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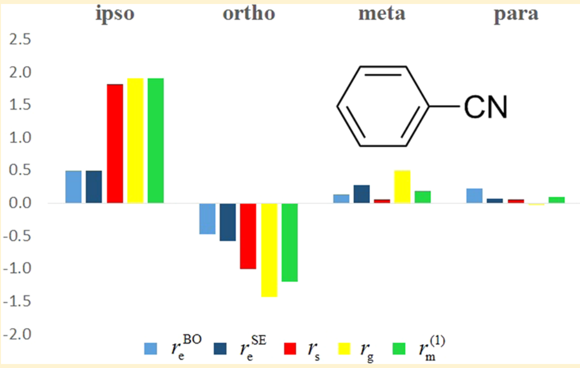
Accurate Determination of the Deformation of the Benzene Ring upon Substitution: Equilibrium Structures of Benzonitrile and Phenylacetylene

Heinz Dieter Rudolph,[†] Jean Demaison,*[,‡] and Attila G. Császár*[,§,∥]

[†]Department of Chemistry, University of Ulm, D-89069 Ulm, Germany
[‡]Laboratoire de Physique des Lasers, Atomes et Molécules, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France
[§]Laboratory of Molecular Structure and Dynamics, Eötvös University, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary
[∥]MTA-ELTE Research Group on Complex Chemical Systems, H-1518 Budapest, Hungary

Ⓢ *Supporting Information*

ABSTRACT: Accurate equilibrium, r_e, structures of the monosubstituted benzene molecules benzonitrile, C_6H_5CN, and phenylacetylene, C_6H_5CCH, have been determined using two different, to some extent complementary techniques. The semiexperimental, r_e^{SE}, structural parameters are the result of a least-squares fit to equilibrium rotational constants derived from experimental effective ground-state rotational constants and rovibrational corrections based principally on an ab initio cubic force field. The composite ab initio Born−Oppenheimer, r_e^{BO}, structural parameters are obtained from frozen-core and all-electron MP2 and the CCSD(T) geometry optimizations using Gaussian basis sets up to quintuple-zeta quality. The DFT(B3LYP) method, with two different Gaussian basis sets, 6-31G* and 6-311+G(3df,2pd), was used to calculate the cubic force field employed during the r_e^{SE} structure determination. With the 6-31G* basis set, the error of the rovibrational correction is to a large extent random, whereas with the 6-311+G(3df,2pd) basis set it is mainly systematic. As shown here, systematic errors do not have a significant effect on the accuracy of the derived structure; the quality of the structural fit, however, is sensitive to the true accuracy of the ground-state rotational constants. An even more important general conclusion of this study is that the addition of extra rotational constants from multisubstituted species does not seem to improve the accuracy of the r_e^{SE} structures, quite in contrast to the highly desirable availability of data corresponding to all singly substituted species.



1. INTRODUCTION

A considerable amount of work has been devoted to understand the effect of substitution on the structure and properties of families of molecules. Substitutions cause a modification of the electronic structure, which affects the reactivity as well as the geometrical structure of the molecule. The effect of replacing a hydrogen atom in the benzene ring by another atom or a functional group, the topic of the present study, has been widely investigated.[1,2]

Up to now, almost all of the experimental structural studies on substituted benzenes relied on gas-phase electron diffraction (GED), microwave (MW) and millimeterwave (MMW) spectroscopies, or X-ray diffraction (XRD). In the case of solid-state XRD, intermolecular interactions may be large, leading to substantial structural distortions, comparable to the intrinsic substitution effects. Furthermore, the derived structures are neither very precise nor accurate. As to GED, molecular interactions become negligible but even in the most favorable cases the obtained structure is significantly different from the equilibrium structure, and even more importantly, GED studies are usually not accurate enough to point out many of the subtle structural trends caused by substitution in the benzene ring. Rotational (primarily MW and MMW) spectroscopy has the reputation of being accurate. This is often true for the primary (observed) data; however, the structures derived by different empirical methods from ground-state rotational constants may be unreliable.

In contrast to the experimental and empirical techniques mentioned, high-level ab initio electronic structure computations have become able to yield Born−Oppenheimer equilibrium structures, r_e^{BO}, of molecules as large as benzene and its derivatives with remarkable accuracy (see, for example, our recent study on fluorobenzenes[3]).[4−6] It must also be mentioned that substituted benzenes are semirigid molecules, i.e., molecules without large-amplitude motions, and for them,

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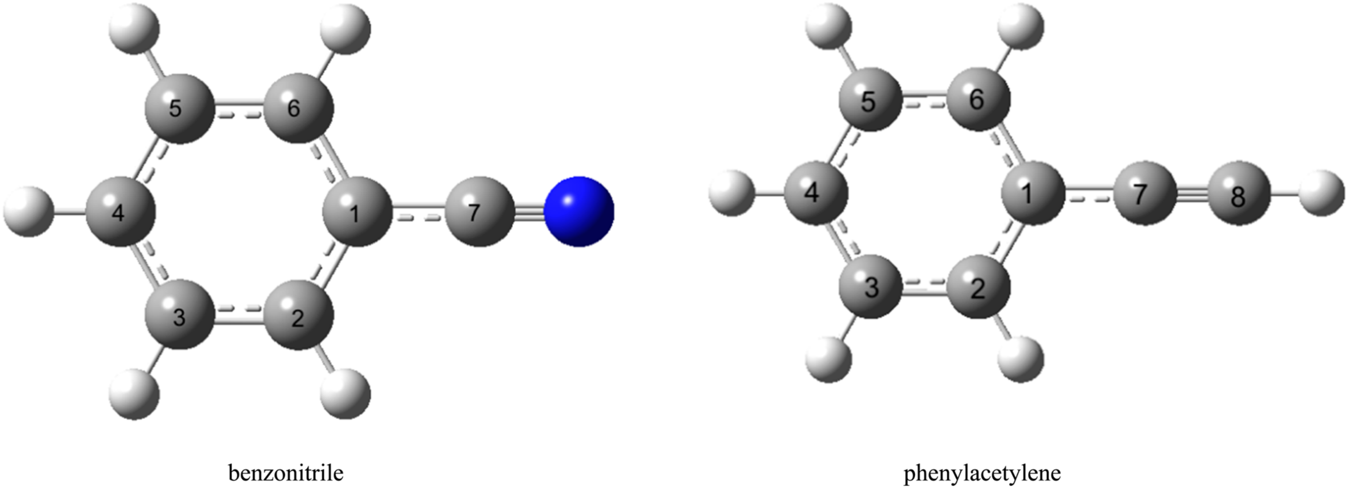

Figure 1. Structure and atomic numbering of the molecules C_6H_5CN, benzonitrile, and C_6H_5CCH, phenylacetylene.

even elementary levels of electronic structure theory, such as 4-21G RHF, yield highly accurate r_e^{BO} estimates.[3,7−9]

The fundamentals of the semiexperimental method, yielding an r_e^{SE} equilibrium structure, have been laid down by Pulay et al.[10] Within this technique a least-squares structural fit is executed with respect to equilibrium rotational constants derived from experimental effective ground-state rotational constants and corrections based principally on an ab initio cubic force field.[11] This method has the reputation of being able to deliver accurate estimates to equilibrium structures of (mostly) semirigid molecules.[12−14] Until today there have been few attempts to determine the equilibrium structure of molecules as large as benzene derivatives. As the size and complexity of the molecule increases, determination of a complete and accurate r_e^{SE} structure becomes more and more difficult either because the system of normal equations in the least-squares fit becomes ill-conditioned or the semiexperimental equilibrium rotational constants become not sufficiently accurate. Among typical examples we mention the case of 1,3,4-oxadiazole (c-$C_2H_2N_2O$),[15] alanine ($C_3H_6NO_2$),[16] glycidol ($C_3H_6O_2$),[17] and *o*-xylene (c-$C_6H_4(CH_3)_2$).[18] Oxadiazole is an oblate symmetric top molecule and there is a large rotation of the principal axis system (PAS) upon isotopic substitution, which amplifies the errors on the rovibrational corrections.[19] For alanine, the somewhat poor performance of the method was explained by the large-amplitude motion of the OH group, which makes accurate computation of the rovibrational correction difficult. For glycidol, it was presumed that the ground-state *A* rotational constant of the OD isotopologue was inaccurate. For *o*-xylene, it was found that the semiexperimental equilibrium rotational constants of the deuterated isotopologues are not fully compatible with those of the nondeuterated ones.

Ill-conditioning is an inherent problem when molecular structure is determined by a nonlinear least-squares fit to the moments of inertia of a set of isotopologues. Dependence of the moments on a sizable number of structural parameters often differs only little from isotopologue to isotopologue. This leads to rather similar and hence nearly collinear fit vectors (column vectors of the Jacobian or design matrix) and a high condition number. The problem is aggravated when the number of structural parameters is not small with respect to that of the isotopologues. In order to reduce the risk of ill-conditioning, it is important to consider two aspects: (*i*) a high point-group symmetry helps to minimize the number of structural parameters to be determined, and (*ii*) accurate ground-state rotational constants should be available for a large number of isotopic species, in particular for all monosubstituted species. Both criteria underlying a successful r_e^{SE} structure determination are satisfied for two substituted benzenes: benzonitrile, C_6H_5CN (PhCN), and phenylacetylene, $C_6H_5CC{\equiv}H$ (PhCCH), see Figure 1. Both molecules are planar and their equilibrium structures have C_{2v} point-group symmetry. The structure of benzonitrile is defined by 12 independent structural parameters, whereas rotational constants are available for ten isotopologues, providing 20 independent observations. The structure of phenylacetylene is defined by 13 independent parameters, while rotational constants are available for 39 isotopologues, yielding 78 independent observations. Thus, besides an intrinsic interest in their structures both molecules are excellent test cases to investigate the utility of determining rotational constants of multiply substituted isotopomers and isotopologues during a structural determination of a medium-sized molecule. A further advantage of these two molecules is that the substituents are quite different: $C{\equiv}N$ is highly electronegative, whereas $C{\equiv}C{-}H$ is a π-electron donor. Thus, interesting and complementary chemical information can be gained via the structural study of these two semirigid substituted benzenes.

