J. Phys. Chem. 1989, 93, 7644-7651

binding enthalpies (ΔH) can be obtained with electrostatic parameterization methods similar to those employed in this work. It is therefore of particular interest to note that the ab initio calculated ΔH_{298} (−2.1 kcal/mol) and the SOLDRI-MM2 ground-state binding energy (−1.3 kcal/mol) are substantially closer (0.8 kcal/mol) than the respective ΔE data. This may suggest that SOLDRI-MM2 binding energies are best compared to ab initio ΔH data.

Conclusions

Using a combination of ab initio and SOLDRI-MM2 techniques, we have performed one of the most complete studies of the CO_2–water potential energy surface reported to date. Our ab initio results at the MP2/6-311+G**//6-31G** level of sophistication are in good agreement with the experimental structure and are somewhat lower than the experimental binding enthalpy (ΔH_{298}). The potential energy surfaces generated by SOLDRI-MM2 and 6-31G**//SOLDRI-MM2 are in very good qualitative agreement and reasonable to good quantitative agreement. Agreement between ground-state binding energies calculated by SOLDRI-MM2 (−1.3 kcal/mol) and MP2/6-311+G**//6-31G** corrected to ΔH_{298} (−2.1 kcal/mol) is very good.

These observations support our previous position[4] regarding the utility of the SOLDRI-MM2 approach.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Academic Computing Services at the University of Delaware for support of this research. We thank Dr. Dean Nairn for useful input regarding graphics. W.C.F.M. thanks the University of Delaware for a University Fellowship.

Registry No. CO_2, 124-38-9.

Supplementary Material Available: Tables of structural parameters for **1b** and **1f** calculated with normal Gaussian 82 optimization convergence criteria (2 pages). Ordering information is given on any current masthead page.

Theoretical Prediction of the Vibrational Spectrum, Geometry, and Scaled Quantum Mechanical Force Field for Phenylacetylene

Attila G. Császár,* Gêza Fogarasi,

Laboratory of Theoretical Chemistry, Eötvös Lorând University, Mûzeum krt, 6-8, H-1088 Budapest, Hungary

and James E. Boggs

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712 *(Received: April 4, 1989)*

The optimized geometry and the complete harmonic force field of phenylacetylene have been determined by ab initio Hartree–Fock calculations, using a 4-21 Gaussian basis set. Systematic errors in the bond lengths, characteristic at this level of theory, were corrected by empirical offset values. Only at the ipso position does the equilibrium geometry obtained in this way differ significantly from the experimental one (MW; r_g). A detailed analysis suggests that while the experimental ipso CCC angle may be correct, the ipso CC distance should be reconsidered. The force field was evaluated at the above geometry as a reference. To remove systematic deficiencies, the final scaled quantum mechanical (SQM) force field was obtained by applying scale factors optimized previously for benzene and acetylene. All force constants that occur both in phenylacetylene and in the isoelectronic molecule benzonitrile are very nearly the same. Frequencies calculated from the SQM force field of phenylacetylene confirm, with only a few exceptions, the published experimental assignments for all four isotopomers investigated. When the C–H (and C–D) stretching frequencies, perturbed by anharmonicity, are not considered, the average deviation between the observed and calculated frequencies is below 10 cm^{-1}. Theoretical dipole moment derivatives are discussed, and infrared intensities are presented. Quartic centrifugal distortion constants, calculated also from the SQM force field, agree well with the results of an incomplete experimental study.

Introduction

Following a basic study on benzene,[1] the harmonic scaled quantum mechanical (SQM) force fields[2] of several monosubstituted benzene derivatives have been determined and discussed by us: fluorobenzene,[3] aniline,[4] toluene,[5] and benzonitrile.[6] The results, obtained from relatively simple ab initio calculations by using empirical corrections to eliminate systematic errors (a procedure called scaling), represent the most reliable force fields available for complex molecules. The calculations were performed to gain insight into the effects of substitution on the force field and electronic structure of these molecules and, since SQM force fields give reliable predictions for calculating vibrational normal modes, to correct possible experimental misassignments of their vibrational spectra. Here, we report similar calculations on phenylacetylene, C_6H_5CCH.

The microwave (MW) spectrum of phenylacetylene (hereafter PA) was studied by Cox et al.,[7] who obtained ground-state rotational constants and a hybrid-type ($r_s - r_0$) geometry, the centrifugal distortion constants (in the symmetric top approximation), and the dipole moment.

The first fairly complete assignment of the vibrational spectrum of PA was published by Evans and Nyquist.[8] In a detailed study by King and So,[9] the infrared and laser Raman spectra of four isotopomers of PA (C_6H_5CCH, C_6H_5CCD, C_6D_5CCH, and C_6D_5CCD) were obtained and fully interpreted. For the nondeuterated molecule, the lowest b_1 and b_2 fundamentals were reassigned from the single vibronic level fluorescence spectra.[10]

---

(1) Pulay, P.; Fogarasi, G.; Boggs, J. E. *J. Chem. Phys.* **1981**, *74*, 3999.

(2) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037.

(3) Fogarasi, G.; Császár, A. G. *Spectrochim. Acta* **1988**, *44A*, 1067.

(4) Niu, Z.; Dunn, K. M.; Boggs, J. E. *Mol. Phys.* **1985**, *55*, 421.

(5) Xie, Y.; Boggs, J. E. *J. Comput. Chem.* **1986**, *7*, 158.

(6) Császár, A. G.; Fogarasi, G. *Spectrochim. Acta, Part A*, in press.

(7) Cox, A. P.; Ewart, I. C.; Stigliani, W. M. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 504.

(8) Evans, J. C.; Nyquist, R. A. *Spectrochim. Acta* **1960**, *16*, 918.

(9) King, G. W.; So, S. P. *J. Mol. Spectrosc.* **1970**, *36*, 468.

