824(18)	1.3832	1.3834(5)
$r(C-C_m)$			1.395	1.3879(30)	1.3946(34)	1.3915	1.3933(13)
$r(C-C_p)$			1.397	1.3996(11)	1.3944(15)	1.3916	1.3910(4)
$r(C-H_o)$			1.081	1.0833(15)	1.0771(14)	1.0796	1.0780(6)
$r(C-H_m)$			1.083	1.0808(9)	1.0785(8)	1.0805	1.0799(3)
$r(C-H_p)$			1.080	1.0814(6)	1.0769(7)	1.0801	1.0801(3)
$r(C-F)$			1.354	1.3594(24)	1.3554(28)	1.3436	1.3435(10)
$\alpha = \angle(C_2C_1C_6)$	123.4(2)	123.14(15)	123.4	122.82(16)	123.12(18)	122.48	122.67(7)
$\beta = \angle(C_1C_2C_3)$	118.0(2)	118.10(12)	117.9	118.34(13)	118.07(12)	118.39	118.27(5)
$\gamma = \angle(C_2C_3C_4)$	120.2(3)	120.34(4)	120.5	120.32(8)	120.45(7)	120.45	120.43(3)
$\delta = \angle(C_3C_4C_5)$	120.2(4)	119.98(20)	119.8	119.87(7)	119.84(7)	119.84	119.93(3)
$\angle(C_1C_2H_2)$		120.06(13)	120.0	119.43(16)	119.84(18)	119.69	119.81(7)
$\angle(C_4C_3H_3)$		120.01(4)	119.9	119.80(10)	119.97(9)	120.11	120.20(4)

^aGas-phase electron diffraction (GED) studies.^bThe bond lengths are not given because they are not directly comparable to the equilibrium values.^c $r_e^{BO(I)} = wCVTZ\ CCSD(T)\ (AE) + wCVQZ\ MP2\ (AE) - wCVTZ\ MP2\ (AE)$, see Table 1.^d r_e^{SE} structure calculated with the 6-31G* B3LYP force field, see Table 4.

equilibrium inertial defect becomes $\Delta_e = -0.012\ \text{u}\text{\AA}^2$, and once the electronic correction is taken into account, it is $\Delta_e = 0.0005\ \text{u}\text{\AA}^2$. If the 6-311 + G(3df,2pd) B3LYP force field is used instead, the equilibrium inertial defect, after electronic correction, is even closer to zero, $\Delta_e = -0.0003\ \text{u}\text{\AA}^2$. This indicates that this time the 6-31G* B3LYP force field is very slightly less accurate. The complete set of results are given in Tables S11 and S12 of the Supplementary Material for 1,2-difluorobenzene and 1,3-difluorobenzene, respectively, and a summary is given in Tables 9 and 10. Inspection of Table S11 indicates that

for 1,2-difluorobenzene the $r(C_3H_3)$ bond length and the $\angle(C_2C_3H_3)$ bond angle are not well determined, the different fits and different force fields give significantly different results. This suggests an accuracy problem with the rotational constants of isotopologue 3- d_1 . This is indeed confirmed by IRLS fits which downweight the A and B rotational constants of this isotopologue. The easiest way to obtain an accurate semiexperimental structure is to add the r_e^{BO} value of the C_3H_3 bond length and of the $\angle(C_2C_3H_3)$ bond angle as predicate observations with a reasonable uncertainty of 0.002 Å and 0.2° for the length and the angle,

Table 9. Equilibrium structures of 1,2-difluorobenzene (distances in Å, angles in degrees).

Method Basis set	r_s^a	CCSD(T)_AE CVTZ	MP2(AE) CVTZ	MP2(AE) wCVQZ	r_e^{BO} ^b	r_e^{SE} ^c	r_e^{SE} ^d + predicates	GED + NMR ^e
$r(C_1-F)$	1.3494	1.3367	1.3354	1.3341	1.3354	1.3357(12)	1.3368(8)	
$r(C_1-C_2)$	1.3755	1.3909	1.3878	1.3850	1.3881	1.3862(16)	1.3852(6)	
$r(C_2-C_3)$	1.3786	1.3849	1.3813	1.3787	1.3823	1.3834(15)	1.3830(8)	
$r(C_3-C_4)$	1.4004	1.3949	1.3903	1.3876	1.3922	1.3915(7)	1.3918(4)	
$r(C_4-C_5)$	1.3917	1.3926	1.3888	1.3863	1.3901	1.3897(15)	1.3892(7)	
$r(C_3-H_3)$	1.0829	1.0808	1.0793	1.0782	1.0797	1.0815(4)	1.0816(4)	
$r(C_4-H_4)$	1.0813	1.0809	1.0791	1.0780	1.0798	1.0796(4)	1.0796(2)	
$\angle(C_1C_2F)$	119.16	119.17	119.17	119.13	119.13	119.105(70)	119.122(29)	
$\angle(C_1C_2C_3)$	121.17	120.47	120.41	120.46	120.52	120.560(31)	120.590(21)	120.7(1)
$\angle(C_2C_3C_4)$	118.59	119.33	119.42	119.33	119.25	119.163(40)	119.130(23)	119.4(2)
$\angle(C_3C_4C_5)$	120.24	120.19	120.17	120.21	120.23	120.278(24)	120.279(13)	119.9(1)
$\angle(C_2C_3H)$	119.58	118.82	118.70	118.74	118.87	118.718(57)	118.729(56)	
$\angle(C_3C_4H)$	119.55	119.54	119.54	119.53	119.53	119.459(61)	119.46(28)	
Predicates								
$r(C_3H_3)$							1.0797(20)	
$\angle(C_2C_3H)$							118.866(200)	

^aRef. [76].^bCVTZ CCSD(T)_AE + wCVQZ MP2(AE) - CVTZ MP2(AE).^cCalculated with the 6-31G* B3LYP force field, Huber weighting, see text.^dCalculated with the 6-31G* B3LYP force field and two predicate observations, see text.^eRef. [75].

Table 10. Equilibrium structures of 1,3-difluorobenzene (distances in Å, angles in degrees)

	r_s^a	MP2(AE) CVTZ	MP2(AE) wCVQZ	CCSD(T)_AE CVTZ	$r_e^{BO\ b}$	$r_e^{SE\ c}$	GED + NMR ^d
$r(C_1-C_2)$	1.3888	1.3830	1.3803	1.3871	1.3844	1.38473(68)	
$r(C_3-C_4)$	1.3745	1.3830	1.3800	1.3869	1.3839	1.3819(12)	
$r(C_4-C_5)$	1.3956	1.3893	1.3868	1.3936	1.3911	1.39070(28)	
$r(C_2-H_2)$	1.0822	1.0780	1.0770	1.0794	1.0784	1.07891(28)	
$r(C_4-H_4)$	1.0820	1.0783	1.0772	1.0799	1.0788	1.07851(18)	
$r(C_5-H_5)$	—	1.0794	1.0783	1.0812	1.0801	1.0795(49)	
$r(C_1-F)$	1.3561	1.3405	1.3399	1.3407	1.3401	1.34164(78)	
$\angle(C_1C_2C_3)$	115.74	117.33	117.18	117.18	117.02	116.853(72)	117.8(3)
$\angle(C_2C_3C_4)$	123.70	122.50	122.62	122.63	122.75	122.866(36)	121.7(3)
$\angle(C_3C_4C_5)$	118.00	118.33	118.28	118.25	118.20	118.164(14)	
$\angle(C_4C_5C_6)$	120.86	121.02	121.01	121.07	121.06	121.087(16)	
$\angle(C_3C_4H_4)$	119.92	119.74	119.76	119.80	119.82	119.810(24)	119.1(2)
$\angle(C_5C_4H_4)$		121.94	121.96	121.96	121.98	122.025(21)	
$\angle(C_2C_1F)$	117.26	118.36	118.29	118.31	118.25	118.07(10)	118.3(2)
$\angle(C_6C_1F)$		119.14	119.09	119.06	119.00	119.068(71)	

^aRef. [77].^bCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).^cCalculated with the 6-311 + G(3df,2pd) B3LYP force field, Huber weighting, see text.^dRef. [78].

respectively. For this fit, the 6-31G* B3LYP force field was preferred because it gives a better fit, the derived parameters being closer to the r_e^{BO} structure and their standard deviations being smaller. The final result is given in the last column of Table 9 and it is quite satisfactory. Inspection of Table S12 shows the superiority of the 6-311 + G(3df,2pd) B3LYP force field but the different fits give compatible results. The largest difference is found for the $r_e^{SE}(C_3C_4)$ bond length, which is shorter, by 0.002 Å, than the corresponding r_e^{BO} value. This difference is not larger than the expected accuracy of the computations. Furthermore, it has to be noted that the $b(C_3)$ coordinate at 0.25 Å is quite small, which may explain its lower accuracy.