2. COMPUTATIONAL DETAILS

2.1. Ab Initio Born−Oppenheimer Equilibrium Structure, r_e^{BO}. The geometry optimizations of this study were mostly performed at the MP2 (second-order Møller−Plesset perturbation theory)[20] and CCSD(T) (coupled cluster theory, including single and double excitations (CCSD)[21] augmented with a perturbational estimate of the effects of connected triple excitations)[22] levels of electronic structure theory. Different atom-centered, fixed-exponent Gaussian basis sets have been utilized, including the correlation-consistent polarized basis sets cc-pVTZ and cc-pVQZ,[23] abbreviated throughout this article as VTZ and VQZ, respectively. Optimizations were also performed with the correlation-consistent polarized weighted core−valence triple-ζ, cc-pwCVTZ,[24] quadruple-ζ, cc-pwCVQZ,[25] and quintuple-zeta, cc-pwCV5Z, basis sets, denoted here as wCVTZ, wCVQZ, and wCV5Z, respectively.

With the wCVTZ, wCVQZ, and wCV5Z basis sets all of the electrons were correlated (AE), whereas with the VTZ and VQZ basis sets the frozen core approximation is normally used. With these basis sets, convergence to the complete basis set (CBS) limit is not fully achieved.[6] Part of the reason is that tight functions are missing from the VTZ and VQZ basis sets and diffuse functions are missing from all the basis sets mentioned. Nevertheless, as shown by Helgaker et al.,[26] the VTZ basis set appears to yield bond distances close to the basis set limit, and as the number of basis functions is relatively small, the optimization is still reasonably fast. In the spirit of the focal-point analysis (FPA) method,[27,28] the corrections to the CCSD(T) results were determined at the MP2 level (vide infra). To check how far away we are with the wCVQZ basis set from the CBS limit the structures were also optimized at the all-electron MP2 level with the aug-cc-pwCV5Z basis set (abbreviated as AwCV5Z). It is comforting to find that the AwCV5Z and wCVQZ basis sets give almost identical results at the MP2(AE) level. Actually, the small wCVQZ → AwCV5Z correction is the sum of two terms that partly compensate each other: the correction wCVQZ → AwCVQZ is positive and of the order of +0.0004 Å for the C−C bond lengths, while the correction AwCVQZ → AwCV5Z is negative and of the order of −0.0006 Å for the C−C bond lengths.

Briefly, composite ab initio r_e^{BO} parameters are obtained in this study for PhCN and PhCCH in four different ways using one of the following equations:

$$\begin{aligned} r_e^{BO}(\mathrm{I}) = {} & \mathrm{wCVTZ\ CCSD(T)\_AE} + [\mathrm{wCVQZ\ MP2(AE)} \\ & - \mathrm{wCVTZ\ MP2(AE)}] + [\mathrm{AwCV5Z\ MP2(AE)} \\ & - \mathrm{wCVQZ\ MP2(AE)}] \end{aligned} \tag{1}$$

$$\begin{aligned} r_e^{BO}(\mathrm{II}) = {} & \mathrm{VTZ\ CCSD(T)\_AE} + [\mathrm{wCVQZ\ MP2(AE)} \\ & - \mathrm{VTZ\ MP2(AE)}] + [\mathrm{AwCV5Z\ MP2(AE)} \\ & - \mathrm{wCVQZ\ MP2(AE)}] \end{aligned} \tag{2}$$

$$\begin{aligned} r_e^{BO}(\mathrm{III}) = {} & \mathrm{VQZ\ CCSD(T)\_FC} + [\mathrm{wCVQZ\ MP2(AE)} \\ & - \mathrm{wCVQZ\ MP2(FC)}] + [\mathrm{AwCV5Z\ MP2(AE)} \\ & - \mathrm{wCVQZ\ MP2(AE)}] \end{aligned} \tag{3}$$

$$\begin{aligned} r_e^{BO}(\mathrm{IV}) = {} & \mathrm{wCVQZ\ CCSD(T)\_AE} \\ & + [\mathrm{AwCV5Z\ MP2(AE)} - \mathrm{wCVQZ\ MP2(AE)}] \end{aligned} \tag{4}$$

In eq 3, the first term in brackets corresponds to a core correlation correction.[29]

In order to determine the cubic force fields,[30] the Kohn−Sham density functional theory (DFT)[31] using Becke's three-parameter hybrid exchange functional[32] and the Lee−Yang−Parr correlation functional,[33] together denoted as B3LYP, was employed. To avoid the nonzero-force dilemma,[34] the cubic force fields were determined at the tightly optimized equilibrium DFT(B3LYP) structures.

The CCSD(T) computations, including the geometry optimizations employing analytic first derivatives,[35] were performed with the CFOUR[36] electronic structure program package. The lower-level, DFT(B3LYP) and MP2, computations utilized the Gaussian09 (G09) program suite.[37]

2.2. Experimental Ground-State Rotational Constants.

During the first structural fits resulting in r_e^{SE} parameters, the published ground-state rotational constants were used. However, it became evident soon that some of the constants are not accurate enough. This observation prompted us to redo the fits of the rotational and centrifugal distortion constants to the observed rotational transitions. Because for many isotopologues the number of measured transitions is small, originally it had not been possible to determine most of the quartic centrifugal distortion constants, they had been set equal to zero in the fits. For this reason, we used the method of predicate observations, in which theoretical centrifugal distortion constants derived from a quadratic 6-311+G(3df,2pd) B3LYP force field are used as supplementary data in a weighted least-squares fit to the transitions.[38,39] The starting uncertainty of these predicate centrifugal distortion constants was 10% of their value. Then, if necessary, the uncertainty of any predicate value was increased until a good fit was obtained. Practically speaking, the objective was to keep the corresponding jackknifed (or studentized) residual, $t(i)$ of any distortion constant i, smaller than about 3, where $t(i)$ is the ith residual divided by its standard deviation calculated by omitting the ith data.[40]

2.3. Semiexperimental Equilibrium Rotational Constants.

To correct the ground-state experimental rotational constants for each isotopologue and to obtain their equilibrium counterparts, cubic force fields were computed at the B3LYP level. Two split-valence basis sets were used, the small 6-31G*, as well as the larger 6-311+G(3df,2pd) basis. The B3LYP functional was chosen for these computations since it is now well established that this level of electronic structure theory generally gives results comparable or even superior to the MP2 method, at a much lower cost.[41−44] Equilibrium rotational constants B_e^β are related to ground-state rotational constants B_0^β to first order by

$$B_e^\beta \approx B_0^\beta + 1/2 \sum_k \alpha_k^\beta \tag{5}$$

where β represents the a, b, and c directions of the principal axes and k scans the normal modes of vibration.[45,46]

In order to deduce correct equilibrium rotational constants from experimental ones, modifications due to the small electronic effect[47] should also be considered besides the larger (first-order) rovibrational corrections. As no experimental values for the related g-constants are known, they were computed, using G09, at the 6-311+G(3df,2pd) B3LYP level using London orbitals.[48] The corrected values of the rotational constants are given by the relation

$$B_{\mathrm{corr}}^\beta = B_{\mathrm{exp}}^\beta \left(1 - \frac{m}{M_p} g_{\beta\beta}\right) \tag{6}$$

where $g_{\beta\beta}$ is expressed in units of the nuclear magneton, m is the electron mass, M_p the proton mass, and $\beta = a$, b, and c.

2.4. Determination of Structural Parameters.

It is common practice in MW spectroscopy to use the Kraitchman substitution method to determine substitution (r_s) structures of molecules.[49] The Kraitchman method does not yield equilibrium structures and is quite sensitive to inherent errors of the rotational constants, in particular when there are atoms with (Cartesian) coordinates, which are small with respect to the principal axes coordinate system. This is the case for PhCN and PhCCH for the two carbon atoms in ortho position relative to the ipso point of substitution.