0022-3654/89/2093-7644$01.50/0

TABLE I: Internal Coordinates for Phenylacetylene[a]

no.	internal coord	description
	In-Plane	
1	r_1	CH str (CH′)
2	r_2	C≡C str (C≡C)
3	r_3	CC str (CC′)
4–8	$r_4, ..., r_8$	CH str (CH)
9–14	$R_1, ..., R_6$	CC str (CC)
15	λ_1	CCC linear bending (λ_1)
16	λ_2	CCH linear bending (λ_2)
17	$\beta_1 = 2^{-1/2}(\varphi_1 - \varphi_1')$	CC deformn (βCC′)
18–22	$\beta_2, ..., \beta_6$	CH deformn (βCH)
23	$q_{23} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$	b_{1u} ring deformn
24	$q_{24a} = 12^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$	e_{2g} ring deformn
25	$q_{24b} = {}^1/_2(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$	e_{2g} ring deformn
	Out-of-Plane	
26	λ_3	CCC linear bending (λ_3)
27	λ_4	CCH linear bending (λ_4)
28	γ_1	CC wag (γCC′)
29–33	$\gamma_2, ..., \gamma_6$	CH wag (γCH)
34	$q_{34} = 6^{-1/2}(\delta_1 - \delta_2 + \delta_3 - \delta_4 + \delta_5 - \delta_6)$	b_{2g} ring deformn
35	$q_{35a} = {}^1/_2(-\delta_1 + \delta_3 - \delta_4 + \delta_6)$	e_{2u} ring deformn
36	$q_{35b} = 12^{-1/2}(-\delta_1 + 2\delta_2 - \delta_3 - \delta_4 + 2\delta_5 - \delta_6)$	e_{2u} ring deformn

[a] See Figure 1. γ_1 is the angle of the C–C′ bond with the $C_6C_1C_2$ plane, etc. All waggings are positive if the X (X = C/H) atom moves toward the positive *Z* direction. δ_1 is the $C_6C_1C_2C_3$ dihedral angle, and so on cyclically; the signs of these torsional coordinates are defined according to: Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955. λ_i (i = 1, 4) are defined as $\pi - \alpha$(CCX; X = C/H); their signs are such that the X = C/H atoms move in the positive *X* direction in λ_1 and λ_2 and in the positive *Z* direction in λ_3 and λ_4.

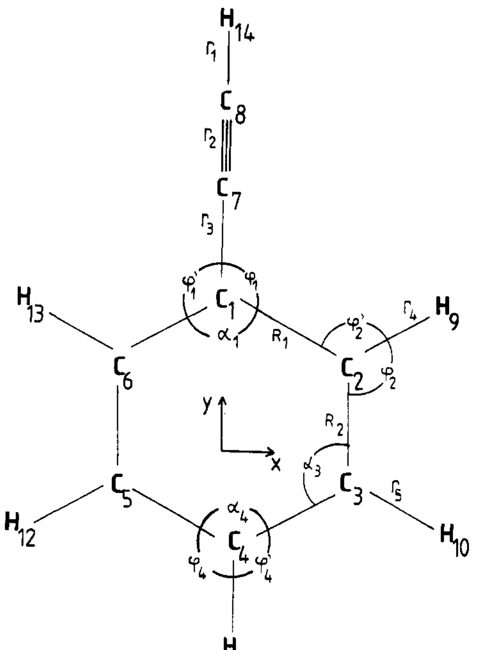

Figure 1. Numbering of atoms and individual internal coordinates in phenylacetylene.

TABLE II: Structural Results for Phenylacetylene[a]

parameter	exptl (MW[7])[b]	theor (4–21)[c]
$r(C_1C_2)$	1.388 (4)	1.402
$r(C_2C_3)$	1.396 (5)	1.392
$r(C_3C_4)$	1.398 (1)	1.395
$r(C_1C_7)$	1.448 (5)	1.440
$r(C_7C_8)$	1.208 (1)	1.206
$r(C_2H_9)$		1.076
$r(C_3H_{10})$		1.077
$r(C_4H_{11})$		1.077
$r(C_8H_{14})$	1.055 (1)	1.061
$\angle(C_6C_1C_2)$	120.8 (4)	119.4
$\angle(C_1C_2C_3)$	119.8 (4)	120.2
$\angle(C_2C_3C_4)$	119.9 (2)	120.2
$\angle(C_3C_4C_5)$	119.9 (2)	119.9
$\angle(C_1C_2H_9)$		119.4
$\angle(C_2C_3H_{10})$		119.8

[a] Distances (r) in angstroms; angles ($\angle$) in degrees. For numbering of atoms, see Figure 1. [b] The atomic coordinates for C_1 and C_2 were not substitution coordinates. For the refinement of the molecular structure, the ring CH parameters have been assumed from benzonitrile.[24b] [c] Present results, corrected theoretical geometry used as reference in the force constant calculations, see text. For comparison, the corresponding values in benzene[1] are r(CC) = 1.395 Å and r(CH) = 1.077 Å and in acetylene[15] r(CC) = 1.203 Å and r(CH) = 1.061 Å.

Simplified overlay valence force fields of PA were published recently by Baranović et al.[11] and by Pietilä et al.[12] Still, it is of interest to calculate a force field for PA a priori, since it is the intrinsic feature of the overlay technique that a considerable number of assumptions regarding the force constants is used. Thus, for example, the overlay calculations of Baranović et al.[11] provided only a set of 24 in-plane and 9 out-of-plane refined force constants for PA.

Since a byproduct of an ab initio calculation of the force field is the equilibrium geometry, this is also presented and discussed in this paper. An analysis of the force field and the vibrational spectra of PA and its above-mentioned deuterated isotopomers then follows. Discussion of the calculated dipole derivatives and infrared intensities comes next. Calculation of quartic centrifugal distortion constants from SQM force fields has proved to be fairly accurate;[13,14] as an additional application, the SQM force field of PA is used to obtain these constants.

Computational Details

In performing the calculations, we exactly followed the scheme described in detail in ref 2 and 15. The actual calculations were carried out by the force method of Pulay,[16] using TEXAS, an ab initio gradient program.[17] The Gaussian basis set used throughout the calculations is denoted as 4-21.[15] Scaling of the force constants was also done as described previously.[2] Infrared intensities were calculated from the theoretical, unadjusted dipole moment derivatives and the SQM force field.

The internal coordinates of PA, selected in accordance with the recommendations of ref 15, are defined in Table I and Figure 1.

In Table II, the experimental and the theoretical geometry of PA are compared. The theoretical geometry presented is the one used in this study for the evaluation of the force constants. It was obtained by empirical correction of the theoretical equilibrium geometry, determined by complete optimization, with use of the following offset values:[15] +0.010 Å for ≡C—H, +0.018 Å for C≡C, +0.002 Å for C—CCH, +0.005 Å for the ring C—H, and +0.010 Å for the ring C—C bonds.

The scale factors used in this study to correct for the systematic deficiencies of the calculated force fields were, when appropriate,

---

(10) Bacon, A. R.; Hollas, J. M.; Ridley, T. *Can. J. Phys.* **1984**, *62*, 1254.