Comparison of the r_e^{BO} and r_e^{SE} structures of benzene, fluorobenzene, and 1,2- and 1,3-difluorobenzenes shows that the accuracy of the r_e^{BO} structure is as good as 0.002 Å for the bond lengths and 0.2° for the bond angles. This observation is in excellent agreement with results of previous studies.

7. Equilibrium structures of trifluorobenzenes

Due to its D_{3h} symmetry, the structure of 1,3,5-trifluorobenzene is completely defined by only six parameters: three bond lengths (CC, CF and CH) and three bond angles, one ring angle, and the exoring $\angle(CCF)$ and $\angle(CCH)$ angles. For this reason, its structure has been determined several times by GED [18,81–83], the most recent study is due to Wann *et al.* [18], who also analyzed the additivity of ring distortions. The structure was also obtained in solid state by X-ray diffraction [17]. There is also a neutron inelastic scattering study of the crystal [84]. As the molecule is centrosymmetric, there is no microwave spectrum available; nevertheless, the rotational constants of the parent species have been derived by rotational Raman spectroscopy [15,85] and more recently by femtosecond degenerate four-wave mixing, a Raman scattering type rotational coherent spectroscopy, which permitted a very high accuracy in the determination of the rotational constants [15]. Kumpli *et al.* [15] also computed estimates to the r_e^{BO}

Table 11. *Ab initio* estimates of the r_e^{BO} structure of 1,4-difluorobenzene (distances in Å, angles in degrees)

	CCSD(T)_FC VQZ	CCSD(T)_AE CVTZ	MP2(AE) CVTZ	MP2(AE) wCVQZ	$r_e^{BO\ a}$	GED + NMR ^b
$r(C_1-C_2)$	1.3870	1.3868	1.3831	1.3802	1.3839	
$r(C_2-C_3)$	1.3943	1.3936	1.3892	1.3868	1.3912	
$r(C_2-H_2)$	1.0809	1.0804	1.0788	1.0777	1.0793	
$r(C_1-F)$	1.3452	1.3435	1.3423	1.3419	1.3431	
$\angle C_6C_1C_2$	122.30	122.10	122.00	122.16	122.27	122.23(15)
$\angle C_1C_2C_3$	118.85	118.95	119.00	118.92	118.87	118.88(7)
$\angle C_1C_2H$	119.79	119.75	119.70	119.74	119.79	119.76(7)

^aCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).^bRef. [80].

structure of 1,3,5-trifluorobenzene at the MP2, QCISD and CCSD(T) levels with the VDZ, VTZ, CVDZ and CVTZ basis sets. They also calculated the cubic force field at three different levels of theory (MP2 level with VDZ and VTZ basis sets and CVTZ QCISD) and derived an r_e^{SE} equilibrium structure by effectively extrapolating the computed ground-state rotational constants to infinite basis size.

Experimental studies on the structures of the other two trifluorobenzenes are much scarcer. 1,2,3-trifluorobenzene has an equilibrium structure of C_{2v} point-group symmetry and its structure is defined by eleven independent parameters. An approximate effective r_0 structure was first obtained from the rotational constants of the parent species by Doraiswamy and Sharma [14]. More recently, the FTMW spectra of all monosubstituted ^{13}C isotopologues were measured in natural abundance and permitted to determine an improved but partial r_0 structure [19]. There is also a GED determination of the structure of 1,2,3-trifluorobenzene [18].

The equilibrium structure of 1,2,4-trifluorobenzene has only C_s point-group symmetry and 21 independent parameters are required to define it. An approximate r_0 structure was estimated from the ground-state rotational constants of the parent species [86]. Later, the FTMW spectra of the six ^{13}C isotopologues were measured in natural abundance by FTMW and permitted to derive a partial r_s structure [87].

In this study, the r_e^{BO} structures of the three trifluorobenzene isomers were computed following the guidelines detailed for fluorobenzene and using Equation (5). The results are given in Tables 12–14 for 1,3,5-, 1,2,3- and 1,2,4-trifluorobenzenes, respectively. As for PhF, the effect of adding diffuse functions was investigated at the AVQZ MP2 level for 1,3,5-trifluorobenzene. Their effect is significant only for the $r_e(\text{CF})$ bond length, which is lengthened by 0.0014 Å when the basis set changes from VQZ to AVQZ, see Table 12. Again similar to PhF, this small change is of the same order of magnitude as the expected accuracy of the BO structure and, furthermore, this increase is partially cancelled by the fact that the basis set is not yet fully converged at the VQZ level. The r_e^{BO} structure of 1,3,5-trifluorobenzene is in excellent agreement with the r_e^{SE} structure of Kummlı *et al.* [15]. For example, the difference in the CCC_i angle is only 0.2° . The exception is the $r(\text{CF})$ bond length, where the r_e^{SE} value is 0.0035 Å too long. This may be explained by the fact that the extrapolation using the CVDZ and CVTZ basis sets is not very accurate for the CF bond. To investigate this, we performed further valence-only CCSD(T) geometry optimizations, employing the basis sets VDZ, VTZ, and VQZ. These results confirm the well-known fact that it is dangerous to extrapolate to the complete basis set limit based on VDZ and VTZ results alone [88]. The approximate equilibrium structure derived from a GED analysis is also given in Table 12. It does not appear to be very accurate.

The r_e^{BO} structure of 1,2,3-trifluorobenzene is compared in Table 13 to an approximate equilibrium structure deter-

mined by GED [18] and to an empirical r_0 structure [19]. The agreement is satisfactory for the bond angles but not for the bond lengths.

The r_e^{BO} structure of 1,2,4-trifluorobenzene is compared in Table 14 to an empirical r_s structure [87]. The agreement is not at all satisfactory.

8. Equilibrium structures of tetrafluorobenzenes

The equilibrium structures of 1,2,3,4- and 1,2,3,5-tetrafluorobenzene are of C_{2v} point-group symmetry and thus defined by eleven independent parameters.

The microwave spectrum of the parent species of 1,2,3,4-tetrafluorobenzene was measured in 1974 by Hartmann and Botskor [89] and CC and CF bond lengths were determined assuming a hexagonal structure for the benzene ring. An approximate r_0 structure was determined in 1983 by Doraiswamy and Sharma [14]. In 1994, improved rotational constants were determined by Onda and co-workers [90]. In 2008, the FTMW spectra of the parent species and the three monosubstituted ^{13}C species were measured and partial r_s and $r_m^{(1)}$ structural parameters were derived [91]. In this study results from lower-level (MP2 and B3LYP) structure optimizations were also reported.

The microwave spectrum of 1,2,3,5-tetrafluorobenzene was measured by Sharma and Doraiswamy [92]. Later, these authors derived an approximate r_0 structure from the rotational constants of the parent species [14]. The NMR spectrum in a nematic phase was also observed and used for a structure analysis [93].

The equilibrium structure of 1,2,4,5-tetrafluorobenzene is centrosymmetric, of point-group symmetry D_{2h} , and its structure is defined by six independent parameters. For this reason, there is no measured microwave spectrum available. However, a structure for this molecule was determined by GED [94].