Table 1. Ab Initio Estimates of the r_e^{BO} Structure of Benzonitrile (Distances, r, in Å; Angles, ∠, in Degrees)

	CCSD(T)				MP2								
	VTZ	wCVTZ	wCVQZ	VQZ	wCVQZ	VTZ	wCVTZ	wCVQZ	AwCV5Z				
parameter[a]	AE	AE	AE	FC	FC	AE	AE	AE	AE	r_e^{BO}(I)[b]	r_e^{BO}(II)[c]	r_e^{BO}(III)[d]	r_e^{BO}(IV)[e]
$r(C_1C_2) \equiv CC_o$	1.3951	1.3980	1.3964	1.3997	1.3968	1.3926	1.3950	1.3936	1.3934	1.3966	1.3961	1.3965	1.3962
$r(C_2C_3) \equiv CC_m$	1.3880	1.3902	1.3884	1.3918	1.3878	1.3844	1.3860	1.3845	1.3843	1.3887	1.3881	1.3885	1.3882
$r(C_3C_4) \equiv CC_p$	1.3920	1.3936	1.3918	1.3952	1.3911	1.3883	1.3894	1.3878	1.3877	1.3920	1.3915	1.3919	1.3917
$r(C_1C_7)$	1.4308	1.4379	1.4362	1.4395	1.4295	1.4217	1.4277	1.4262	1.4259	1.4364	1.4352	1.4362	1.4359
$r(C{\equiv}N)$	1.1610	1.1605	1.1585	1.1614	1.1698	1.1692	1.1686	1.1669	1.1667	1.1588	1.1587	1.1585	1.1583
$r(C_2H) \equiv CH_o$	1.0769	1.0807	1.0802	1.0817	1.0801	1.0759	1.0793	1.0786	1.0787	1.0800	1.0796	1.0802	1.0803
$r(C_3H) \equiv CH_m$	1.0771	1.0811	1.0803	1.0819	1.0802	1.0761	1.0795	1.0787	1.0787	1.0803	1.0797	1.0804	1.0803
$r(C_4H) \equiv CH_p$	1.0773	1.0814	1.0806	1.0822	1.0803	1.0761	1.0796	1.0788	1.0788	1.0806	1.0800	1.0807	1.0806
$\angle(C_2C_1C_6) \equiv CCC_i$	120.29	120.47	120.49	120.52	120.49	120.27	120.44	120.46	120.47	120.49	120.49	120.50	120.50
$\angle(C_1C_2C_3) \equiv CCC_o$	119.70	119.53	119.52	119.50	119.45	119.65	119.48	119.46	119.46	119.52	119.52	119.52	119.52
$\angle(C_2C_3C_4) \equiv CCC_m$	120.07	120.14	120.14	120.14	120.28	120.21	120.27	120.27	120.26	120.13	120.13	120.13	120.13
$\angle(C_3C_4C_5) \equiv CCC_p$	120.15	120.19	120.20	120.21	120.07	120.01	120.10	120.07	120.08	120.21	120.20	120.21	120.22
$\angle(C_1C_2H_2)$	119.53	119.61	119.62	119.62	119.60	119.52	119.60	119.60	119.60	119.62	119.62	119.62	119.61
$\angle(C_2C_3H_3)$	119.75	119.71	119.71	119.71	119.63	119.67	119.63	119.63	119.64	119.71	119.71	119.71	119.72

[a] *i* = ipso, *o* = ortho, *m* = meta, and *p* = para. [b] See eq 1. [c] See eq 2. [d] See eq 3. [e] See eq 4.

Therefore, it is advantageous to use a least-squares fit (LSQ) of the equilibrium structural parameters to the semiexperimental equilibrium moments of inertia. Further advantages of the fitting method are that the first-moment equations are automatically obeyed, that the errors are smoothed, and that an analysis of the residuals permits to estimate the quality of the structural fit. One difficulty remains, the choice of correct weights. They are usually chosen as the reciprocal square of the uncertainty. Because the experimental ground-state rotational constants are usually highly accurate, the uncertainty of the equilibrium rotational constants is determined mainly by the (computed) rovibrational corrections. The accuracy of these corrections ($1/2\alpha$ sums, see eq 5) is usually a few percent of the magnitude of the rovibrational correction.[50] However, the error is mainly systematic, and it is difficult to assess its true magnitude. For this reason, within the present study the weights of the semiexperimental rotational constants were determined iteratively. At each step, an analysis of the residuals permitted checking the appropriateness of the weights and the compatibility of the rotational constants and the predicate observations. It is possible to automate, at least partly, this procedure by using the iteratively reweighted least squares (IRLS) method, whereby data with large residuals are weighted down.[38,51] The advantage of the IRLS method is that it is robust, i.e., it mitigates the influence of outliers. Two different weighting schemes are used in this study: Huber weighting, where the weight linearly decreases as the residual increases, and biweight weighting, where, in addition, data with large residuals are eliminated. Furthermore, as the number of data is small, some of them are influential, i.e., they have a very small residual even if they are quite inaccurate. If their weight is too high, it may lead to biased parameters, i.e., to parameters affected by a systematic error, with corresponding standard deviations which are too small. For this reason, it is important to identify these influential data. Details of the method may be found in refs 33, 35, and 45.

3. BENZONITRILE, PhCN

3.1. Previous Studies. Benzonitrile (also called cyanobenzene), C_6H_5CN, is a singly substituted benzene, with an equilibrium structure of C_{2v} point-group symmetry. Its structure is defined by 12 independent parameters.

The rotational spectrum of PhCN was first measured in 1954 by Erlandson[52] and independently by Lide.[53] Later, the Copenhagen group analyzed the MW spectra of the parent species as well as of nine isotopologues and determined a complete r_s structure.[54] Because PhCN is a molecule of astrophysical interest and is involved in several van der Waals complexes, its microwave spectrum has been reinvestigated several times.[55−60]

Besides ref 54, two investigations are particularly relevant for a structural study. In ref 57, very accurate rotational constants were obtained for the normal species, thanks to MMW spectroscopy. In ref 59, accurate rotational constants were derived for the heavy-atom isotopic species (^{13}C and ^{15}N) with the help of Fourier transform microwave (FTMW) spectroscopy.

The structure of PhCN was also investigated by GED[61] and by a nuclear magnetic resonance (NMR) study in a nematic phase.[62] These last two structures were found to be in good agreement with the r_s structure; in particular, the value of the angle at the *ipso* carbon was found to be $\angle(C_2C_1C_6) = 121.9(3)°$.

3.2. Born−Oppenheimer Equilibrium Structures, r_e^{BO}. Estimates to the Born−Oppenheimer equilibrium structure (r_e^{BO}) of PhCN were computed using eqs 1−4. The results are given in Table 1. The final structures, r_e^{BO}(I), r_e^{BO}(II), r_e^{BO}(III), and r_e^{BO}(IV), are in extremely good agreement, the largest difference is only 0.001 Å for the C_1C_7 bond length. It is also worth noting that the wCVTZ and VTZ CCSD(T)_AE structures are rather close to the best estimate of the r_e^{BO} structure. The latter method provides slightly worse structural parameters; in particular, the CH bond lengths are, as usual, about 0.0027 Å too short, and the VTZ → wCVQZ correction is large for the C_1C_7 bond length, +0.0045 Å.

Table 2. Ground-State and Semiexperimental[a] Equilibrium Rotational Constants of Benzonitrile (MHz)

		N	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	$^{13}C_7$	^{15}N	2D	3D	4D
ground state	A_0	5655.265	5655.526	5563.915	5565.666	5655.453	5655.256	5655.281	5379.403	5383.786	5655.048
	B_0	1546.876	1545.552	1546.803	1535.713	1523.655	1528.641	1502.148	1546.110	1526.279	1496.595
	C_0	1214.404	1213.602	1210.090	1203.373	1200.058	1203.137	1186.659	1200.714	1188.928	1183.208
6-31G*	A_e^{SE}	5695.819	5696.105	5603.590	5605.359	5695.823	5695.587	5695.830	5417.087	5421.594	5695.910
	B_e^{SE}	1553.036	1551.641	1552.930	1541.805	1529.737	1534.737	1508.063	1552.250	1532.359	1502.514
	C_e^{SE}	1220.304	1219.437	1215.950	1209.202	1205.873	1208.982	1192.364	1206.522	1194.686	1188.896
	Δ_e[b]	0.0002	0.0065	0.0005	0.0004	0.0003	−0.0052	0.0002	0.0005	0.0018	0.0001
	ΔA[c]	−0.022	0.264	0.004	0.036	−0.018	−0.254	−0.011	0.018	0.040	0.069
	ΔB[c]	0.001	0.004	0.005	−0.001	0.001	−0.003	0.001	0.001	0.003	−0.002
	ΔC[c]	−0.001	−0.005	0.002	0.000	−0.001	0.001	−0.001	−0.001	−0.002	0.001
6-311+G(3df,2pd)	A_e^{SE}	5698.035	5698.071	5605.689	5607.627	5698.030	5698.050	5698.038	5418.942	5423.687	5698.088
	B_e^{SE}	1553.159	1551.771	1553.047	1541.934	1529.836	1534.854	1508.190	1552.399	1532.500	1502.607
	C_e^{SE}	1220.476	1219.618	1216.115	1209.382	1206.028	1209.143	1192.534	1206.698	1194.867	1189.043
	Δ_e[b]	0.0022	0.0029	0.0024	0.0021	0.0022	0.0026	0.0024	0.0026	0.0041	0.0023
	ΔA[c]	0.031	0.067	0.085	0.045	0.026	0.046	0.034	0.054	0.082	0.084
	ΔB[c]	0.004	0.006	0.000	0.003	0.004	0.006	0.005	0.005	0.007	0.003
	ΔC[c]	−0.003	−0.002	−0.003	−0.002	−0.002	−0.003	−0.003	−0.003	−0.004	−0.002

[a] Rovibrational correction calculated with a B3LYP cubic force field with a basis as indicated in the first column. The semiexperimental equilibrium rotational constants were calculated using eqs 5 and 6; see text. [b] Semiexperimental equilibrium inertial defect. [c] Residuals (obsd − calcd) of the least-squares fit, biweight weighting. They correspond to semiexperimental equilibrium values.