(11) Baranović, G.; Colombo, L.; Skare, D. *J. Mol. Struct.* **1986**, *147*, 275.

(12) (a) Pietilä, L.-O.; Mannfors, B.; Palmö, K. *Spectrochim. Acta* **1988**, *44A*, 141. (b) Palmö, K.; Mannfors, B.; Pietilä, L.-O. *Spectrochim. Acta* **1986**, *42A*, 1265.

(13) (a) Wlodarczak, G.; Martinache, L.; Demaison, J.; van Eijck, B. P. *J. Mol. Spectrosc.* **1988**, *127*, 200. (b) Wlodarczak, G.; Burie, F.; Demaison, F.; Vormann, K.; Császár, A. G. *J. Mol. Spectrosc.* **1989**, *134*, 297.

(14) Császár, A. G.; Fogarasi, G. *J. Chem. Phys.* **1988**, *89*, 7646.

(15) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550.

(16) (a) Pulay, P. *Mol. Phys.* **1969**, *17*, 197. (b) Pulay, P. In *Modern Theoretical Chemistry*; Schafer, H. F., III, Ed.; Plenum: New York, 1977; Vol. 4, pp 153–185.

(17) Pulay, P. *Theor. Chim. Acta* **1979**, *50*, 299.

taken from benzene (set II in Table VIII of ref 1). To get scale factors for the C≡C and C—H′ (C_8—H_{14}) stretching and for the CCH linear bending motions, we optimized the 4-21 force constants of acetylene, calculated as part of this study in exactly the same way as for PA, by fitting to the observed vibrational frequencies.[18] The optimized scale factors of acetylene are as follows: 0.86 for C≡C stretching, 0.08 for C—H stretching, and 0.60 for CCH linear bending. (The scaled force constants are listed in a footnote to Table III.) Then, as a necessary simplification, equal scale factors were assumed for all the linear bending motions of PA (λ_i, $i = 1$–4 in Table I). For CC′ (C_1C_7) stretching, CC′ bending, and CC′ wagging, the same scale factors were used as for the ring CC stretchings (0.911), CH bendings (0.797), and CH waggings (0.739), respectively.

At this point, it is necessary to discuss a discrepancy found in acetylene. For the linear bending frequencies, the performance of our simple scaling procedure is much poorer than usual. With the optimized bending scale factor (0.60), the calculated vs experimental (anharmonic) frequencies are as follows: $\pi_g = 659$ vs 613 cm^{-1}, $\pi_u = 683$ vs 730 cm^{-1}. Clearly, the basic problem is the drastic underestimation of the splitting. In terms of individual bending coordinates, this splitting depends mainly on the coupling force constant connecting the HCC and CCH linear bendings in the 2 × 2 force constant matrix. The directly calculated 4-21 value of this coupling, 0.093 aJ rad^{-2}, is very close to the experimental result of Suzuki and Overend,[18] 0.10 aJ rad^{-2}, while the final scaled value is 0.056 aJ rad^{-2}, obviously too low. In our standard scaling scheme,[2] $F^{\mathrm{SQM}} = \mathbf{C}^{1/2}F^{\mathrm{th}}\mathbf{C}^{1/2}$ (the diagonal **C** matrix containing the scale factors), thus an F_{ij} off-diagonal constant is multiplied by $(c_ic_j)^{1/2}$. This handling of the couplings has no strict theoretical basis but makes the scaling invariant against most coordinate transformations. In most cases, the exact validity of this treatment is not a crucial question, because a reasonable estimate of the small coupling constants is perfectly satisfactory. In the present case, however, two modes are connected that are degenerate in zero order, thus becoming extremely sensitive to the coupling constant. The underestimation of the coupling of linear bendings will have its consequences in the calculated vibrational spectrum of PA.

Calculation of vibrational amplitudes, Coriolis coupling, and quartic centrifugal distortion constants has been performed with a slightly modified version of the ASYM20 program of Hedberg.[19]

Results and Discussion

Geometry. An available check to judge the quality of the theoretical (corrected) equilibrium geometry of PA is the calculation of the moments of inertia from it. From the geometry given in the third column of Table II, the calculated moments (amu Å^2) are as follows: $I_a = 88.67$, $I_b = 331.13$, and $I_c = 419.80$. For comparison, the experimental I^0 values[7] in this order are as follows: 88.970 (5), 330.3668 (6), and 419.416 (1). The latter values are subject to vibrational averaging, as indicated also by the inertia defect $\Delta = I_c - I_a - I_b = 0.08$ amu Å^2. Using our SQM force field to be discussed in the next section, we have calculated the harmonic vibrational corrections to obtain the following I^z values: $I_a = 88.98$, $I_b = 330.40$, and $I_c = 419.37$ amu Å^2, i.e., the inertia defect has been lowered to practically zero. It can also be concluded that vibrational effects on the moments of inertia are small, and the agreement between theory and experiment is very satisfactory.

Considering the individual geometry parameters (see Table II), the theoretical results are fairly close to the reported MW structure.[7] Agreement for the bond lengths in the substituent is very reasonable. The ring structure shows very little change from that of benzene in both cases. There is, however, a notable difference between the two structures at the ipso position. Calculation predicts a ring bond angle decrease and, at the same time, a CC bond distance increase, while the experimental structure shows a bond angle increase and a distance decrease, if compared to the undistorted benzene values.

When the ipso angle is discussed, it seems more reasonable, as suggested by Domenicano,[20] to try to separate steric and electronic effects of the substituent. To this aim, we take toluene as the reference molecule, assuming the substituent effect in it to be primarily steric. The ipso angle in toluene is about 118°,[5] and then, both the theoretical and the experimental ipso angles in PA, 119.4° and 120.8°, respectively, show an increase, in agreement with VSEPR predictions[21] based on the relatively large electronegativity of the CCH group.[22] Comparing the magnitudes of change, shows, however, a significant difference. One has to take into consideration that both in fluorobenzene[3] and in benzonitrile[6] and in fact in most benzene derivatives[23] Hartree–Fock calculations (also with larger basis sets) seem to slightly underestimate the ipso angle. Thus, in PA, the somewhat larger experimental value cannot be questioned.