The r_e^{BO} structures of the three isomers were computed in a similar way as for fluorobenzene, using Equation (5). The results are given in Tables 15–17 for 1,2,3,4-, 1,2,3,5- and 1,2,4,5-fluorobenzene, respectively. The r_e^{BO} structure of 1,2,3,4-tetrafluorobenzene is compared in Table 15 to the mass-dependent, $r_m^{(1)}$, and the substitution, r_s , structures of Ref. [91]. The agreement is not at all satisfactory for the bond lengths and somewhat satisfactory for the bond angles. We expect that the computed r_e^{BO} structure is considerably more accurate than the experimental structures of Ref. [91].

9. Equilibrium structure of pentafluorobenzene

The equilibrium structure of pentafluorobenzene is of point-group symmetry C_{2v} , and it is defined by eleven independent geometry parameters. An approximate r_0 structure was first determined for this molecule by Doraiswamy and Sharma based on the ground-state rotational constants of the parent species [14]. Recently, the rotational spectrum of

Table 12. *Ab initio* estimates of the r_e^{BO} structure of 1,3,5-trifluorobenzene (distances in Å, angles in degrees).

	MP2(FC) VQZ	MP2(FC) AVQZ	MP2(AE) CVTZ	MP2(AE) wCVQZ	CCSD(T)_AE CVTZ	r_e^{BO} ^a	r_e^{SE} ^b	GED ^c
$r(\text{C-H})$	1.0779	1.0783	1.0773	1.0763	1.0787	1.0777	1.0763(10)	1.084
$r(\text{C-F})$	1.3397	1.3411	1.3380	1.3372	1.3378	1.3370	1.3405(20)	1.346
$r(\text{C-C})$	1.3837	1.3840	1.3828	1.3800	1.3870	1.3843	1.3842(10)	1.392
$\angle(\text{C}_1\text{C}_2\text{C}_3)$	116.915	116.828	117.065	116.956	116.940	116.832	116.60	116.8
$\angle(\text{C}_1\text{C}_2\text{H})$	121.542	121.586	121.468	121.522	121.530	121.584		
$\angle(\text{FC}_1\text{C}_2)$	118.458	118.414	118.532	118.478	118.470	118.416		
$\angle(\text{C}_2\text{C}_3\text{C}_4)$	123.085	123.172	122.935	123.044	123.060	123.168	123.40	123.2

^aCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).

^bRef. [15].

^cEquilibrium structure, Ref. [18].

the parent species was measured by chirped-pulse FTMW spectroscopy and the microwave spectra of the four ^{13}C isotopologues were observed by FTMW [95]. This permitted the determination of partial r_0 and r_s structures. NMR spectroscopy has also been utilized to derive a structure [96].

The r_e^{BO} structure was computed in a similar way as for fluorobenzene and using Equation (5). The results are given in Table 18, where they are compared with the previous determinations confirming that the latter are not accurate.

10. Equilibrium structure of hexafluorobenzene

The equilibrium structure of hexafluorobenzene, C_6F_6 , has D_{6h} point-group symmetry. Thus, it is completely defined by only two structural parameters and the molecule does not

have a microwave spectrum. Nevertheless, the ground-state rotational constant B_0 has been determined by Raman spectroscopy permitting to obtain a r_0 structure [85]. There are also GED investigations of the structure of C_6F_6 [97,98]. Its structure was also obtained in solid state by X-ray diffraction [17,99]. There is also a neutron inelastic scattering study of the crystal [84]. The NMR spectrum in a nematic phase was also observed [93].

The r_e^{BO} structure was computed in a similar way as for PhF and using Equation (5). The results are given in Table 19. Comparison of the r_e^{BO} structure with the previous determinations is not meaningful because the latter are not accurate enough. However, there is another way to check the accuracy of the r_e^{BO} structure. The experimental value of B_0 is known [85]. The rovibrational correction

Table 13. *Ab initio* estimates of the r_e^{BO} structure of 1,2,3-trifluorobenzene (distances in Å, angles in degrees).

	MP2(AE) CVTZ	MP2(AE) wCVQZ	CCSD(T)_AE CVTZ	r_e^{BO} ^a	GED ^b	r_0 ^c
$r(\text{C}_{1/2}\text{-C}_{2/3})$	1.3870	1.3845	1.3900	1.3875	1.395	1.3895
$r(\text{C}_{3/1}\text{-C}_{4/6})$	1.3820	1.3792	1.3860	1.3832	1.391	1.3832
$r(\text{C}_{4/5}\text{-C}_{5/6})$	1.3888	1.3863	1.3931	1.3906	1.399	1.3988
$r(\text{C}_{1/3}\text{-F}_{1/3})$	1.3340	1.3326	1.3347	1.3333	1.341	1.3398
$r(\text{C}_2\text{-F}_2)$	1.3284	1.3264	1.3303	1.3283	1.334	1.3348
$r(\text{C}_{4/6}\text{-H}_{4/6})$	1.0785	1.0775	1.0801	1.0791		1.082
$r(\text{C}_5\text{-H}_5)$	1.0787	1.0776	1.0804	1.0793		1.082
$\angle(\text{C}_1\text{C}_2\text{C}_3)$	118.872	118.837	118.881	118.85	118.8	118.75
$\angle(\text{C}_{2/2}\text{C}_{3/1}\text{C}_{4/6})$	121.098	121.136	121.149	121.19	121.3	121.50
$\angle(\text{C}_{3/1}\text{C}_{4/6}\text{C}_{5/5})$	119.101	119.055	119.021	118.98	119.0	118.68
$\angle(\text{C}_4\text{C}_5\text{C}_6)$	120.732	120.781	120.778	120.83	120.8	120.89
$\angle(\text{F}_{1/3}\text{C}_{1/3}\text{C}_{2/2})$	118.331	118.279	118.381	118.33	118.3	118.09
$\angle(\text{F}_{1/3}\text{C}_{1/3}\text{C}_{4/6})$	120.571	120.585	120.469	120.48	120.5	120.41
$\angle(\text{F}_{2/2}\text{C}_{2/2}\text{C}_{1/3})$	120.564	120.582	120.560	120.58		120.62
$\angle(\text{H}_{4/6}\text{C}_{4/6}\text{C}_{5/5})$	122.006	122.019	121.986	122.00	122.1	121.96
$\angle(\text{H}_{4/6}\text{C}_{4/6}\text{C}_{1/3})$	118.894	118.926	118.993	119.03		119.36
$\angle(\text{H}_{5/5}\text{C}_{5/5}\text{C}_{4/6})$	119.634	119.610	119.611	119.59		119.55

^aCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).

^bEquilibrium structure, Ref. [19].

^cEffective structure, Ref. [20].

Table 14. *Ab initio* estimates of the r_e^{BO} structure of 1,2,4-trifluorobenzene (distances in Å, angles in degrees).