Table 3. Semiexperimental Equilibrium Structures of Benzonitrile (Distances in Å, Angles in Degrees)

basis set[a]	6-31G*			6-311+G(3df,2pd)			
weighting[b]	Kraitchman[c]	Huber	biweight	Huber	biweight	scaled[d]	$r_e^{BO}(IV)$[e]
$r(C_1C_2) \equiv CC_o$	1.3974	1.3977(5)	1.3978(4)	1.3968(6)	1.3968(6)	1.3969(1)	1.3962
$r(C_2C_3) \equiv CC_m$	1.3863	1.3875(6)	1.3875(4)	1.3884(8)	1.3884(7)	1.3881(2)	1.3882
$r(C_3C_4) \equiv CC_p$	1.3916	1.3919(3)	1.3919(2)	1.3917(3)	1.3917(3)	1.3915(1)	1.3917
$r(C_1C_7)$	1.4322	1.4327(7)	1.4326(5)	1.4347(8)	1.4347(8)	1.4343(2)	1.4359
$r(C{\equiv}N)$	1.1611	1.1591(2)	1.1591(2)	1.1582(3)	1.1582(3)	1.15829(6)	1.1583
$r(C_2H) \equiv CH_o$	1.0792	1.0819(6)	1.0819(4)	1.0780(8)	1.0780(8)	1.0780(2)	1.0803
$r(C_3H) \equiv CH_m$	1.0802	1.0796(2)	1.0796(2)	1.0799(3)	1.0799(3)	1.08003(8)	1.0803
$r(C_4H) \equiv CH_p$	1.0800	1.0802(2)	1.0802(1)	1.0800(2)	1.0800(2)	1.07995(5)	1.0806
$\angle(C_2C_1C_6) \equiv CCC_i$	120.42	120.34(8)	120.33(5)	120.55(9)	120.55(9)	120.53(2)	120.50
$\angle(C_1C_2C_3) \equiv CCC_o$	119.55	119.60(5)	119.60(3)	119.42(6)	119.42(6)	119.43(2)	119.52
$\angle(C_2C_3C_4) \equiv CCC_m$	120.15	120.13(2)	120.13(2)	120.27(3)	120.27(3)	120.274(7)	120.13
$\angle(C_3C_4C_5) \equiv CCC_p$	120.20	120.22(2)	120.22(1)	120.07(2)	120.07(2)	120.066(6)	120.22
$\angle(C_1C_2H_2)$	119.46	119.31(8)	119.30(6)	119.77(10)	119.77(10)	119.76(3)	119.61
$\angle(C_2C_3H_3)$	119.69	119.74(3)	119.74(2)	119.63(4)	119.63(4)	119.62(1)	119.72
$\angle(C_4C_3H_3)$	120.16	120.13(2)	120.13(2)	120.10(3)	120.10(3)	120.10(1)	120.10

[a] Basis set used to compute the cubic force field with the B3LYP method. [b] Weighting method used in the least-squares fit, see text. [c] Structure calculated with Kraitchman's equations. [d] The rovibrational corrections are scaled, see text, and the weights used are (in kHz): 20 for A, 1.2 for B, and 0.4 for C. [e] See Table 1.

3.3. Semiexperimental Equilibrium Structure, r_e^{SE}.

The anharmonic force fields of the ten isotopologues listed in Table 2 were computed at the 6-31G* and 6-311+G(3df,2pd) B3LYP levels of electronic structure theory. The optimized structures are given in Table S1 of the Supporting Information. The derived α-constants were combined with the experimental ground-state rotational constants to yield estimates of semiexperimental equilibrium rotational constants, which were also corrected for the electronic contribution. The calculated values of the molecular g-tensor for the parent species are g_{aa} = −0.0825, g_{bb} = −0.0391, and g_{cc} = +0.0111. The experimental ground state inertial defect is Δ_0 = +0.080 uÅ^2 for the parent species, after the rovibrational correction it is −0.0132 uÅ^2 with the 6-31G* B3LYP force field, and after the electronic correction it is Δ_e = 0.0002 uÅ^2, i.e., practically zero. This confirms that the rovibrational correction is likely to be accurate and that the electronic correction, although small, is not negligible. The 6-311+G(3df,2pd) B3LYP force field gives similar results. The semiexperimental equilibrium rotational constants obtained are listed in Table 2.

The structure of PhCN was first determined in this study via Kraitchman's equations. The a-coordinate of the two *ortho*-carbon atoms is small, $a(C_o)$ = 0.151 Å, and the b coordinates of the *para*-carbon, cyano-carbon, and nitrogen atoms turn out to be imaginary and thus had to be zeroed. For this reason, the derived structure, given in Table 3, is not expected to be accurate, as can be seen by comparing the values of Tables 1 and 3.

Next, the structure was determined using the LSQ method. Different weighting schemes were used, as described in section 2.4. In the first fits, the published ground-state rotational constants were used to derive the semiexperimental equilibrium

Table 4. Comparison of Different Structures of Benzonitrile (Distances in Å, Angles in Degrees)

method	r_e^{BO}(IV)	r_e^{SE}	r_s	r_s	$r_m^{(1)}$	r_g	r_α
ref	*a*	*b*	54	59	*c*	61	62
$r(C_1C_2) \equiv CC_o$	1.3962	1.3968	1.3876(5)	1.398	1.389(2)	1.400(3)	1.402(2)
$r(C_2C_3) \equiv CC_m$	1.3882	1.3884	1.3956(4)	1.395	1.395(2)		
$r(C_3C_4) \equiv CC_p$	1.3917	1.3917	1.3974(4)	1.397	1.395(1)		
$r(C_1C_7)$	1.4359	1.4347	1.4509(6)	1.444	1.449(2)	1.438(5)	1.434(3)
$r(C{\equiv}N)$	1.1583	1.1582	1.1581(2)	1.156	1.1574(7)	1.168(3)	1.166(6)
$r(C_2H) \equiv CH_o$	1.0803	1.0780	1.0803(6)	1.081	1.077(2)	1.086(3)	1.082(2)
$r(C_3H) \equiv CH_m$	1.0803	1.0799	1.0822(3)	1.081	1.0808(7)		
$r(C_4H) \equiv CH_p$	1.0806	1.0800	1.0796(4)	1.080	1.0791(6)		
$\angle(C_2C_1C_6) \equiv CCC_i$	120.498	120.554	121.82(5)	121.16	121.9(2)	121.90(14)	120.8(9)
$\angle(C_1C_2C_3) \equiv CCC_o$	119.516	119.421	119.00(4)	119.15	118.8(1)	118.57(8)	119.4(2)
$\angle(C_2C_3C_4) \equiv CCC_m$	120.127	120.266	120.06(3)	120.15	120.18(6)	120.49(3)	119.7(4)
$\angle(C_3C_4C_5) \equiv CCC_p$	120.217	120.073	120.05(3)	120.21	120.10(7)	119.98(9)	121.0(6)
$\angle(C_1C_2H_2)$	119.611	119.772			120.5(3)		
$\angle(C_2C_3H_3)$	119.717	119.631	120.01(3)		119.85(8)		
$\angle(C_4C_3H_3)$	120.156	120.103			119.97(7)		
$\angle(C_3C_2H_2)$	120.872	120.807	120.36(5)		120.7(2)		

[a] This work, see Table 1. [b] This work, see Table 3. [c] Empirical mass-dependent structure, this work.

rotational constants. Some rotational constants were downweighed during the IRLS fits and, in particular, the *A*-constant of the d_4 species was excluded. Furthermore, inspection of the equilibrium inertial defects shows rather large variations: their range is 0.019 uÅ^2 with the 6-31G* B3LYP force field and 0.013 uÅ^2 with the 6-311+G(3df,2pd) B3LYP force field. For these reasons, the ground-state rotational constants were redetermined as described in section 2.2. With these new constants the range of the equilibrium inertial defect becomes much smaller: 0.0012 uÅ^2 with the 6-31G* B3LYP force field and 0.0020 uÅ^2 with the 6-311+G(3df,2pd) B3LYP force field. The situation is not yet perfect because the A_0 constant of the PhCN-d_4 species is still not very accurate. This is due to the fact that only a few *a*-type transitions were measured for this near-prolate top. If this species is excluded, the range of the inertial defect decreases to 0.0008 uÅ^2 (6-311+G(3df,2pd) B3LYP value), which is very pleasing. Furthermore, the fits are now of high quality, the IRLS weights being almost identical for all species. These results are also given in Table 3. Both IRLS weighting schemes, Huber and biweight, give practically identical results, which is again highly satisfactory. The two force fields give compatible results, and their precision is quite similar. However, small differences are observed for the $r(C_2H)$ bond length, 0.0029(10) Å, the $\angle(C_2C_1C_6)$ angle, 0.22(7)°, and the $\angle(C_1C_2H)$ angle, 0.47(12)°. This may be explained by the small value of the *a*-coordinate of the C_2 atom, $a(C_2) = 0.1509(5)$ Å. In each case, the structure derived with the help of the 6-311+G(3df,2pd) B3LYP force field is in better agreement with the r_e^{BO} structure. The better overall accuracy of this force field is confirmed by the analysis of the inertial defects, see above.

There are two further points worth discussing. First, it has to be noted that the two B3LYP force fields give semiexperimental equilibrium rotational constant estimates which are slightly different, the difference, 6-311+G(3df,2pd) − 6-31G*, in MHz being 2.16(17) for A_e^{SE}, 0.12(2) for B_e^{SE}, and 0.17(1) for C_e^{SE}. The standard deviation of the differences is given in parentheses. It shows that these differences are mainly systematic. This is the reason why they do not significantly affect the results, although they are not negligible. Then, inspection of the residuals of the structure derived from the 6-311+G(3df,2pd) B3LYP force field, see Table 2, shows that they are affected by systematic deviations, they are all positive for *A* and *B*, and all negative for *C*, their median (in MHz) is 0.05(2) for *A*, 0.004(1) for *B*, and −0.003(0) for *C*. This is in agreement with the fact that the semiexperimental inertial defects are different from zero with values close to 0.002 uÅ^2. It is known that the rovibrational correction is affected mainly by a systematic error, which is a few percent of the rovibrational correction.[50] It is possible to correct for this error by multiplying all the rovibrational corrections by a constant factor *f* of 1.0236; with this choice the equilibrium inertial defect of the parent species becomes zero. The subsequent fit is much better: the reduced standard deviation of the fit is $s = 1.6$, the standard deviations of the parameters and the systematic deviations of the residuals are much smaller. However, the parameters of this new fit are almost identical to those of the previous fits, confirming that small systematic errors do not have much effect on the values of the structural parameters.[63] The results of this last fit are given in the last column of Table 3.