At the same time, all our experience suggests that the relative values of the calculated ring CC bond lengths are quite reliable, so that the MW results, giving the ortho length as the shortest one, should be reconsidered. This is the more reasonable, because some assumptions had to be made in the evaluation of the MW data; as the most important approximation, the positions of atoms C_1 and C_2 were obtained from second-moment equations based on an assumed analogy with benzonitrile.[24]

The calculated dipole moment of PA coincides, accidentally, with the measured value, 0.656 (5) D.[7]

Force Field. Our results for the complete harmonic in-plane and out-of-plane force fields of PA are compiled in Tables III and IV. To conserve space, several columns that follow from symmetry have been omitted.

The small changes in the geometry of PA compared to that of benzene already suggest that the force field of PA should be fairly similar to that of benzene.[1] It is even more important to notice the close relationship with benzonitrile,[6] a molecule isoelectronic with PA: all the force constants that occur in both compounds agree almost perfectly. This fact in itself is an important conclusion of the present paper. In the following, we focus our attention on the remaining part of the force field that is novel in PA.

First, one should comment on the scale factor used for the linear bending motions. Its value of 0.60 (obtained in acetylene, see Computational Details above) is significantly lower than typical bending scale factors (0.75–0.85);[2] in fact, this is not surprising since a similar value was found for the linear bending in HCN, 0.65.[6] Apparently, description of the shape of the potential curve of a linear bending involving a triple bond is expectionally poor. It should be emphasized that this cannot be attributed to the relatively simple theoretical model (Hartree–Fock, small basis set) used in the present study: even in highest level calculations with large basis sets and including electron correlation, the calculated frequencies of the linear bendings are extremely sensitive to the particular theoretical model assumed.[25] Having no better choice for an a priori prediction of the vibrational spectrum, we use the same scale factor for all four linear bending motions, although it is clear that the error in the description of the "in-plane" and "our-of-plane" linear bendings (which no longer form a degenerate pair, as in HCN or HCCH) could be different.

Starting the discussion of the force field with the stretchings, an obvious observation is that the acetylenic CH′ force constant

---

(18) Suzuki, I.; Overend, J. *Spectrochim. Acta* **1969**, *25A*, 977.

(19) Hedberg, L. *Abstracts of Papers*, 8th Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, March 1978, p 49.

(20) Domenicano, A.; Mazzeo, P.; Aciago, A. *Tetrahedron Lett.* **1976**, *13*, 1029.

(21) Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* **1957**, *11*, 389. Gillespie, R. J. *Molecular Geometry*; Van Nostrand Reinhold: New York, 1972.

(22) Bergmann, D.; Hinze, J. *Struct. Bonding (Berlin)* **1987**, *66*, 146.

(23) (a) Bock, C. W.; Trachtmann, M.; George, P. *J. Mol. Struct.* **1985**, *122*, 155. (b) Bock, C. W.; Trachtmann, M.; George, P. *J. Comput. Chem.* **1985**, *6*, 592.

(24) (a) Bak, B.; Christensen, D.; Dixon, W. B.; Hansen-Nygaard, L.; Rastrup-Andersen, J. *J. Chem. Phys.* **1962**, *37*, 2027. (b) Casado, J.; Nygaard, L.; Sorensen, G. O. *J. Mol. Struct.* **1971**, *8*, 211.

(25) Simandiras, E. D.; Rice, J. E.; Lee, T. J.; Amos, R. D.; Handy, N. C. *J. Chem. Phys.* **1988**, *88*, 3187.

TABLE III: In-Plane SQM Force Field of Phenylacetylene[a]

no.[b]	1 $r(CH')$	2 $r(C{\equiv}C)$	3 $r(CC')$	4 $r(CH)$	5 $r(CH)$	6 $r(CH)$	9 $r(CC)$	10 $r(CC)$	11 $r(CC)$	15 λ_1	16 λ_2	17 $\beta CC'$	18 βCH	19 βCH	20 βCH	23 ring	24 ring	25 ring
1	5.858																	
2	−0.146	15.561																
3	0.007	0.067	5.430															
4	0.001	0.008	0.010	5.211														
5	−0.001	0.004	0.007	0.014	5.178													
6	0.000	0.002	0.001	0.003	0.014	5.175												
7	−0.001	0.004	0.007	0.001	0.003	0.014												
8	0.001	0.008	0.010	0.004	0.001	0.003												
9	0.003	−0.052	0.388	0.060	−0.007	−0.022	6.397											
10	−0.001	0.025	−0.014	0.070	0.079	−0.004	0.697	6.646										
11	0.002	−0.015	−0.056	−0.003	0.081	0.078	−0.422	0.733	6.565									
12	0.002	−0.015	−0.056	−0.020	−0.004	0.078	0.391	−0.420	0.723									
13	−0.001	0.025	−0.014	−0.021	−0.024	−0.004	−0.400	0.415	−0.420									
14	0.003	−0.052	0.388	−0.007	−0.022	−0.022	0.703	−0.400	0.391									
15	0.0	0.0	0.0	0.002	0.001	0.0	0.016	0.004	−0.007	0.272								
16	0.0	0.0	0.0	0.0	0.000	0.0	0.007	0.000	−0.001	0.059	0.231							
17	0.0	0.0	0.0	−0.019	0.007	0.0	0.245	0.009	−0.012	0.067	0.022	0.728						
18	−0.001	−0.006	0.014	−0.005	−0.005	0.007	−0.185	0.163	0.010	−0.001	0.000	0.007	0.511					
19	0.000	−0.004	−0.009	0.005	−0.001	−0.005	−0.008	−0.172	0.168	−0.002	−0.001	−0.010	0.007	0.511				
20	0.0	0.0	0.0	−0.006	0.005	0.0	0.019	−0.011	−0.170	0.000	0.000	0.000	−0.010	0.008	0.510			
21	0.000	0.004	0.009	0.000	−0.007	0.005	−0.020	0.019	−0.009	−0.002	−0.001	−0.010	−0.001	−0.010	0.008			
22	0.001	0.006	−0.014	0.006	0.000	−0.007	0.007	−0.020	0.016	−0.001	0.000	0.007	−0.011	−0.001	−0.010			
23	0.002	−0.022	−0.227	0.101	−0.100	0.101	−0.024	−0.001	0.009	0.0	0.0	0.0	−0.002	−0.001	0.0	1.272		
24	0.004	−0.028	−0.265	0.053	0.051	−0.096	0.081	−0.240	0.130	0.0	0.0	0.0	−0.068	0.067	0.0	0.021	1.287	
25	0.0	0.0	0.0	−0.079	0.082	0.0	0.201	−0.007	−0.206	0.017	0.004	0.078	−0.035	−0.039	0.078	0.0	0.0	1.256

[a] Units are consistent with energy measured in attojoules, stretching coordinates in angstroms, and bending coordinates in radians. The values listed are ab initio 4–21 values scaled with empirical factors optimized previously for benzene and for acetylene (see text). Columns that follow from symmetry have been omitted. For comparison with benzene, see its SQM force field in ref 1. The corresponding force constants of acetylene, obtained for the purpose of the present study, are as follows (for the reference geometry, see footnote *c* to Table II; for the internal coordinates, see ref 15; for scale factors, see text): CC, 15.94; CH, 5.86; CC/CH, −0.145; CH/CH′, 0.013; $\lambda(CCH) = 0.232$; $\lambda/\lambda' = 0.056$. [b] See Table I for the definition of the internal coordinates.