	MP2(AE) CVTZ	MP2(AE) wCVQZ	CCSD(T)_AE wCVTZ	r_e^{BO} ^a	r_s^{b}
$r(\text{C}_1\text{-C}_2)$	1.3880	1.3852	1.3911	1.3883	1.378
$r(\text{C}_2\text{-C}_3)$	1.3815	1.3791	1.3853	1.3829	1.369
$r(\text{C}_3\text{-C}_4)$	1.3840	1.3812	1.3883	1.3855	1.378
$r(\text{C}_4\text{-C}_5)$	1.3817	1.3790	1.3852	1.3825	1.404
$r(\text{C}_5\text{-C}_6)$	1.3900	1.3874	1.3947	1.3921	1.365
$r(\text{C}_1\text{-C}_6)$	1.3809	1.3783	1.3843	1.3817	1.409
$r(\text{C}_1\text{-F})$	1.3349	1.3336	1.3366	1.3353	
$r(\text{C}_2\text{-F})$	1.3330	1.3316	1.3338	1.3324	
$r(\text{C}_3\text{-H})$	1.0782	1.0772	1.0796	1.0786	
$r(\text{C}_4\text{-F})$	1.3400	1.3394	1.3407	1.3401	
$r(\text{C}_5\text{-H})$	1.0781	1.0770	1.0796	1.0785	
$r(\text{C}_6\text{-H})$	1.0789	1.0779	1.0804	1.0794	
$\angle(\text{C}_1\text{C}_2\text{C}_3)$	120.723	120.765	120.803	120.845	121.81
$\angle(\text{C}_2\text{C}_3\text{C}_4)$	118.184	118.025	118.018	117.858	117.83
$\angle(\text{C}_3\text{C}_4\text{C}_5)$	122.225	122.383	122.362	122.520	122.35
$\angle(\text{C}_4\text{C}_5\text{C}_6)$	118.685	118.657	118.639	118.612	118.56
$\angle(\text{C}_1\text{C}_6\text{C}_5)$	120.035	119.942	119.960	119.867	119.93
$\angle(\text{C}_2\text{C}_1\text{C}_6)$	120.148	120.228	120.218	120.298	119.50
$\angle(\text{C}_2\text{C}_1\text{F})$	119.281	119.227	119.273	119.219	
$\angle(\text{C}_6\text{C}_1\text{F})$	120.571	120.545	120.509	120.483	
$\angle(\text{C}_1\text{C}_2\text{F})$	119.357	119.323	119.335	119.302	
$\angle(\text{C}_3\text{C}_2\text{F})$	119.921	119.912	119.862	119.853	
$\angle(\text{C}_3\text{C}_4\text{F})$	118.454	118.384	118.390	118.321	
$\angle(\text{C}_5\text{C}_4\text{F})$	119.321	119.233	119.248	119.159	
$\angle(\text{C}_2\text{C}_3\text{H})$	120.490	120.569	120.612	120.692	
$\angle(\text{C}_4\text{C}_3\text{H})$	121.326	121.406	121.370	121.450	
$\angle(\text{C}_4\text{C}_5\text{H})$	119.932	119.933	119.974	119.976	
$\angle(\text{C}_6\text{C}_5\text{H})$	121.384	121.410	121.386	121.412	
$\angle(\text{C}_1\text{C}_6\text{H})$	118.763	118.807	118.869	118.913	
$\angle(\text{C}_5\text{C}_6\text{H})$	121.202	121.251	121.172	121.220	

^aCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).^bSubstitution structure, Ref. [87].Table 15. *Ab initio* estimates of the r_e^{BO} structure of 1,2,3,4-tetrafluorobenzene (distances in Å, angles in degrees).

	MP2(AE) CVTZ	MP2(AE) wCVQZ	CCSD(T)_AE wCVTZ	r_e^{BO} ^a	r_s^{b}	$r_m^{(1)}$ ^c
$r(\text{C}_1\text{-C}_2)$	1.3879	1.3853	1.3912	1.3886	1.382(3)	1.388(4)
$r(\text{C}_2\text{-C}_3)$	1.3864	1.3842	1.389	1.3868	1.366(3)	1.360(3)
$r(\text{C}_4\text{-C}_5)$	1.3802	1.3776	1.3837	1.3811	1.393(3)	1.389(3)
$r(\text{C}_5\text{-C}_6)$	1.3898	1.3872	1.3944	1.3918	1.386(3)	1.378(5)
$r(\text{C}_1\text{-F})$	1.3336	1.3322	1.3347	1.3333		
$r(\text{C}_2\text{-F})$	1.3271	1.3250	1.3284	1.3263		
$r(\text{C}_5\text{-H})$	1.0782	1.0772	1.0798	1.0788		
$\angle(\text{C}_1\text{C}_2\text{C}_3)$	119.569	119.530	119.561	119.52	120.11(40)	119.97(40)
$\angle(\text{C}_3\text{C}_4\text{C}_5)$	120.759	120.832	120.830	120.90	120.52(37)	120.49(14)
$\angle(\text{C}_4\text{C}_5\text{C}_6)$	119.672	119.638	119.609	119.58	119.37(35)	119.55(07)
$\angle(\text{FC}_1\text{C}_2)$	118.453	118.399	118.476	118.42		
$\angle(\text{FC}_1\text{C}_6)$	120.788	120.769	120.695	120.68		
$\angle(\text{FC}_2\text{C}_3)$	119.753	119.758	119.801	119.81		
$\angle(\text{FC}_2\text{C}_1)$	120.678	120.712	120.638	120.67		
$\angle(\text{HC}_5\text{C}_4)$	119.014	119.030	119.101	119.12		
$\angle(\text{HC}_5\text{C}_6)$	121.314	121.332	121.290	121.31		

^aCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).^bSubstitution structure of Ref. [91].^cMass-dependent structure of Ref. [91].

Table 16. *Ab initio* estimates of the r_e^{BO} structure of 1,2,3,5-tetrafluorobenzene (distances in Å, angles in degrees).

	MP2(AE) CVTZ	MP2(AE) wCVQZ	CCSD(T)_AE wCVTZ	r_e^{BO} ^a
$r(\text{C}_1\text{-C}_2)$	1.3867	1.3842	1.38967	1.3872
$r(\text{C}_3\text{-C}_4)$	1.3824	1.3797	1.38654	1.3838
$r(\text{C}_4\text{-C}_5)$	1.3823	1.3796	1.38639	1.3837
$r(\text{C}_1\text{-F}_1)$	1.3318	1.3302	1.33200	1.3304
$r(\text{C}_2\text{-F}_2)$	1.3283	1.3262	1.33037	1.3283
$r(\text{C}_5\text{-F}_5)$	1.3379	1.3371	1.33801	1.3372
$r(\text{C}_4\text{-H}_4)$	1.0776	1.0767	1.07898	1.0781
$\angle(\text{C}_1\text{C}_2\text{C}_3)$	118.567	118.574	118.602	118.61
$\angle(\text{C}_2\text{C}_3\text{C}_4)$	121.563	121.588	121.611	121.64
$\angle(\text{C}_3\text{C}_4\text{C}_5)$	117.848	117.742	117.709	117.60
$\angle(\text{C}_4\text{C}_5\text{C}_6)$	122.612	122.768	122.759	122.92
$\angle(\text{C}_3\text{C}_2\text{F}_2)$	120.717	120.713	120.699	120.70
$\angle(\text{C}_2\text{C}_3\text{F}_3)$	118.491	118.445	118.525	118.48
$\angle(\text{C}_4\text{C}_3\text{F}_3)$	119.947	119.967	119.864	119.88
$\angle(\text{C}_4\text{C}_5\text{F}_5)$	118.694	118.616	118.621	118.54
$\angle(\text{C}_3\text{C}_4\text{H}_4)$	120.613	120.678	120.717	120.78
$\angle(\text{C}_5\text{C}_4\text{H}_4)$	121.538	121.580	121.574	121.62

^aCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).

$\varepsilon = I_0 - I_e$ is small because the molecule is rigid and the rotational constant is small. Furthermore, it is possible to estimate its order of magnitude using the known values for the mono-, di- and trifluorobenzenes and assuming that ε varies as the square root of I_e [100]. It allows us to estimate $B_e^{\text{exp.}} = 1033.4$ MHz, to be compared with the value derived from the r_e^{BO} structure, $B_e^{\text{BO}} = 1034.5$ MHz. Taking into account the uncertainties, it may be concluded that the agreement is very good and that the r_e^{BO} structure of C_6F_6 is accurate.

11. Substitution effects of F on the benzene ring

Fluorine has a high EN and a small size, these are properties which make F an especially important substituent in many fields of chemistry.

The high EN value of F means that it is an electron-withdrawing substituent. Consequently, the inductive effect governs the structural changes occurring upon substitution

of H by F, the most important of which is the pushing of the F atom toward the center of the benzene ring.

First, let's interpret the substituent effects of F in PhF in a qualitative way. It is natural to assume that the polarizability of the π electrons of the benzene ring are larger than that of the σ electrons. Consequently, the F substituent preferably withdraws charge from the 2p electron of C, leading to a move from sp^2 to sp hybridization at the ipso C atom. As a follow up, the ortho C atoms rehybridize toward sp^3 . Thus, the ipso CCC angle increases and the ortho CCC angle decreases relative to their reference value in benzene, 120° . At the same time, these rehybridizations lead to a contraction of the CH_σ bond. The distortions caused by F substitution have also been rationalized via VSEPR arguments [4].

The $r_e^{\text{SE}}(\text{I})$ structure of PhF reveals that the change in the ipso CCC angle, $+2.67(7)^\circ$, is considerably less than twice as large and of opposite direction as the change at the ortho CCC angle, $-1.73(5)^\circ$. This means that while the

Table 17. *Ab initio* estimates of the r_e^{BO} structure of 1,2,4,5-tetrafluorobenzene (distances in Å, angles in degrees).