Finally, it has to be noted that with the 6-31G* B3LYP force field the deviations of the residuals of the fit are less systematic. It is perhaps due to the fact that the basis set is much smaller, which apparently induces more random noise.

3.4. Comparison with Previous Studies.

Table 4 compares the different determinations of the structure of PhCN. The r_e^{BO} and r_e^{SE} structures are in extremely good agreement. Furthermore, they appear to be accurate. Bond angles determined either by GED or NMR should generally be close to the values of the equilibrium angles. However, in the present case the experimental determinations are, unfortunately, rather inaccurate. For example, the r_g-type estimate of the ipso bond angle distortion obtained by GED is some 350% too large when compared to the equilibrium distortion, which we consider as well determined. Such a large discrepancy in the ipso angle transfers into significant errors of the GED distortions in the other bond angles.

It is not possible to directly compare the equilibrium bond lengths with the values obtained by either GED or NMR because the latter are vibrationally averaged values.[64] Also, it was necessary to make several assumptions to determine them.

Table 5. Ab Initio Estimates of the r_e^{BO} Structure of Phenylacetylene (Distances, r, in Å; Angles, ∠, in Degrees)

	CCSD(T)				MP2								
	VTZ	wCVTZ	wCVQZ	VQZ	wCVQZ	VTZ	wCVTZ	wCVQZ	wCV5Z				
parameter[a]	AE	AE	AE	FC	FC	AE	AE	AE	AE	r_e^{BO}(I)[b]	r_e^{BO}(II)[c]	r_e^{BO}(III)[d]	r_e^{BO}(IV)[e]
$r(C_1C_2) \equiv CC_o$	1.3973	1.4003	1.3987	1.4027	1.3995	1.3952	1.3976	1.3962	1.3960	1.3987	1.3981	1.3992	1.3985
$r(C_2C_3) \equiv CC_m$	1.3884	1.3904	1.3888	1.3921	1.3880	1.3847	1.3861	1.3847	1.3846	1.3888	1.3883	1.3887	1.3886
$r(C_3C_4) \equiv CC_p$	1.3919	1.3934	1.3917	1.3950	1.3912	1.3884	1.3894	1.3879	1.3878	1.3917	1.3913	1.3916	1.3915
$r(C_1C_7)$	1.4274	1.4341	1.4325	1.4356	1.4253	1.4181	1.4237	1.4221	1.4219	1.4323	1.4312	1.4322	1.4322
$r(C_7C_8)$	1.2092	1.2096	1.2076	1.2107	1.2147	1.2131	1.2133	1.2116	1.2115	1.2078	1.2075	1.2074	1.2075
$r(C_2H) \equiv CH_o$	1.0779	1.0811	1.0806	1.0821	1.0806	1.0769	1.0797	1.0791	1.0791	1.0805	1.0801	1.0806	1.0806
$r(C_3H) \equiv CH_m$	1.0776	1.0815	1.0808	1.0823	1.0806	1.0765	1.0799	1.0791	1.0791	1.0808	1.0803	1.0809	1.0808
$r(C_4H) \equiv CH_p$	1.0775	1.0814	1.0808	1.0823	1.0805	1.0763	1.0797	1.0790	1.0790	1.0807	1.0801	1.0808	1.0808
$r(C_8H)$	1.0590	1.0628	1.0619	1.0632	1.0611	1.0575	1.0607	1.0598	1.0597	1.0618	1.0612	1.0618	1.0618
$\angle(C_2C_1C_6) \equiv CCC_i$	119.28	119.45	119.45	119.47	119.39	119.21	119.37	119.37	119.38	119.46	119.45	119.46	119.45
$\angle(C_1C_2C_3) \equiv CCC_o$	120.30	120.13	120.13	120.12	120.12	120.29	120.13	120.13	120.13	120.13	120.13	120.13	120.13
$\angle(C_2C_3C_4) \equiv CCC_m$	120.16	120.21	120.21	120.21	120.29	120.24	120.29	120.29	120.29	120.21	120.21	120.21	120.21
$\angle(C_3C_4C_5) \equiv CCC_p$	119.81	119.86	119.87	119.87	119.80	119.74	119.79	119.80	119.80	119.87	119.87	119.87	119.87
$\angle(C_1C_2H_2)$	119.26	119.26	119.26	119.26	119.20	119.19	119.20	119.20	119.19	119.25	119.26	119.25	119.26
$\angle(C_4C_3H_3)$	120.12	120.10	120.10	120.10	1.3995	120.08	120.06	120.06	1.3960	120.09	120.10	120.09	120.09

[a] *i* = ipso, *o* = ortho, *m* = meta, and *p* = para. [b] See eq 1. [c] See eq 2. [d] See eq 3. [e] See eq 4.

It appears that the different empirical structures, substitution, r_s, and even mass-dependent,[65] r_m, cannot be relied upon for PhCN.

4. PHENYLACETYLENE, PhCCH

4.1. Previous Studies. Phenylacetylene (also called ethynylbenzene), $C_6H_5C{\equiv}CH$, is a singly substituted benzene with an equilibrium structure of C_{2v} point-group symmetry. Its structure is defined by 13 independent parameters.

The rotational spectrum of PhCCH was first measured by Zeil et al.[66] Later, Cox et al.[67] conducted a thorough study of the rotational spectra of several isotopologues and were able to derive a complete empirical structure, mostly r_s, but only with the help of data from the structurally similar PhCN. More recently, the rotational spectrum of PhCCH was reinvestigated by FTMW spectroscopy, and the rotational constants of 39 isotopologues were determined.[68] In this work, empirical structures, mainly mass-dependent ones,[65] were calculated and compared with an ab initio structure of CCSD(T) quality using a simple complete basis set extrapolation method. Despite the large number of isotopologues, the mass-dependent structures were not able to give an accurate structure. A problem with this method is that it introduces additional parameters (three or six or more) to take into account the rovibrational contribution: whereas the quality of the model improves, the ill-conditioning of the fit worsens. PhCCH was also investigated by GED.[69] The authors point to a significant difference between their GED results and the MW results of Cox et al.[67] in the ipso region of the carbon ring, the discrepancy in the $\angle(C_2C_1C_6)$ angle being 1°.

4.2. Born−Oppenheimer Equilibrium Structure, r_e^{BO}. Estimates of the Born−Oppenheimer equilibrium structure (r_e^{BO}) of PhCCH were computed using eqs 1−4. The results are given in Table 5. The final r_e^{BO} structure is close to the wCVTZ CCSD(T)_AE and VTZ CCSD(T)_AE ones but rather different from the approximate CCSD(T) structure of ref 68. The final structures are in extremely good agreement, the only significant difference, as small as 0.001 Å, is for the C_1C_7 bond length. For the VTZ CCSD(T)_AE structure the CH bond lengths are, as usual, about 0.0026 Å too short. The large VTZ → wCVQZ correction for the C_1C_7 bond length, +0.004 Å, is also worth noting.

4.3. Semiexperimental Structure, r_e^{SE}. The rotational constants are given in Table 6 for the monosubstituted species and Table S3 of the Supporting Information for all species. The ground-state rotational constants of PhCCH were redetermined in this study in the same same way as for PhCN, i.e., using the method of predicate observations (see section 2.2). In general good agreement was found with the previous determination.[68] For the B_0 and C_0 rotational constants, the differences are negligible, of the order of 1 kHz. However, the differences for the A_0 constants are a few tens of kHz, up to 120 kHz. This is easily explained by the fact that the centrifugal distortion constants were kept fixed in the previous study. The required anharmonic force fields for the 39 isotopologues of ref 68 were computed at the 6-31G* and 6-311+G(3df,2pd) B3LYP levels of electronic structure theory. The structures optimized at these levels of theory are given in Table S2 of the Supporting Information. It is interesting to compare the rovibrational corrections calculated with the two force fields. For the B and C constants, the differences are small, their range is only 0.10 MHz. For the A constants the situation is more complex: the median of the differences is 1.74 MHz but with a rather large range of 1.54 MHz.