TABLE IV: Out-of-Plane SQM Force Field of Phenylacetylene[a]

no.	26 λ_3	27 λ_4	28 $\gamma CC'$	29 γCH	30 γCH	31 γCH	34 ring	35 ring	36 ring
26	0.297								
27	0.053	0.216							
28	−0.049	−0.014	0.479						
29	0.009	0.002	−0.071	0.435					
30	−0.001	0.000	−0.002	−0.071	0.437				
31	0.003	0.001	−0.018	−0.002	−0.068	0.436			
32	−0.001	0.000	−0.002	−0.016	−0.001	−0.068			
33	0.009	0.002	−0.071	0.001	−0.016	−0.002			
34	0.023	0.005	−0.144	0.142	−0.144	0.141	0.365		
35	−0.022	−0.005	0.144	−0.071	−0.072	0.144	0.004	0.302	
36	0.0	0.0	0.0	−0.126	0.129	0.0	0.0	0.0	0.311

[a] See footnotes *a* and *b* to Table III.

is considerably larger than the aromatic ones (5.86 vs ≈5.2 aJ Å^{-2}). This was, of course, previously reproduced in the experimental force fields based on a series of benzene derivatives ("overlay" force fields).[11,12] A comparison with acetylene force constants (see footnote *a* to Table III) shows the following: 5.86 vs 5.86 aJ Å^{-2} for CH′ and 15.56 vs 15.94 aJ Å^{-2} for $C\equiv C$. Changes in both pairs are in line with the theoretical bond lengths (Table II): r(CH′) is practically the same in the two molecules; while changes in $R(C\equiv C)$ in various acetylene derivatives are hardly detectable experimentally,[26] the theoretical result for PA shows an increase of 0.003 Å compared to acetylene. The force constant of 5.43 aJ Å^{-2} for the CC′ stretching suggests a partial double bond character of the CC′ bond.

The subject of the linear bending motions of the $-C\equiv C-$ group in conjugation has been carefully studied by Pietilä et al.[12,27] by comparing overlay valence force fields of a number of compounds containing the $C\equiv C$ group. The main question is whether the in- and out-of-plane linear bending force constants split significantly. On the basis of the argument[27] that no significant difference was found between the C(sp)—$C\equiv C$ and C(sp^3)—$C\equiv C$ bending force constants, they conclude that the splitting is negligible and, in fact, they use the same value for the in-plane and out-of-plane force constants both for CCC and CCH. Baranovič et al.[11] have also calculated these force constants, although for a less wide range of compounds. Their out-of-plane linear bending constants are larger than the in-plane ones, although for CCH the difference is within the reported error limits. It is of interest to investigate whether the present ab initio results would support the above findings of the overlay force field studies.

The scaled linear bending force constant in acetylene, calculated at the 4-21 level, is 0.23 aJ rad^{-2}. In PA, the force constants for the linear bendings $C\equiv C$—H are 0.231 (in-plane) and 0.216 aJ rad^{-2} (out-of-plane), while for C—$C\equiv C$ 0.272 (in-plane) and 0.297 aJ rad^{-2} (out-of-plane). As can be seen, theory gives a significant—but not dramatic—splitting (7–10%). It is interesting that the trend is different for the two types of bendings: while for CCC the in-plane deformation is more flexible, the opposite is true for the CCH bending. This basically confirms the results of Baranovič et al.[11] and is also in line with the work of Tørneng et al. on vinylacetylene.[28] (For the sake of completeness, it should be added, however, that for divinylacetylene, Tørneng et al. found the in-plane linear bending CCC force constant to be considerably larger than the out-of-plane one.[29])

In their series of force field studies of monosubstituted benzenes, Pietilä et al.[12,30] observed that the βCC′ and γCC′ force constants in PA agree closely with their counterparts in toluene, while the βCC′ constants of styrene and benzaldehyde are significantly different. Unfortunately, quantum chemical calculations of similar accuracy as the present one are not available for the latter two compounds. The scaled 4-21 diagonal force constants in toluene[5] and in PA for βCC′ are 0.83 and 0.73 aJ rad^{-2}, while for γCC′ they are 0.52 and 0.48 aJ rad^{-2}, respectively. Thus, for both the βCC′ and γCC′ force constants, we find a moderate but significant difference. (Note that in toluene[5] a different scale factor was used for βCC′; with our present PA scale factor, the toluene βCC′ force constant would be 0.79 aJ rad^{-2}, which does not alter the above conclusion.)

Among the coupling force constants there are several that deserve discussion.

It is well-known that the CH/CC coupling constant is small and positive in most hydrocarbons, while in acetylene a fairly large negative value can be found both experimentally[31] and theoretically.[32] The coupling between C—H′ and $C\equiv C$ in PA is −0.146 aJ Å^{-2} (practically the same as in acetylene, −0.145 aJ Å^{-2}). This is a relatively large value, e.g., the largest ring CH/CC coupling in PA is 0.08 aJ Å^{-2}. Experimental determination of this constant is rather uncertain, as is shown by the fact that the two overlay force field calculations resulted in rather different values. Baranovič et al.[11] obtained −0.19 (7) aJ Å^{-2}, a result similar to our calculated value, while Pietilä et al.[12] assumed +0.066 aJ Å^{-2}, which seems to be wrong even in its sign.

The two overlay force fields differ considerably also in the $C\equiv C$/CC′ force constant. Pietilä et al.[12] report 0.775, while Baranovič et al.[11] constrained this constant to 0.0 aJ Å^{-2}. Our calculated value is 0.067 aJ Å^{-2}; thus, it supports again the work of Baranovič et al. and suggests that the refined value of 0.775 is much too large for $C\equiv C$/CC′.