	MP2(AE) CVTZ	MP2(AE) wCVQZ	CCSD(T)_AE wCVTZ	r_e^{BO} ^a
$r(\text{C}_1\text{-C}_2)$	1.3865	1.3838	1.3892	1.3865
$r(\text{C}_2\text{-C}_3)$	1.3823	1.3798	1.3863	1.3838
$r(\text{C-F})$	1.3328	1.3314	1.3340	1.3326
$r(\text{C-H})$	1.0784	1.0774	1.0797	1.0787
$\angle(\text{C}_1\text{C}_2\text{C}_3)$	120.380	120.464	120.479	120.56
$\angle(\text{C}_1\text{C}_6\text{C}_5)$	119.240	119.072	119.042	118.87
$\angle(\text{C}_6\text{C}_1\text{F})$	120.025	120.009	119.952	119.94
$\angle(\text{C}_1\text{C}_2\text{F})$	119.595	119.527	119.569	119.50
$\angle(\text{C}_2\text{C}_3\text{H})$	120.380	120.464	120.479	120.56

^aCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).

Table 18. *Ab initio* estimates of the r_e^{BO} structure of pentafluorobenzene (distances in Å, angles in degrees) along with previous experimental determinations.

	MP2(AE) CVTZ	MP2(AE) wCVQZ	CCSD(T)_AE wCVTZ	r_e^{BO} ^a	r_0^{b}	r_s^{b}	NMR ^c
$r(\text{C}_1\text{-C}_2)$	1.3859	1.3834	1.3889	1.3864	1.375(13)	1.368(4)	1.388(16)
$r(\text{C}_2\text{-C}_3)$	1.3873	1.3849	1.3903	1.3879	1.395(10)	1.393(10)	1.387(8)
$r(\text{C}_1\text{-C}_6)$	1.3817	1.3791	1.3858	1.3832	1.390(7)	1.386(11)	1.389(11)
$r(\text{C}_1\text{-F}_1)$	1.3317	1.3302	1.3323	1.3308			
$r(\text{C}_2\text{-F}_2)$	1.3270	1.3249	1.3286	1.3265			1.335(7)
$r(\text{C}_3\text{-F}_3)$	1.3259	1.3237	1.3267	1.3245			1.330(4)
$r(\text{C}_6\text{-H})$	1.0779	1.0769	1.0792	1.0782			
$\angle(\text{C}_1\text{C}_2\text{C}_3)$	119.179	119.185	119.206	119.21	119.5(9)	119.7(9)	119.6(2)
$\angle(\text{C}_2\text{C}_3\text{C}_4)$	120.458	120.404	120.415	120.36	119.8(10)	119.3(10)	119.8(3)
$\angle(\text{C}_1\text{C}_6\text{C}_5)$	118.888	118.780	118.715	118.61	118.0(7)	117.7(11)	117.2(2)
$\angle(\text{C}_6\text{C}_1\text{C}_2)$	121.148	121.224	121.229	121.30	121.6(10)	121.8(11)	121.7(3)
$\angle(\text{F}_1\text{C}_1\text{C}_2)$	118.734	118.666	118.746	118.68			
$\angle(\text{C}_6\text{C}_1\text{F}_1)$	120.118	120.111	120.025	120.02			119.9(3)
$\angle(\text{C}_3\text{C}_2\text{F}_2)$	119.870	119.866	119.889	119.89	118.9(8)		120.1(2)
$\angle(\text{C}_1\text{C}_2\text{F}_2)$	120.952	120.949	120.905	120.90	121.7(17)		1203(2)
$\angle(\text{C}_2\text{C}_3\text{F}_3)$	119.771	119.798	119.793	119.82	120.1(5)	120.4(1)	120.1(1)
$\angle(\text{C}_1\text{C}_6\text{H})$	120.556	120.610	120.642	120.70			121.2(1)

^aCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).

^bEffective structure, Ref. [95].

^bSubstitution structure, Ref. [95].

^cFrom the spin-spin coupling constants of ^{19}F and ^{13}C nuclei, Ref. [96].

CCC angle distortion at the para position is minuscule, on the order of -0.1° , fluorine substitution results in a substantial change at the meta position, $+0.43(4)^\circ$. This alternate angle distortion is characteristic for most monosubstituted benzenes (though there are both positive and negative ipso angle changes, depending upon the substituent).

It is also interesting to take a look at the bond length changes of PhF. At $r_e^{\text{SE}}(\text{CC}_0) = 1.383(1)$ Å, the ortho CC bond length is significantly shorter than the value found in benzene, $1.392(1)$ Å, see Table 1. The CH bond lengths between $1.078(1)$ Å for CH_o and $1.080(1)$ Å for CH_p are close to, but smaller than the reference value of benzene, $1.081(1)$ Å. The CF bond length at $1.344(1)$ Å is extremely different from the substitution value, $r_s = 1.354$ Å [17], as well as from the effective value, $r_0 = 1.359(2)$ Å, and the mass-dependent value, $r_m = 1.355(3)$ Å [16]. This equilibrium value is much shorter than the value found for methyl fluoride, 1.383 Å [101], but it is almost identical to the values found for vinyl fluoride, 1.343 Å [102], and *cis,trans*-1,4-difluorobutadiene, 1.339 and 1.343 Å [103]. Thus, it appears that the different empirical structures, r_0 , r_s , and even r_m , are not reliable for the bond lengths. However, it may be noted that the effective bond angles \angle_0 are rather close to the equilibrium values. This observation strengthens the conclusion of Domenicano [21] that the \angle_0 bond angles are often considerably more accurate than the r_0 bond lengths.

From a substantial body of GED and X-ray studies it has been deduced that the distortion of the ring may be

interpreted, at least in the first approximation, as arising from the superposition of independent contributions from each substituent [4,18,21,104]. This assumption is particularly obvious for bond angles. On the other hand, for bond lengths, the effects are not convincing, because the accuracy of these former studies was not sufficient. Let $\Delta\alpha$, $\Delta\beta$, $\Delta\gamma$ and $\Delta\delta$ denote the variations from 120° of the endocyclic bond angles at the ipso, ortho, meta, and para positions for the substituent, respectively (Figure 1). Based on GED results, Domenicano proposed the following variations: $\Delta\alpha = 3.4^\circ$, $\Delta\beta = -2.0^\circ$, $\Delta\gamma = 0.3^\circ$ and $\Delta\delta = 0$ [21]. Our r_e^{BO} results for PhF provide $\Delta\alpha = 2.48^\circ$, $\Delta\beta = -1.61^\circ$, $\Delta\gamma = 0.45^\circ$ and $\Delta\delta = -0.16^\circ$. Instead of using fluorobenzene and the fluorine atom, it is possible to use the structure of pentafluorobenzene and investigate the effect of hydrogen substitution. The values should be the same but with opposite signs. Actually, we obtain: $\Delta\alpha(\text{H}) = -1.39^\circ$, $\Delta\beta(\text{H}) = 1.30^\circ$, $\Delta\gamma(\text{H}) = -0.79^\circ$ and $\Delta\delta(\text{H}) = 0.36^\circ$. The increments have indeed the same sign pattern but they are not fully compatible and they do not allow us to make an accurate prediction of the angles of all polyfluorobenzenes.

A more satisfactory method is to determine the increments from a least-squares fit of all the 39 inner-ring CCC angles determined. The fit proves to be good with a correlation coefficient close to 1, $\rho = 0.980$, and a small standard deviation, $\sigma = 0.24^\circ$. The fitted values are: $\Delta\alpha = 1.954(69)^\circ$, $\Delta\beta = -1.460(42)^\circ$, $\Delta\gamma = 0.625(42)^\circ$ and $\Delta\delta = -0.247(69)^\circ$. It is still possible to slightly improve the fit by using the constraint $\Delta\alpha + 2\Delta\beta + 2\Delta\gamma +$

Table 19. *Ab initio* estimates of the r_e^{BO} structure of hexafluorobenzene (distances in Å, angles in degrees).