The computed α constants were combined with the known experimental ground-state rotational constants to yield semi-experimental equilibrium rotational constants, which were also corrected for the electronic contribution. As there are no experimental values available for the molecular g-tensor, they were computed at the 6-311+G(3df,2pd) B3LYP level. The results for the parent species are $g_{aa} = -0.088$, $g_{bb} = -0.0244$, and $g_{cc} = +0.0210$. The rotational constants are given in Table 6. Before discussing the determination of the structure, it is interesting to have a look at the equilibrium inertial defects Δ_e, which should be zero in the absence of errors. With the 6-31G*

Table 6. Ground-State, B_0^β, and Semiexperimental Equilibrium, B_e^β, Rotational Constants (MHz) as Well As Inertial Defects, Δ (uÅ^2), of Phenylacetylene

force field			6-31G*		6-311+G(3df,2pd)		6-311+G(3df,2pd) + scaling	
species	β	B_0^β	B_e^β	o − c	B_e^β	o − c	B_e^β	o − c
parent	*a*	5680.3467	5721.631	−0.078	5723.420	0.056	5725.770	−0.032
	b	1529.7419	1535.729	0.002	1535.604	0.008	1535.925	0.002
	c	1204.9551	1210.755	−0.001	1210.742	−0.006	1211.061	0.000
	Δ	0.0787	−0.0005		0.0048		0.0000	
$^{13}C_1$	*a*	5680.5717	5721.630	−0.079	5723.414	0.049	5725.752	−0.050
	b	1528.3268	1534.248	0.007	1534.127	0.010	1534.445	0.002
	c	1204.0902	1209.835	0.003	1209.824	−0.005	1210.140	0.000
	Δ	0.0776	−0.0008		0.0045		−0.0002	
$^{13}C_2$	*a*	5588.8164	5629.207	−0.025	5630.943	0.065	5633.242	−0.034
	b	1529.6857	1535.637	0.005	1535.513	0.009	1535.832	0.001
	c	1200.7461	1206.506	0.003	1206.494	−0.005	1206.811	−0.001
	Δ	0.0797	−0.0005		0.0047		−0.0001	
$^{13}C_3$	*a*	5590.2442	5630.670	−0.059	5632.454	0.090	5634.757	−0.015
	b	1518.9770	1524.901	−0.009	1524.778	0.009	1525.096	0.001
	c	1194.2018	1199.935	−0.007	1199.926	−0.003	1200.241	0.001
	Δ	0.0801	−0.0003		0.0045		−0.0004	
$^{13}C_4$	*a*	5680.5317	5721.620	−0.089	5723.424	0.059	5725.764	−0.038
	b	1507.1748	1513.089	−0.003	1512.960	0.011	1513.276	0.003
	c	1190.9212	1196.639	−0.004	1196.623	−0.003	1196.937	0.002
	Δ	0.0774	−0.0007		0.0043		−0.0004	
$^{13}C_7$	*a*	5680.3165	5721.679	−0.031	5723.420	0.055	5725.772	−0.030
	b	1511.5669	1517.455	−0.012	1517.350	0.004	1517.666	−0.004
	c	1193.6501	1199.371	−0.007	1199.367	−0.008	1199.681	−0.003
	Δ	0.0782	−0.0007		0.0045		−0.0003	
$^{13}C_8$	*a*	5680.3748	5721.649	−0.060	5723.435	0.071	5725.785	−0.017
	b	1483.8219	1489.593	0.009	1489.466	0.006	1489.775	−0.002
	c	1176.2757	1181.896	0.004	1181.878	−0.007	1182.186	−0.002
	Δ	0.0812	−0.0003		0.0049		−0.0001	
D2	*a*	5402.6588	5440.987	−0.059	5442.522	0.067	5444.697	−0.027
	b	1528.9637	1534.931	−0.005	1534.835	0.005	1535.156	−0.001
	c	1191.4888	1197.200	−0.002	1197.200	−0.005	1197.515	0.001
	Δ	0.0780	−0.0016		0.0040		−0.0008	
D3	*a*	5406.4958	5444.976	−0.016	5446.516	0.057	5448.699	−0.024
	b	1509.8365	1515.742	−0.010	1515.651	0.007	1515.970	0.001
	c	1180.0221	1185.682	−0.005	1185.684	−0.006	1185.995	0.000
	Δ	0.0787	−0.0008		0.0047		−0.0001	
D4	*a*	5680.1342	5721.739	0.029	5723.519	0.154	5725.886	0.084
	b	1480.7553	1486.510	−0.011	1486.384	0.002	1486.692	−0.005
	c	1174.3652	1179.959	−0.004	1179.939	−0.007	1180.246	−0.002
	Δ	0.0711	−0.0007		0.0052		0.0008	
D8	*a*	5680.5204	5721.639	−0.071	5723.425	0.060	5725.766	−0.036
	b	1450.2368	1455.573	−0.004	1455.502	0.009	1455.790	0.003
	c	1155.0710	1160.375	−0.006	1160.390	−0.006	1160.683	0.000
	Δ	0.0833	0.0003		0.0052		0.0002	

B3LYP force field, Δ_e is small, its median value is only −0.0006 uÅ^2, but its range is rather large at 0.0352 uÅ^2. This indicates that there is probably some random noise in the rovibrational correction, as described for PhCN. With the 6-311+G(3df,2pd) B3LYP force field, Δ_e is larger, its median value being 0.0049 uÅ^2 but its range at 0.0064 uÅ^2 is much smaller. This indicates that the error is now mainly systematic. It is also noteworthy that $\Delta_e(D_2{}^{13}C_4)$ = 0.0005 uÅ^2 is probably an outlier. Indeed, for this species, the A_0 rotational constant is significantly less accurate.

The semiexperimental equilibrium structure, r_e^{SE}, of PhCCH was first determined in this study with the help of Kraitchman's equations.[49] Next, it was determined by the least-squares method, first using the experimental uncertainties of the ground-state constants for the weighting, then using the IRLS method with Huber weighting and biweight weighting. The results are given in Table 7.

On the basis of the comparison of the results obtained, we note that the use of the experimental uncertainties for the weighting gives the worst results. This is not surprising because the experimental uncertainty of the ground-state rotational constants is not expected to be a good approximation of the uncertainty of the semiexperimental constants. In particular, it appears that the *A* constants of the isotopologues are much less accurate than assumed. Kraitchman's equations give satisfactory results, except for the $r(C_2C_3)$ bond length, which may be

Table 7. Semiexperimental Equilibrium Structures r_e^{SE} of Phenylacetylene (Distances in Å, Angles in Degrees)

force field[a]	L	S	S	L	L	L + scaling[b]	L + scaling[b]	L + scaling[b]	
method	Kraitchman	Huber	biweight	Huber	biweight	Huber	biweight	biweight[c]	r_e^{BO}(IV)
C_1C_2	1.3986	1.4013(5)	1.4011(4)	1.3989(4)	1.3989(4)	1.3990(2)	1.3990(2)	1.3990(1)	1.3985
C_2C_3	1.3891	1.3854(7)	1.3856(5)	1.3890(5)	1.3890(5)	1.3886(2)	1.3886(2)	1.3882(1)	1.3886
C_3C_4	1.3912	1.3918(3)	1.3918(2)	1.3916(2)	1.3916(2)	1.3912(1)	1.3912(1)	1.3912(1)	1.3915
C_1C_7	1.4315	1.4300(7)	1.4301(5)	1.4310(5)	1.4310(5)	1.4304(2)	1.4304(2)	1.4309(1)	1.4322
C_7C_8	1.2070	1.2067(2)	1.2067(2)	1.2071(2)	1.2071(2)	1.2071(1)	1.2071(1)	1.2069(1)	1.2075
C_2H_2	1.0769	1.0819(7)	1.0815(5)	1.0776(5)	1.0776(5)	1.0776(2)	1.0776(2)	1.0777(2)	1.0806
C_3H_3	1.0805	1.0809(3)	1.0808(2)	1.0802(2)	1.0802(2)	1.0802(1)	1.0802(1)	1.0803(1)	1.0808
C_4H_4	1.0805	1.0804(2)	1.0804(2)	1.0802(2)	1.0802(2)	1.0802(1)	1.0802(1)	1.0805(1)	1.0808
C_8H_8	1.0602	1.0613(2)	1.0613(1)	1.0603(1)	1.0603(1)	1.0607(1)	1.0607(1)	1.0605(1)	1.0618
$C_6C_1C_2$	119.50	119.19(8)	119.21(5)	119.47(6)	119.47(6)	119.42(2)	119.42(2)	119.42(2)	119.45
$C_1C_2C_3$	120.07	120.23(5)	120.22(3)	120.09(4)	120.10(4)	120.12(2)	120.12(1)	120.11(1)	120.13
$C_2C_3C_4$	120.28	120.27(2)	120.26(2)	120.26(2)	120.26(2)	120.26(1)	120.26(1)	120.27(1)	120.21
$C_3C_4C_5$	119.82	119.82(2)	119.83(2)	119.83(2)	119.83(2)	119.82(1)	119.82(1)	119.82(1)	119.87
$C_1C_2H_2$	119.48	118.91(9)	118.96(6)	119.52(6)	119.52(6)	119.49(3)	119.49(3)	119.47(2)	119.26
$C_4C_3H_3$	120.13	120.03(3)	120.04(2)	120.13(2)	120.13(2)	120.14(1)	120.14(1)	120.13(1)	120.09
$C_3C_2H_2$	120.46	120.860(7)	120.82(5)	120.39(5)	120.39(5)	120.39(2)	120.40(2)	120.42(1)	120.62
$C_2C_3H_3$	119.60	119.71(3)	119.70(3)	119.61(2)	119.61(2)	119.60(1)	119.60(1)	119.60(1)	119.70

[a] L = 6-311+G(3df,2pd) B3LYP; S = 6-31G* B3LYP. [b] See text. [c] Fit using only the 11 singly substituted species.