The coupling between the C—$C\equiv C$ and $C\equiv C$—H linear bending motions, according to our calculation with the standard scaling procedure, is 0.059 and 0.053 aJ rad^{-2} for the in-plane and the out-of-plane blocks, respectively. As discussed above (see Computational Details), the corresponding HCC/CCH constant in acetylene is 0.056 aJ/rad^{-2} and is certainly somewhat underestimated. This must, of course, be assumed for PA, too. For the in-plane coupling, Baranovič et al.[11] reported no value, while for the out-of-plane coupling a value of 0.09 (2) aJ rad^{-2} was obtained. Pietilä et al.[12] assumed the same value for these two constants, 0.074 aJ rad^{-2}. All this supports the conclusion that the scaling procedure has indeed underestimated this type of coupling force constant. We come back to this point in the discussion on the frequencies.

Pietilä et al.[12] assumed the coupling between βCC′ and the HCC and CCC linear bendings to be zero. For βCC′/HCC, our calculated value, +0.022 aJ rad^{-2}, is indeed small. However, the coupling between βCC′ and CCC is 0.067 aJ rad^{-2}, a small but definitely nonzero value. Baranovič et al.[11] included βCC′/HCC in their optimization and obtained a value of 0.35 (3) aJ rad^{-2} for it, which seems to be greatly overestimated.

Although the γCC′/γCH and γCH/γCH′ coupling constants are almost negligible (Table IV), it should be noted that Pietilä et al.[12] find the following order: ortho ≈ −meta > −para. According to the present calculation, the right order is as follows: ortho ≫ meta (∼0.0) < para. The results of Baranovič et al.[11] are qualitatively the same as ours.

It is well-known that although experimentally derived force fields can reproduce the vibrational frequencies extremely well, they still may contain uncertainties, mainly in the interaction force constants. The two overlay force fields obtained for PA[11,12] are basically the same as the present quantum chemical one, but the work of Baranovič et al.[11] seems to be closer to our results, while the force field of Pietilä et al.[12] contains some questionable points.

Frequencies and Assignment. The theoretical frequencies obtained from the SQM force field of Tables III and IV are compared with experimental assignments in Table V. The vibrational modes are numbered simply according to the order of frequencies obtained in this study. Characterization is based on the present theoretical results (using the **M** matrix criterion $\mathbf{M}_{ip} = L_{ip}^{-1} L_{pi}$,[33] where i refers to a normal and p to an internal coordinate). The dominant internal coordinates are indicated by their serial numbers defined in Table I. Similar results for the three deuterated isotopomers (C_6H_5CCD, C_6D_5CCH, and C_6D_5CCD) are compiled in Table VI.

As is well-known, most of the normal modes in the vibrational spectra of monosubstituted benzenes (C_6H_5X) are, in good approximation, independent of the nature of the substituent X. Furthermore, benzonitrile, a thoroughly studied molecule both experimentally[34] and theoretically,[6] is isoelectronic with PA.

---

(26) (a) Pauling, L.; Springall, H. D.; Palmer, K. J. *J. Am. Chem. Soc.* **1939**, *61*, 927. (b) Collins, M. J.; Britt, C. O.; Boggs, J. E. *J. Chem. Phys.* **1972**, *56*, 4262. (c) Császár, A. G.; Hedberg, K.; Terjeson, R. J.; Gard, G. L. *Inorg. Chem.* **1987**, *26*, 955.

(27) Mannfors, B.; Pietilä, L.-O.; Palmö, K. *J. Mol. Struct.* **1986**, *144*, 287.

(28) Tørneng, E.; Nielsen, C. J.; Klaeboe, P.; Hopf, H.; Priebe, H. *Spectrochim. Acta* **1980**, *36A*, 975.

(29) Tørneng, E.; Nielsen, C. J.; Klaeboe, P.; Hopf, H.; Schull, V. *J. Mol. Struct.* **1981**, *71*, 71.

(30) Mannfors, B.; Pietilä, L.-O.; Palmö, K. in *Studies in Physical and Theoretical Chemistry*; Stepanek, J., Anzenbacher, P., Sedlacek, B., Eds.; Elsevier: Amsterdam–Oxford–New York–Tokyo, 1987; Vol. 45, pp 151–157.

(31) McKean, D. C.; Duncan, J. L. *Spectrochim. Acta* **1971**, *27A*, 1879.

(32) Pulay, P.; Meyer, W. *Mol. Phys.* **1974**, *27*, 473.

(33) (a) Pulay, P.; Török, F. *Acta Chim. Acad. Sci. Hung.* **1965**, *44*, 287. (b) Keresztury, G. Jalsovszky, G. *J. Mol. Struct.* **1971**, *10*, 304.

(34) (a) Green, J. H. S.; Harrison, D. J. *Spectrochim. Acta* **1976**, *32A*, 1279. (b) Kuwae, A.; Machida, K. *Spectrochim. Acta* **1979**, *35A*, 841.

TABLE V: Fundamental Vibrational Frequencies of Phenylacetylene (cm^{-1})