	MP2(AE) CVTZ	MP2(AE) wCVQZ	CCSD(T)_AE wCVTZ	r_e^{BO} a
$r(\text{C-C})$	1.3864	1.3840	1.3894	1.3871
$r(\text{C-F})$	1.3260	1.3239	1.3271	1.3249

^aCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).

$\Delta\delta = 0$, but the improvement is marginal. Although the fit seems to be good, there are four outliers with residuals of the order of 0.5° : the ipso angles in monofluoro- and parafluorobenzenes and the angles with H at the apex for 1,2,3,5-tetrafluorobenzene and pentafluorobenzene, see Table S11 of the Supplementary Material for a complete list of residuals. In particular, $\Delta\alpha$ seems to be too small and $\Delta\beta$ too large (in absolute values). This clearly shows that an additivity rule is simply not accurate enough once accurate structures are available. It is possible to slightly improve the fit by introducing interaction terms but the rather small improvement does not justify the increase in the complexity of the underlying model.

The range of the CC bond length changes, 0.011 \AA , is small. Furthermore, the accuracy of the GED bond lengths is limited. For these reasons, there have been no reliable analyses of the bond length changes. The high accuracy of the r_e^{BO} results of this work and their number should permit such an analysis. We assume that the CC bond length can be written as $r = r_0 + \Delta r$, where r_0 is the value in benzene. There will be three independent bond length changes when there is a F in ortho, meta, or para positions which we denote as Δr_o , Δr_m and Δr_p , respectively. From the results for PhF, see Table 3, we see that Δr_o at -0.0076 \AA is large and negative, whereas Δr_m and Δr_p are almost negligible. Indeed, a least-squares fit to 35 bond lengths, including that of benzene, confirms that Δr_m and Δr_p are not determined. On the other hand, when there are two fluorine atoms in ortho position, the additivity rule breaks down (indicating that the assumption of separate, independent contributions from each substituent becomes invalid), and it is necessary to use two different Δr_o , one, Δr_{o1} , for the first fluorine in ortho position and a second one, Δr_{o2} , when there is a second fluorine in ortho position. The resulting fit is of excellent quality with a large correlation coefficient, $\rho = 0.940$, and a small standard deviation, $\sigma = 0.0009 \text{ \AA}$. The fitted values are $r_0 = 1.39135(27) \text{ \AA}$, $\Delta r_{o1} = -0.00790(35) \text{ \AA}$ and $\Delta r_{o2} = 0.00399(35) \text{ \AA}$. The largest residual, 0.0021 \AA , is found for the bond length $\text{C}_3\text{--C}_4$ in 1,2,4-trifluorobenzene, see Table S12 of the Supplementary Material for a complete list of residuals. It is worth pointing out that the value found for r_0 is in excellent agreement with the CC bond length in benzene.

The range of the CH bond length changes, 0.003 \AA , is even smaller. However, the r_e^{BO} values are accurate enough

to permit a meaningful analysis of the changes. We assume that the CH bond length can be written as $r = r_0 + \Delta r$, where r_0 is the value in benzene. There will be three independent bond length changes when there is an F in *ortho*, *meta* or *para* positions which we denote as Δr_o , Δr_m and Δr_p , respectively. As in the case of the CC bond length, Δr_o will be the largest increment, whose approximate value may be derived from fluorobenzene: $\Delta r_o = -0.0014 \text{ \AA}$. A least-squares fit of 20 values, including that of benzene, gives a good fit with a large correlation coefficient, $\rho = 0.919$, and a very small standard deviation, $\sigma = 0.0003 \text{ \AA}$. The fitted values are $r_0 = 1.08054(14) \text{ \AA}$, $\Delta r_o = -0.000922(76) \text{ \AA}$, $\Delta r_m = -0.000086(76) \text{ \AA}$ and $\Delta r_p = -0.00069(12) \text{ \AA}$, see Table S13 of the Supplementary Material for a complete list of values and residuals. It has to be noted that r_0 is in good agreement with the r_e^{BO} value of benzene, 1.081 \AA , that Δr_m is quite small and not well determined, and that all increments are negative.

The range of the CF bond length changes at 0.019 \AA is rather large, the longest CF bond length is in PhF. We again assume that the CF bond length can be written as $r = r_0 + \Delta r$, where r_0 is the value in fluorobenzene. There will be three independent bond length changes when there is a F in ortho, meta, or para positions which we denote as Δr_o , Δr_m and Δr_p , respectively. A least-squares fit to 20 bond lengths shows that Δr_p is not determined. When there are two fluorine atoms in ortho position, the additivity rule breaks down, and it is necessary to use two different Δr_o , one, Δr_{o1} , for the first fluorine in ortho position and a second one, Δr_{o2} , when there is the second fluorine in ortho position. The resulting fit is of excellent quality with a large correlation coefficient, $\rho = 0.993$, and a minuscule standard deviation, $\sigma = 0.00053 \text{ \AA}$. The fitted values are $r_0 = 1.34261(27) \text{ \AA}$, $\Delta r_{o1} = -0.00724(29) \text{ \AA}$, $\Delta r_{o2} = -0.00647(29) \text{ \AA}$ and $\Delta r_m = -0.00243(15) \text{ \AA}$, see Table S14 of the Supplementary Material for a complete list of values and residuals. It has to be noted that r_0 is in good agreement with the r_e^{BO} value of fluorobenzene.

There is another way to predict the variation of the CF bond length. When the negative charge on the fluorine atom, $q(\text{F})$, increases, the radius of the atom increases and the bond becomes longer. The quantum theory of atom in molecules (QAIM) [105] with its implementation in G03 by Cioslowski *et al.* [106] was used to calculate the atomic charges. The B3LYP level of theory was used for this purpose with the 6-311 + G(2d,2p) basis set. The results are given in Table S14 of the Supplementary Material. A least-squares fit to the 21 bond lengths gives $r_e(\text{CF}) = 0.9927(99) - 0.536(16)q(\text{F})$. The correlation coefficient, $\rho = 0.985$, is close to 1 and the standard deviation, $\sigma = 0.0007 \text{ \AA}$, is quite small. In principle, it is still possible to improve the fit by taking into account the charges of the carbon atoms, $q(\text{C})$, but, actually, $q(\text{F})$ and $q(\text{C})$ are fully correlated and the fit becomes ill-conditioned.

12. Comparison of the structure of fluorobenzene with the structures of other benzene derivatives

It is instructive to compare the deformations of the benzene ring in fluorobenzene with those arising in other substituted benzenes. Although the effects of substitution on the benzene ring have been extensively investigated, most studies are not accurate enough to point out subtle effects, as shown above. However, in parallel to our work on fluorobenzenes, the r_e^{BO} and r_e^{SE} structures of cyanobenzene, $\text{C}_6\text{H}_5\text{CN}$ (also called benzonitrile), and ethynylbenzene, $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ (also called phenylacetylene), have been accurately determined by us. Furthermore, the r_e^{BO} structure of isocyanobenzene, $\text{C}_6\text{H}_5\text{NC}$, has been determined in the same way as for the fluorobenzenes, *i.e.*, using Equation (5). The results are presented in Table 20. Before going into detail about the comparison, it is useful to summarize the main results obtained previously by GED and X-ray crystallography and summarized in the review papers of Domenicano [21].

The ipso angle α is sensitive to the σ -inductive effect of the substituent and increases linearly with the EN of the substituent. The increase of α is associated with a decrease of the ortho angle β , a small increase of the meta angle γ , a decrease of the para angle δ , and a shortening of the ortho CC bond, CC_o . The other bonds are barely affected. On the other hand, when the substituent is a π -electron donor, the effect is the opposite and, in particular, the α angle decreases with increasing conjugation. Furthermore, an empirical correlation has been found between the variations of the angles α and β ,

$$\Delta\beta = -0.591(7)\Delta\alpha - 0.301(15). \quad (8)$$

This relation is in degrees and is valid for first-row substituents. Finally, Domenicano [21] also found a rough

correlation between the decrease of $r(\text{CC}_o)$ and the increase of α , $r(\text{CC}_o)$ decreasing by 0.0027 \AA each time that α increases by one degree.