explained by the fact that one coordinate of C_2 is small, $a(C_2)$ = 0.143 Å. The two IRLS fits are excellent, and the resulting parameter values differ little among the different fits, mostly even less than the very small parameter errors, and this holds for all three approaches used, see Table 7. The largest differences are found for the $r(C_2C_3)$ and $r(C_2H_2)$ bond lengths and for the $\angle(C_1C_2H_2)$ bond angle. This may be partly explained by the fact that the *a*-coordinate of C_2 is tiny and therefore quite sensitive to small errors in the rotational constants. The particular case of the $r(C_2H_2)$ bond length will be discussed below. For the $r(C_2C_3)$ bond length and the $\angle(C_1C_2H_2)$ bond angle, the structure derived with the help of the 6-311+G(3df,2pd) B3LYP cubic force field seems to be more accurate. Furthermore, the biweight weighting does not outweigh any of the 117 observations, whereas seven are outweighed from the fit when using the 6-31G* B3LYP force field. Generally, the structure derived from the 6-311+G-(3df,2pd) B3LYP cubic force field seems to be slightly better. This is confirmed by a comparison with the r_e^{BO} structure, and this is in agreement with the more constant residual value of the equilibrium inertial defect. However, besides the value of $r(C_2H_2)$, which seems to be slightly too small, the fit is still not fully satisfactory; we provide the following arguments and possible improvements: (*i*) the residuals of the fit are not random, as can be seen in Table 6, for the *A* rotational constant, all residuals are positive with a median value of 87 kHz, and for the *C* constant, all residuals are negative with a median value of −5 kHz; (*ii*) in both IRLS fits, the condition number is rather large, around 1300, and the variance-decomposition proportions indicate a potentially harmful collinearity between $r(C_1C_2)$, $\angle(C_1C_2C_7)$, $r(C_3C_4)$, and $r(C_1C_7)$, which is mainly a consequence of the small coordinate of C_2; (*iii*) comparison of the r_e^{SE} parameters with the r_e^{BO} ones of Table 5 indicates that the former are accurate, and as the standard deviations of the correlated parameters are quite small, the collinearity should not be harmful, apart from the fact that their confidence intervals are larger than the usually accepted three times standard deviations; and (*iv*) the systematic deviations observed for the residuals of the fit are in agreement with the fact that the semiexperimental inertial defects are different from zero with values close to 0.005 uÅ^2. As for PhCN, it is easy to reduce them by multiplying all the rovibrational corrections by a constant factor *f* of 1.0549, chosen to make the equilibrium inertial defect of the parent species zero. The resulting fit, given in the last column of Table 7, is much better, the standard deviations of the parameters are 2.4 times smaller and the systematic deviations of the residuals are much smaller. However, the parameters of this new fit are almost identical to those of the previous fits, confirming again that small systematic errors do not have much effect on the values of the structural parameters.

It is informative to analyze the origin of the small discrepancy concerning the $r_e^{SE}(C_2H_2)$ bond length. It is tempting to attribute this disagreement to the small coordinate of the C_2 carbon atom. However, inspection of the Cartesian coordinates (Table 8) clearly shows that the inconsistency is due to the *a*-coordinate of H_2. Use of Kraitchman's equations shows that it is enough to reduce the *B* rotational constant (either B_0 or B_e) of the D_2 isotopologue by 15.8 kHz to obtain a good agreement. This value is quite small, although larger than the standard deviation of the B_0 rotational constant, 0.07 kHz; this standard deviation does not take into account the systematic errors due, in particular, to the centrifugal distortion. The conclusion is that the *a*-coordinate of H_2 happens to be quite sensitive to the value of the *B* rotational constant of the D_2 isotopologue, due to the small value of $\Delta I_b = I_b(D_2) - I_b(\text{parent})$ = 0.165 uÅ^2.

Table 8. Cartesian Coordinates (Å) of the C_2 Carbon Atom and the H_2 Hydrogen Atom of Phenylacetylene

	semiexperimental r_e^{SE}		ab initio r_e^{BO}		difference	
	a	*b*	*a*	*b*	Δ*a*	Δ*b*
C_2	0.1403	1.2080	0.1408	1.2082	−0.0005	−0.0002
H_2	−0.4021	2.1391	−0.4071	2.1395	0.0050	−0.0004
C_2H_2	1.0776		1.0805		−0.0030	

It is tempting to incorporate other substitution sequences in the analysis in order to try to improve the accuracy of the *a*-coordinate, for instance, $^{13}C_n \rightarrow D_2{}^{13}C_n$ with n = 1−8. The

Table 9. Comparison of Different Structures of Phenylacetylene (Distances in Å, Angles in Degrees)

parameter[a]	r_e^{BO}(IV)	r_e^{SE}	CBS[b]	GED[c]	r_g	$r_m^{(2)}$
ref	this work	this work	68	69	68	68
$r(C_1C_2) \equiv CC_o$	1.3985	1.3990(2)	1.3988	1.407(3)	1.3926(8)	1.3945(7)
$r(C_2C_3) \equiv CC_m$	1.3886	1.3886(2)	1.3890	1.397(3)	1.3957(6)	1.3914(7)
$r(C_3C_4) \equiv CC_p$	1.3915	1.3912(1)	1.3920	1.400(3)	1.3955(3)	1.3932(4)
$r(C_1C_7)$	1.4322	1.4304(2)	1.4311	1.436(4)	1.4447(7)	1.4407(7)
$r(C_7C_8)$	1.2075	1.2071(1)	1.2059	1.205(5)	1.2074(2)	1.2057(3)
$r(C_2H) \equiv CH_o$	1.0806	1.0776(2)	1.0766		1.0763(6)	1.0991(26)
$r(C_3H) \equiv CH_m$	1.0808	1.0802(1)	1.0768		1.0813(2)	1.0850(5)
$r(C_4H) \equiv CH_p$	1.0808	1.0802(1)	1.0766		1.0794(2)	1.0832(5)
$r(C_8H)$	1.0618	1.0607(1)	1.0569	1.086(14)	1.0544(1)	1.0570(3)
$\angle(C_2C_1C_6) \equiv CCC_i$	119.45	119.42(2)	119.43	119.8(4)	120.72(9)	120.24(9)
$\angle(C_1C_2C_3) \equiv CCC_o$	120.13	120.12(1)	120.16	120.0(4)	119.52(5)	119.73(4)
$\angle(C_2C_3C_4) \equiv CCC_m$	120.21	120.26(1)	120.20	120.1(5)	120.22(2)	120.23(2)
$\angle(C_3C_4C_5) \equiv CCC_p$	119.87	119.82(1)	119.86	120.1(7)	119.81(2)	119.83(2)
$\angle(C_1C_2H_2)$	119.26	119.49(3)	119.26		120.27(9)	118.03(25)
$\angle(C_4C_3H_3)$	120.09	120.14(1)	120.10		119.99(2)	119.70(4)

[a] *i* = ipso, *o* = ortho, *m* = meta, and *p* = para. [b] CCSD(T) structure with extrapolation using the VDZ and VTZ basis sets. [c] Gas-phase electron diffraction, r_g structure.

results of Kraitchman's equations with the 6-31G* B3LYP force field and with the 6-311+G(3df,2pd) B3LYP force field without and with scaling are given in Table S4 of the Supporting Information. For the *a* coordinate, the 6-31G* B3LYP force field gives results close to the r_e^{BO} structure but with a larger scattering than with the 6-311+G(3df,2pd) B3LYP force field. With the latter force field there is a systematic deviation of about 0.006 Å, the effect of the scaling being almost negligible. For the *b* coordinate, the agreement between the r_e^{BO} structure and the different r_e^{SE} structures is extremely good. It confirms our previous results that (*i*) random errors are smaller with the 6-311+G(3df,2pd) B3LYP force field but with a larger systematic error; and (*ii*) scaling does not improve significantly the situation indicating that it is not able to completely eliminate the systematic error. The failure to improve the accuracy of the *a* coordinate is due to the fact that for all substitution schemes ΔI_b remains quite small because H_2 stays close to the principal axis *b*.

These results make one wonder whether the multiply substituted species (MSS) are really useful in a structure determination. It is generally recognized that it is advisable to have the rotational constants of all singly substituted species in order to avoid the problem of ill-conditioning. However, the usefulness of MSS is less clear. From the statistical point of view, it is recommended to have a number of degrees of freedom larger than about 20 in order to have a reliable and as small as possible confidence interval, assuming that the errors are mainly random. However, it is not obvious whether MSS bring new information, i.e., that they really improve the accuracy of the parameters. Indeed, it is possible to estimate the rotational constants of the MSS once the rotational constants of all singly substituted species are known.[70] In other words, MSS do not bring truly new information. However, a small coordinate is extremely sensitive to small errors of the rotational constants. One way to reduce the extent of this problem, at least in theory, is to use a MSS for which the substitution shifts the center of mass in the right direction, i.e., increases the absolute value of the coordinate. The problem is that the shift is usually small, in particular for larger molecules. Furthermore, the rotational constants of the MSS are often less accurate because only a limited number of transition frequencies could be measured. For these reasons the use of MSS does not result in a significant improvement of the accuracy of the fitted structural parameters. PhCCH is a prime example to study this problem: the C_2 carbon atom has a very small *a* coordinate, 0.14 Å, and a large number of MSS is available. However, when the hydrogen farthest from the center of mass is substituted by deuterium, the *a* coordinate of C_2 becomes only slightly larger, 0.18 Å. Comparison of the fit with the full set of 39 isotopologues with the much smaller set of the 11 singly substituted species does not show any significant difference, see the last column of Table 7. In conclusion, it seems more important to try to improve the accuracy of the ground-state rotational constants of the monosubstituted species than to determine constants for multisubstituted ones.

4.4. Comparison with Previous Studies.

Table 9 compares the different determinations of the structure of PhCCH. The r_e^{BO} and r_e^{SE} structures of this study are in extremely good agreement. Furthermore, they appear to be accurate. The agreement with the previous CCSD(T) optimization with an attempted extrapolation to the CBS limit is of moderate quality, but it has to be noted that the extrapolation was made using the VDZ and VTZ basis set results and such extrapolations starting from the very small VDZ basis set will likely give inaccurate results.[71]

The angles determined by GED should be close to the values of the equilibrium angles. Although this statement is confirmed, in the present case the experimental angles from GED are rather inaccurate.