				exptl^b		
	calcd (SQM)^a			ref 9		
no.	freq	IR intens, km/mol	characterization	IR vap	Raman liq	ref 10
			A_1 (In-Plane)			
1	463	0.1	24 (ring); 3 (CC′)	(465) vw	466	463
2	754	4.1	24 (ring); 9, 14 (CC); 3 (CC′)	760^c	760	
3	998	~0.0	23 (ring)	(998) vw	994	1002
4	1026	~0.0	11, 12 (CC)	1028 s	1024	
5	1181	4.7	18, 22 (βCH)	(1175) w	1174	
6	1188	6.7	19, 21 (βCH); 10, 13 (CC); 3 (CC′)	(1192) vw	1192	1196
7	1490	1.3	19, 21, 18, 22 (βCH)	1488 vs	1485	
8	1605	3.0	10, 13 (CC)	1601 ms	1597	
9	2139	~0.0	2 ($C\equiv C$)	2120 m	2107	
10	3057	0.3	6, 5, 7 (CH)	3047 w		
11	3078	18.9	6, 4, 8 (CH)	(3067) ms	3065	
12	3094	5.3	4, 8, 5, 7, 6 (CH)	3078 m		
13	3324	90.0	1 (CH′)	3332 vs	3290	
			B_2 (In-Plane)			
14	146	1.7	15 (λ_1)	349 s^d	353	152
15	499	8.1	17 (βCC′); 15 (λ_1)	513 w	514	514
16	625	1.5	25 (ring)	613 s^d	621	624
17	672 (650)	44.0	16 (λ_2)	649 s		
18	1076	0.7	10, 13 (CC); 18, 22 (CH)	1070 ms		
19	1168	3.1	19, 21, 20 (βCH); 11, 12 (CC)	(1157) w	1157	
20	1258	0.6	9, 14, 10, 13, 11, 12 (CC)	(1282) w		
21	1327	14.3	18, 22 (βCH)	(1330) w	1327	
22	1443	3.5	19, 21, 20 (βCH); 10, 13 (CC)	1447 vs	1440	
23	1574	3.1	11, 12, 9, 14 (CC)	(1573) ms		
24	3067	4.2	5, 7, 4, 8 (CH)	3058 vw	3058	
25	3087	21.5	4, 8, 5, 7 (CH)	3096 vw		
			B_1 (Out-of-Plane)			
26	130	2.0	28 (γCC′); 26 (λ_3); 35 (ring)		162	140
27	342	3.9	35 (ring); 26 (λ_3)	349 s^d	353	
28	516	1.9	28 (γCC′); 26 (λ_3)	530 s	530	
29	650 (630)	68.7	27 (λ_4)	613 s^d	621	
30	682	36.3	34 (ring)	689 vs		
31	749	44.3	30, 32 (γCH); 34 (ring); 31 (γCH)	756 vs		
32	918	5.1	29, 33, 31 (γCH)	915 s		
33	988	~0.0	30, 32, 31 (γCH); 34 (ring)	(985) vvw		
			A_2 (Out-of-Plane)			
34	399	0.0	36 (ring)	(418) vvw		
35	837	0.0	29, 33, 30, 32 (γCH)	(842) vw		
36	969	0.0	30, 32, 29, 33 (γCH)	(968) vvw		

[a] Results of the present study, obtained from the force field given in Tables III and IV. In the approximate characterization of a normal mode, coordinates dominant according to the M-matrix criterion[33] are indicated by their serial number defined in Table I. In parentheses, those frequencies are indicated that changed considerably when the λ_1/λ_2 and λ_3/λ_4 coupling force constants were not scaled (see text). [b] Qualitative IR intensities were measured in liquid phase and are indicated as usual. Infrared frequency values in parentheses were measured in liquid phase. [c] No IR liquid-phase intensity is reported. [d] Frequency used a second time.

Therefore, PA must have most of its fundamentals (including some X-sensitive modes) at frequencies very similar to those of benzonitrile. This allows a simplification of the discussion of the vibrational spectrum of PA; in the following special attention is paid only to a few X-sensitive modes.

The only significant discrepancy between the calculated and the experimentally assigned normal frequencies[9] concerns the lowest in-plane mode (species b_2). In the assignment of King and So,[9] this frequency is at 350 cm^{-1}, while calculations predict it at about 140 cm^{-1}. This misassignment has already been corrected by Bacon et al.[10] As a consequence of the reassignment, the $b_2 - b_1$ coincidence at 350 cm^{-1} assumed in ref 9 is no longer justified. At the same time, however, the in- and out-of-plane CCC bending modes (the latter strongly mixed) do appear very close to each other around 140 cm^{-1}.

The $C\equiv C$—H bending modes of an acetylenic group appear at about 640 cm^{-1} in substituted acetylenes.[35] According to the present calculation, the two components in PA can easily be identified and both are very pure CCH bendings. The in-plane mode appears at 672 cm^{-1} (with large intensity), while its out-of-plane counterpart is an even stronger absorption at 650 cm^{-1}. King and So[9] put these two frequencies at 649 and 613 cm^{-1}, respectively. Concerning the calculated results, we noted in the section on the force field that the CCC/CCH coupling force constants (λ_1/λ_2 and λ_3/λ_4) are rather uncertain, probably underestimated by the scaling. Because the frequencies in question may be sensitive to the CCC/CCH couplings, we made a test calculation, in which these coupling constants were constrained to their directly calculated (unscaled) values. Then, the calculated frequencies are 650 and 630 cm^{-1}, in reasonable agreement with the measured frequencies. King and So also argue that "probably, as in the case of propynal,[36] the two $\equiv$C—H bending modes are strongly Coriolis coupled by rotation about the *a*-axis." Calculation of the Coriolis coupling constants is straightforward from the SQM force field, and we obtained a value of 0.98. This suggests that λ_2 and λ_4 are, indeed, strongly Coriolis coupled, supporting the explanation for the observed band profiles in the 600–650-cm^{-1} region.[9] It is interesting to note in this respect that the two $C—C\equiv C$ bending modes (146 and 130 cm^{-1}, calc) are also strongly Coriolis coupled. Our calculated value is 0.84, significantly larger than the value of 0.4–0.6 assumed in ref 10. (On

---

(35) Nyquist, R. A.; Potts, W. J. *Spectrochim. Acta* **1960**, *16*, 419.

(36) Brand, J. C. D.; Callomon; J. H.; Watson, J. K. G. *Discuss. Faraday Soc.* **1963**, *35*, 175.

TABLE VI: Fundamental Vibrational Frequencies of C_6H_5CCD, C_6D_5CCH, and C_6D_5CCD (cm^{-1})

	C_6H_5CCD		C_6D_5CCH		C_6D_5CCD	
no.	calcd[a]	exptl[b]	calcd[a]	exptl[b]	calcd[a]	exptl[b]
			A_1 (In-Plane)			
1	457	(459)	453	(454)	448	(448)
2	750	758	710	716	707	707
3	998	(998)	835	839	835	838
4	1026	1025	868	(868)	868	(867)
5	1178	(1175)	955	956	955	(952)
6	1185	1193	1124	1136	1119	1136
7	1490	1488	1368	1379	1366	1378
8	1604	1600	1569	1572	1569	1571
9	1986	(1984)	2138	2122	1986	(1980)
10	2603	2609	2255	2282	2255	2284
11	3057	3046	2277	2291	2277	2292
12	3078	(3066)	2296	2300	2296	2300
13	3094	3078	3324	3332	2603	2610
			B_2 (In-Plane)			
14	137	340[c]	141	330[c]	133	322[c]
15	461 (474)	482[c]	486	502	452 (466)	477
16	560 (522)	531[c]	600	(602)	554 (518)	513
17	627	(623)	671 (649)	648	604	(601)
18	1076	1070	822	822	822	821
19	1168	(1157)	846	(842)	846	(841)
20	1258	(1278)	1039	(1034)	1039	(1034)
21	1327	(1329)	1252	(1274)	1252	(1275)
22	1443	1447	1314	(1323)	1314	(1323)
23	1574	(1573)	1535	(1557)	1535	(1556)
24	3067	3058	2266	(2279)[d]	2266	(2279)[d]
25	3087	3096	2287	(2287)[d]	2287	(2287)[d]
			B_1 (Out-of-Plane)			
26	124	(154)	124	(161)	119	(146)
27	328 (332)	340[c]	323	330[c]	311	322[c]
28	488	482[c]	457	470	444 (450)	475
29	547 (520)	531[c]	540	553	520 (497)	491
30	682	691	625	612	548 (541)	553
31	749	757	651 (633)	639	627	637
32	918	916	765	768	765	767
33	988	(985)	836	(825)	836	(825)
			A_2 (Out-of-Plane)			
34	399	(419)	347	(348)	347	(348)
35	837	(841)	651	(704)	651	(704)
36	969	(968)	789	(766)	789	(765)