The results of the present study for fluoro-, isocyano, cyano- and ethynyl-benzene are given in Table 21. The first observation is that the agreement between the r_e^{BO} and r_e^{SE} structures is excellent. Second, the accuracy of the GED data is much worse than indicated by the standard deviations given by the original sources. Third, the mass-dependent $r_m^{(2)}$ structure of ethynylbenzene does not seem to be reliable. Fourth, the order of magnitude and the sign of the variations of the angles agree with the conclusions of Domenicano [21] mentioned above. Moreover, the prediction of the empirical correlation, Equation (8), is satisfactory. Fifth, the CC_o bond length decreases when α increases but the decrease of 0.0027 \AA per degree is not confirmed and there are not enough data to find a quantitative correlation. Finally, it is worth noting that $\Delta\alpha$ in cyanobenzene is small, although the substituent CN is electronegative. It may be interpreted by the fact that this substituent is a π -electron donor which also explains the large increase in the CC_o bond length. $\Delta\alpha$ in isocyanobenzene is larger than in cyanobenzene. This is in agreement with the fact that NC is more electronegative than CN.

Domenicano also noted that the angle $\angle(\text{C}_2\text{C}_1\text{C}_6)$ and the non-bonded distance $r(\text{C}_1\cdots\text{C}_4)$ are linearly correlated for symmetrically para-disubstituted benzenes. Actually, as shown here for the r_e^{BO} structures of several monosubstituted benzenes, optimized at the CVTZ CCSD(T)_AE level of theory, the excellent correlation also applies to monosubstituted benzenes. The results are given in Table S15 of the Supplementary material and represented in Figure 2. It appears that the correlation is quite accurate. An electronegative substituent such as F distorts the ring by pushing the ipso C_1 and the para C_4 atoms towards

Table 20. *Ab initio* estimates of the r_e^{BO} structure of isocyanobenzene, $\text{C}_6\text{H}_5\text{NC}$ (distances in \AA , angles in degrees).

	MP2(AE) CVTZ	MP2(AE) wCVQZ	CCSD(T)_AE wCVTZ	r_e^{BO} ^a
$r(\text{C}_1\text{-C}_2)$	1.3914	1.3888	1.3948	1.3922
$r(\text{C}_2\text{-C}_3)$	1.3874	1.3848	1.3918	1.3892
$r(\text{C}_3\text{-C}_4)$	1.3905	1.3879	1.3945	1.3919
$r(\text{C}_1\text{-N})$	1.3816	1.3794	1.3898	1.3876
$r(\text{N}=\text{C})$	1.1803	1.1772	1.1768	1.1737
$r(\text{C}_2\text{-H})$	1.0793	1.0783	1.0808	1.0798
$r(\text{C}_3\text{-H})$	1.0797	1.0786	1.0814	1.0803
$r(\text{C}_4\text{-H})$	1.0797	1.0786	1.0814	1.0803
$\angle(\text{C}_2\text{C}_1\text{C}_6)$	121.222	121.273	121.186	121.24
$\angle(\text{C}_1\text{C}_2\text{C}_3)$	119.070	119.036	119.099	119.07
$\angle(\text{C}_2\text{C}_3\text{C}_4)$	120.289	120.285	120.310	120.31
$\angle(\text{C}_3\text{C}_4\text{C}_5)$	120.061	120.085	119.998	120.02
$\angle(\text{C}_1\text{C}_2\text{H})$	119.419	119.430	119.482	119.49
$\angle(\text{C}_2\text{C}_3\text{H})$	119.535	119.545	119.520	119.53

^aCVTZ CCSD(T)_AE + wCVQZ MP2(AE) – CVTZ MP2(AE).

Table 21. Distortion of the benzene ring in a few monosubstitute benzenes, C_6H_5X with $X = F, NC, CN, C\equiv CH$ (angles in degree and distances in Å).

		$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$	$\Delta\delta$	$\Delta\beta(\text{pred})^a$	$\Delta(\text{CC}_o)^b$	Ref.
F	GED	3.40(20)	-2.00(20)	0.30(30)	0.00(40)	-2.3	-0.012(3)	[65]
	$r_e^{\text{BO}}(\text{I})$	2.48	-1.61	0.45	-0.16	-1.8	-0.0084	This work
	r_e^{SE}	2.67(7)	-1.73(5)	0.43(3)	-0.07(3)	-1.9	-0.0082(5)	This work
NC	$r_e^{\text{BO}}(\text{I})$	1.24	-0.93	0.31	0.02	-1.0	0.0006	This work
CN	GED	1.9(3)	-1.4(2)	0.5(7)	0.0(14)	-1.4	0.001(3)	[109]
	$r_e^{\text{BO}}(\text{I})$	0.49	-0.54	0.27	0.07	-0.6	0.005	This work
	r_e^{SE}	0.54(3)	-0.56(2)	0.26(1)	0.07(1)	-0.6	0.0053(2)	This work
CCH	$r_e^{(2) \text{ c}}$	0.70(8)	-0.47(5)	0.22(2)	-0.19(2)	-0.7	0.0012(8)	[110]
	$r_e^{\text{BO}}(\text{I})$	-0.55	0.13	0.21	-0.13	0.0	0.0073	This work
	r_e^{SE}	-0.78(7)	0.21(4)	0.27(2)	-0.18(7)	0.2	0.0095(5)	This work

^aCalculated with Equation (8), see text.

^b $\Delta(\text{CC}_o) = r(\text{CC}_o) - r(\text{CC}_{\text{benzene}})$ with $r_e(\text{CC}) = 1.3916 \text{ \AA}$ and $r_g(\text{CC}) = 1.399 \text{ \AA}$ [111].

^cEmpirical mass-dependent structure from the ground state rotational constants.

the ring center, whereas electropositive substituents such as Li pull C_1 and C_4 away from the ring center. It has to be noted that the distortion of the ring along C_1 - C_4 is much larger than the changes of the CC bond lengths. For instance, when going from C_6H_5Li to C_6H_5F $r(C_1 \dots C_4)$ increases by 0.11 Å, whereas the sum $r(C_1-C_2) + r(C_2-C_3) + r(C_3-C_4)$ increases only by 0.03 Å, although the latter sum is about twice as large. Actually, this behavior is expected as it is much easier to deform bond angles than bond lengths.

The additivity of the distortions is also worth investigating. For this, the structure of 2,6-difluoro-benzonitrile,

$F_2C_6H_3CN$, was optimized at the CVTZ CCSD(T)_AE level of theory. The optimized structure is compared in Table 22 with structures, computed at the same level of theory, of 1,3-difluorobenzene and benzonitrile. This level was chosen because it was found to give structures rather close to the best r_e^{BO} ones for fluorinated benzenes. For the ring angles, it appears that the additivity approximation indeed works rather well, at least in this particular case. For the bond lengths the distortions are much smaller, however, the additivity also seems to be roughly verified, although the agreement is significantly worse for the CC_o bond. It is also worth noting that in 2,6-difluoro-benzonitrile the CF bond

Table 22. Comparison of the CVTZ CCSD(T)_AE structure of 2,6-difluoro-benzonitrile with those of its parents, 1,3-difluorobenzene and benzonitrile (angles in degree and distances in Å).

Parameter ^a	$C_6H_4F_2$	C_6H_5CN	$F_2C_6H_3CN$	Pred. ^b
$\angle(C_2C_1C_6) = \alpha$	117.18	120.48	117.42	
$\angle(C_1C_2C_3) = \beta$	122.63	119.53	122.12	
$\angle(C_2C_3C_4) = \gamma$	118.25	120.14	118.55	
$\angle(C_3C_4C_5) = \delta$	121.07	120.19	121.22	
$r(C_1-C_2) = a$	1.387	1.399	1.397	
$r(C_2-C_3) = b$	1.387	1.391	1.384	
$r(C_3-C_4) = c$	1.394	1.395	1.393	
$r(C_3-H_3)$	1.080	1.081	1.080	
$r(C_4-H_4)$	1.081	1.082	1.081	
$r(C-F)$	1.341		1.331	
$r(C_1-C_7)$		1.438	1.431	
$r(C_7-N)$		1.162	1.161	
$\Delta\alpha^c$	-2.82	0.48	-2.58	-2.34
$\Delta\beta^c$	2.63	-0.47	2.12	2.16
$\Delta\gamma^c$	-1.76	0.14	-1.45	-1.62
$\Delta\delta^c$	1.07	0.19	1.22	1.26
Δa^d	-0.007	0.005	0.003	-0.003
Δb^d	-0.007	-0.003	-0.010	-0.011
Δc^d	-0.001	0.000	-0.001	-0.001

^aThe numbering of the atoms corresponds to 2,6-difluoro-benzonitrile.