The comparison with the empirical mass-dependent structures is also interesting. It confirms that these structures are not reliable for molecules as large as PhCCH. Here, they are not even able to predict the sign of the distortions of the ring angles.

It is of general interest to try to understand why the r_m method fails to deliver an accurate estimate of the equilibrium structure. The first reason is rather obvious: the r_m method introduces supplementary parameters, three for $r_m^{(1)}$, six for $r_m^{(2)}$, and even up to nine when the rotation of the principal axis system upon isotopic substitution is large. As the number of structural parameters is already large, 13 in the present case, the least-squares system becomes ill-conditioned, as noted in ref 68.

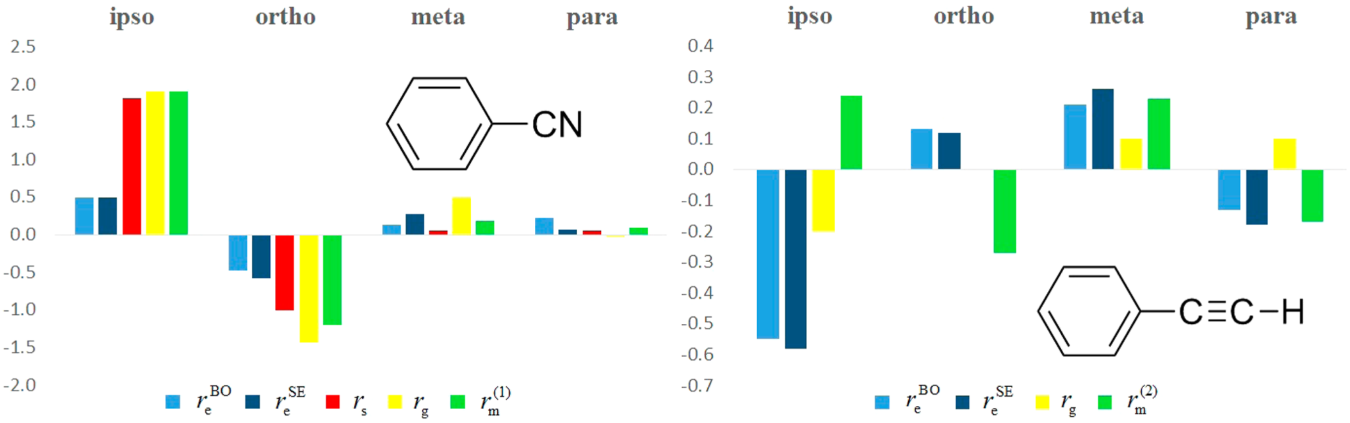

Figure 2. Comparison of inner-ring angle distortions of benzonitrile and phenylacetylene obtained with different techniques, using benzene as reference.

The second reason is that there are several small coordinates, in particular C_1, C_2, and H_2, which require extremely accurate rotational constants for their determination. The third reason is that the molecule contains six hydrogen atoms, and it is known that the r_m method has difficulties to determine the position of these atoms accurately. There is a fourth reason, as well: the r_m method is only an approximate one, and therefore, the small errors inherent to the r_m model may be amplified considerably when the least-squares system is not extremely well conditioned, or when there are small coordinates. For instance, using the rovibrational corrections calculated at the 6-311+G(3df,2pd) B3LYP level, it appears that the $r_m^{(1)}$ model is able to predict the rovibrational corrections with an accuracy of about 0.2 MHz, which seems quite good. Indeed, if we assume that the $r_m^{(1)}$ structure is identical to the r_e one it is possible to write the relationship between the ground-state inertial moments, I_0^β, and the equilibrium inertial moments, I_e^β, as

$$I_0^\beta = I_e^\beta + c_\beta\sqrt{I_e^\beta} \qquad (7)$$

and the parameters c_β may be determined by a least-squares fit to the ab initio rovibrational corrections. However, the errors of the fit do not show any systematic deviation, contrary to the semiexperimental rovibrational corrections. These nonsystematic errors are the cause of the poor behavior of the $r_m^{(1)}$ method. This may be compared with the need to have accurate ground-state rotational constants, although their random errors are orders of magnitude smaller than the mainly systematic errors of the semiexperimental rovibrational corrections.

For the sake of completeness, the substitution r_s structure derived from Kraitchman's equations is compared to the r_e^{BO} structure in Table S5 of the Supporting Information. The accuracy of the r_s Cartesian coordinates, including the hydrogen atoms, is about 0.004 Å, but it is significantly worse for the small coordinates, in particular the *a* coordinate of the C_2 carbon atom, $a_e^{BO}(C_2) = 0.141$ Å, for which the error is as large as 0.031 Å. It has to be noted that Costain's rule[72,73] underestimates the errors by a factor larger than two.

5. CONCLUSIONS

Accurate equilibrium structures have been determined for benzonitrile and phenylacetylene using two different methods: a composite ab initio approach based on all-electron MP2 and CCSD(T) optimizations with basis sets up to quintuple-zeta quality (r_e^{BO}), and the semiexperimental method (r_e^{SE}), which combines the experimental ground-state rotational constants and rovibrational corrections derived from ab initio cubic force fields. Results from the two methods are in good agreement, indicating that these estimates of the equilibrium structures are accurate.

The B3LYP method was employed to compute the rovibrational corrections used in the r_e^{SE} structure determination with the following two Gaussian basis sets: the small 6-31G* and the much larger 6-311+G(3df,2pd). The two basis sets give compatible results but with the larger basis set the error on the rovibrational corrections is mainly systematic, which does not, however, affect the accuracy of the r_e^{SE} structure. In the particular case of phenylacetylene, it appears that the Cartesian *a* coordinate of the H_2 hydrogen atom in the principal axis system is extremely sensitive to the value of the rotational constant of the D_2 isotopologue. It is shown that this is due to the small value of $\Delta B = B(D_2) - B(\text{parent})$, which renders it very sensitive to small errors. It is confirmed again in this study that highly accurate, in extreme cases on the order of a few kHz, ground-state rotational constants are required to obtain an accurate r_e^{SE} structure. It is also observed that the addition of extra rotational constants from multisubstituted species does not seem to improve the accuracy of the r_e^{SE} structure (although it may improve its precision).

The accurate equilibrium structure estimates of this study can be compared to the empirical substitution (r_s) and mass-dependent (r_m) structures of previous studies. For the r_s structure, the error is about twice as large as predicted by Costain's rule; furthermore, the small coordinates exhibit a very large error. Results of the r_m method are not satisfactory either. This is mainly due to the fact that the number of parameters to be determined is large, making the least-squares system ill-conditioned.

For benzonitrile, the present results are in moderate agreement with those of a previous GED study, and they are much more accurate. In particular, the deformation of the ipso angle at +0.50(9)° is much smaller than the incorrect GED value, 1.90(14)°, see Figure 2. Furthermore, the bond length changes upon substitution are accurately determined for the first time. For phenylacetylene, the disagreement between the GED and the empirical structures is explained as follows: the small coordinates of the C_1 and C_2 carbon atoms do not permit to obtain a reliable structure from the ground-state rotational constants.

As discussed in our previous study on fluorobenzenes,[3] the best estimates for the structure of benzene are $r_e^{SE}(CC)$ = 1.3914(10) and $r_e^{SE}(CH)$ = 1.0802(20) Å. These values, along with bond angles of 120°, provide the reference values for the present study of the structural effects of substitution of a H atom by the substituents CN and CCH.

The ipso angle α is sensitive to the σ-inductive effect of the substituent and increases linearly with the electronegativity of the substituent. This increase is correlated with a decrease of the ortho angle β. With an electronegative substituent a shortening of the ortho CC bond, CC_o is expected, as in fluorobenzene. The other bonds are barely affected. However, when the substituent is a π-electron donor, the effect is the opposite, and in particular, the α angle decreases with increasing conjugation, see Figure 2.

Indeed, in benzonitrile, the increase of α, +0.49°, the r_e^{BO} estimate, is associated with a decrease of the ortho angle β, −0.48°. The meta angle γ and the para angle δ are barely affected. It is worth noting that $\Delta\alpha$ in cyanobenzene is quite small, although the substituent CN is electronegative. It may be interpreted by the fact that this substituent is also a π-electron donor, which explains the large increase in the CC_o bond length, +0.005 Å, whereas a decrease is expected for an electronegative substituent. As expected, one observes in phenylacetylene a small decrease of α, −0.55°. In this case, the other angles are barely affected. In good agreement with this decrease, $r(CC_o)$ = 1.3989 Å is substantially longer than in benzene, while the other bond lengths are very close to the benzene value. The $r(CH)$ bond lengths in both molecules are not significantly different from the value found in benzene.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table S1 contains estimates of the structure of benzonitrile computed at the B3LYP level of theory. Table S2 contains estimates of the structure of phenylacetylene computed at the B3LYP level of theory. Table S3 contains ground-state and semiexperimental equilibrium rotational constants of phenylacetylene. Table S4 contains Cartesian coordinates of the H_2 hydrogen atom in the principal axis system of the parent molecule phenylacetylene using different substitution schemes. Table S5 contains a comparison of the substitution r_s and the r_e^{BO} structures of phenylacetylene. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*(A.G.C.) E-mail: csaszar@chem.elte.hu.
*(J.D.) E-mail: Jean.demaison@gmail.com.

Notes

The authors declare no competing financial interest.

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