^bAssuming that the deformations are additive.

^cDeviation from 120° .

^dDeviation from the CVTZ CCSD(T)_AE value for benzene, $r(\text{CC}) = 1.3944 \text{ \AA}$, see Table 1.

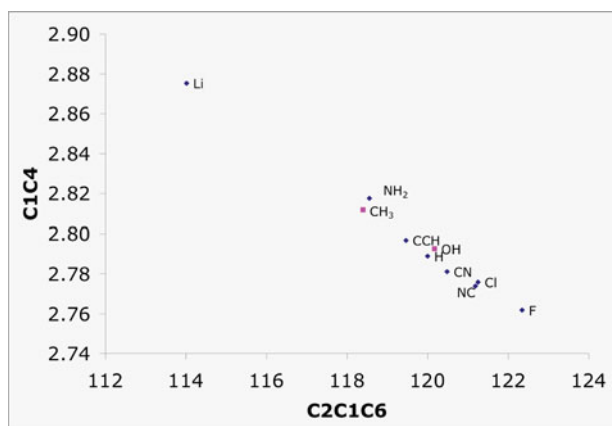


Figure 2. Plot of the non-bonded distance $r(C_1 \dots C_4)$ as a function of the ipso angle $\angle(C_2C_1C_6)$ for monosubstituted benzene rings. Blue dots refer to molecules with an equilibrium structure of C_{2v} point-group symmetry, while purple dots to molecules of lesser symmetry.

and the C_1C_7 bond are shorter than in 1,3-difluorobenzene and benzonitrile, respectively, where C_7 is the cyano carbon atom. It is also useful to check whether Equation (8) may still be used to predict the CF bond length. Indeed, with $q(F) = -0.637$ au, it gives $r(CF) = 1.335$ Å, which is not too far from the CVTZ CCSD(T)_AE value, 1.331 Å.

13. Conclusions

For a long time, a heated debate characterized the community of researchers dealing with the gas-phase structures of molecules, arguing whether GED or MW spectroscopy provide experimental estimates of structures with more accurate structural parameters. As electronic structure theory started to produce more and more dependable results and the convergence of structural results obtained with wavefunction-based electronic structure methods could be investigated, it became clear that quantum chemistry is able to provide converged, dependable, accurate structures, both equilibrium and rovibrationally averaged ones [25,107,108]. At this point it also became clear that equilibrium structures are preferable for structural comparisons over rovibrationally averaged ones and that the most accurate equilibrium structures are the so-called semiexperimental ones, r_e^{SE} , obtained by a careful combination of measured spectroscopic and computed quantum chemical data.

The present investigation of the equilibrium structures of benzene and all possible fluorobenzenes supports the view that the best equilibrium structures are provided by the semiexperimental approach not only for small but also for medium-sized molecules. At the same time, the optimized CCSD(T) r_e^{BO} structure estimates, when all electrons are correlated and at least TZ-quality atom-centered, fixed-exponent Gaussian basis sets are employed, appear to be

highly reliable for the semirigid molecules containing no unusual structural elements investigated here.

Nevertheless, it is important to emphasize that the r_e^{SE} structures will be dependable only if accurate experimental ground-state rotational constants are employed in the structural analysis. It is not always straightforward to estimate the true accuracy of the experimental spectroscopic constants but some of the statistical measures employed in this study and the equilibrium inertial defect in case of planar molecules are able to indicate accuracy problems. The accuracy of the computed anharmonic force field and the consideration of the electronic g -factors also appear to be important when only a limited amount of rotational constants are available, which is usually the case for all but the smallest molecules. Proper weighting, conditioning, and especially the use of predicate observations during the least-squares structural refinement procedure appear to be crucial to ensure the accuracy of the least-squares structural fitting and the subsequent results.

A highly accurate r_e^{SE} structure, dependent upon only two parameters, has been determined for benzene, taking into account the electronic g -factors, which were not considered before for this molecule. The new best estimates are $r_e^{SE}(CC) = 1.3914(10)$ and $r_e^{SE}(CH) = 1.0802(20)$ Å, in perfect agreement with the best previous estimate of the equilibrium structure of benzene [52]. These values, along with bond angles of 120° , provide the reference values for the present study of the structural effects of F substitution.

The r_e^{BO} and r_e^{SE} structures of fluorobenzene, C_6H_5F , determined as part of this study are in extremely good agreement. Furthermore, they appear to be significantly more accurate than the structures obtained in previous GED, MW, and NMR investigations. In particular, the ipso angle α , whose r_e^{SE} value is $122.7(1)^\circ$, is closer to the reference 120° than the values given by GED, $123.4(2)^\circ$ [65], microwave spectroscopy, 123.4° [2] or NMR spectroscopy, $123.14(15)^\circ$ [66]. While the discrepancy of the previous results may appear to be relatively small, the new accurate r_e^{SE} value shows some 20% reduction in the ipso bond angle effect of F substitution.

The conclusion about the improved accuracy of the r_e^{SE} structures compared to previous determinations also applies to the structures of 1,2-difluorobenzene and 1,3-difluorobenzene, for which accurate r_e^{BO} and r_e^{SE} structures have also been determined here. For 1,4-difluorobenzene, our r_e^{BO} estimate clearly supports the joint GED + NMR ring angle distortions [80] and points out the incorrectness of a pure GED study [79].

While the quantitative results, not all summarized here, are certainly important, it is also of special interest to determine qualitatively the structural effects of F substitution on the benzene ring. The structural changes upon F substitution have been determined through a least-squares fit, employing all fluorinated benzenes plus the structure of the reference

benzene molecule. The fitted values of the ring angle distortions are: $\Delta\alpha = 1.95(7)^\circ$, $\Delta\beta = -1.46(4)^\circ$, $\Delta\gamma = 0.63(4)^\circ$ and $\Delta\delta = -0.25(7)^\circ$. Note that deviations up to 0.5° occur in a few random cases for individual fluorinated benzenes, showing the limitations of this empirical approach. Bond length distortions can be determined straightforwardly by assuming $r_{o/m/p} = r_0 + \Delta r_{o/m/p}$ for them, where r_0 is a reference value (like the CC or CH bond lengths in benzene) and performing a least-squares fit to r_c^{BO} results from all-electron cc-pCVTZ CCSD(T) geometry optimizations. For the CC bond lengths of the ring in fluorinated benzenes, from a least-squares fit to 35 bond lengths, including that of benzene, we obtain that $r_0 = 1.39135(27)$ Å, Δr_o is large and negative at $-0.00790(35)$ Å, whereas Δr_m and Δr_p are almost negligible and impossible to determine. For the CH bond lengths, we determine $r_0 = 1.08054(14)$ Å, $\Delta r_o = -0.000922(76)$ Å, $\Delta r_m = -0.000086(76)$ Å and $\Delta r_p = -0.00069(12)$ Å. Note that Δr_m is very small and badly determined and that all CH bond length increments are negative. Note also that the two r_0 values are in good agreement with the r_c^{BO} values of benzene. As to the CF bond length changes, a least-squares fit to 20 r_c^{BO} bond lengths shows that Δr_p is not determined, $r_0 = 1.34261(27)$ Å, $\Delta r_{o1} = -0.00724(29)$ Å, $\Delta r_{o2} = -0.00647(29)$ Å and $\Delta r_m = -0.00243(15)$ Å. Again, r_0 is in good agreement with the reference r_c^{BO} value of fluorobenzene and the bond length corrections are all negative.

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