[a] Results of the present study, obtained from the force field given in Tables III and IV. In parentheses, frequency values are indicated that changed considerably when the λ_1/λ_2 and λ_3/λ_4 coupling force constants were not scaled (see text). [b] Infrared vapor-phase frequency values, except those in parentheses, that were measured in the liquid phase (IR or Raman).[9] [c] Frequency used a second time. [d] Estimated value.

the other hand, we confirm their assumption that these values in PA and benzonitrile agree closely, since from our SQM force field[6] we obtain 0.83 for the latter compound.)

An interesting experimental observation is the fact that the C≡C stretching frequency in PA is significantly higher than that in acetylene (2120 vs 1974 cm^{-1}). The calculated value of 2139 cm^{-1} in PA confirms this trend (of course, in acetylene the calculated frequency agrees with the experimental one, because this was the molecule used for optimization of the scale factors). This increase of the frequency may seem somewhat surprising in the light of the C≡C force constants, which show the opposite trend: 15.56 (PA) vs 15.94 aJ $Å^{-2}$ (acetylene). Obviously, the C≡C coordinate must be in fairly strong coupling with CC′, which cannot be explained by the force field (their coupling is practically negligible). Thus, the coupling is a kinematic effect (coming from the **G** matrix), as can be easily checked by a simple calculation. Note that this frequency increase is also observed in methylacetylene.[37]

The present results basically confirm the study of King and So[9] also for the deuterated isotopomers (C_6H_5CCD, C_6D_5CCH, and C_6D_5CCD; Table VI); only the few discrepancies deserve discussion. Naturally, misassignment of the two lowest frequencies (ν_{14} and ν_{26} in our notation), a problem already discussed for the parent compound, should be taken into account for all the deuterated isotopomers.

In C_6H_5CCD, two in-plane frequencies have errors larger than 20 cm^{-1}, those at 461 and 560 cm^{-1}. If the higher, unscaled value (see above) is used for the λ_1/λ_2 coupling force constant, then the calculated values change to 474 and 522 cm^{-1}, in good agreement with the measured values. A similar problem with a similar solution exists for the 671 cm^{-1} band (calc) in C_6D_5CCH and for the 452, 554 (b_2), and 520 cm^{-1} (b_1) bands in C_6D_5CCD. In the latter, there remains a slight discrepancy in ν_{28} (calculated values, 444–450 cm^{-1}; experimental value, 475 cm^{-1}). As to the inactive a_2 frequencies, Baranović et al.[11] observed that King and So[9] misassigned the second highest a_2 fundamentals in C_6D_5CCH and C_6D_5CCD. Our calculations support the conclusion that this frequency should be set to around 650 cm^{-1} instead of 704 cm^{-1}.

There are a number of in-plane–out-of-plane coincidences assumed in the experimental study of the three deuterated isotopomers:[9] ν_{14}–ν_{27}, ν_{15}–ν_{28}, and ν_{16}–ν_{29} in C_6H_5CCD; ν_{14}–ν_{27} in C_6D_5CCH; and ν_{14}–ν_{27} in C_6D_5CCD. The erronous assignment of ν_{14} was already discussed; thus, coincidences involving this band are clear artifacts. The other assumed coincidences are clearly supported by the present calculations, although for the ν_{15}–ν_{28} pair only after the above mentioned correction of the linear bending couplings. There are also some near-coincidences assumed by King and So:[9] ν_2–ν_{31} in C_6H_5CCD; ν_3–ν_{19} and ν_{18}–ν_{33} in C_6D_5CCH;

---

(37) (a) Duncan, J. L.; McKean, D. C.; Nivellini, G. D. *J. Mol. Struct.* **1976**, *32*, 255. (b) Priebe, H.; Nielsen, C. J.; Klaeboe, P. *Spectrochim. Acta* **1980**, *36A*, 1017.

TABLE VII: Calculated and Experimental Quartic Centrifugal Distortion Constants[a]

	calcd[b]		
parameter	*A* reductn	*S* reductn	exptl[c]
1	0.0420	0.0299	0.0298
2	1.0475	1.1199	1.047
3	0.1474	0.1143	
4	0.0100	−0.0100	
5	0.6493	−0.0060	

[a] I^r representation. All values in kilohertz. For the *A* reduction, the five distortion constants are, respectively: Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K, and for the *S* reduction, the appropriate constants are D_J, D_{JK}, D_K, d_1, and d_2. The two experimental constants are D_J and D_{JK}. [b] Asymmetric top approximation. [c] Symmetric top approximation. From ref 7.

and ν_3–ν_{19} and ν_{15}–ν_{28} in C_6D_5CCD. The largest calculated difference for any of these pairs is 16 cm^{-1}, a significant but not yet conclusive value; thus, the present calculation gives general support to the experimental assignments.[9]

Infrared Intensities. We list, as part of Table V, the IR intensities of the normal modes of PA, calculated from the theoretical (unadjusted) dipole moment derivatives and the scaled theoretical force fields of Tables III and IV.

No reliable experimental intensity data are available for this complex molecule; the qualitative IR intensities, measured in the liquid phase, are indicated in Table V for the parent molecule. The calculated intensity values show, somewhat unexpectedly, rather poor agreement with them. Still, a discussion of the dipole derivatives—the direct results of the quantum chemical calculations—may be interesting from the structural point of view. In the following, the sign of the derivative is positive if the change of the dipole moment vector—the latter directed from negative toward positive charge—points in the same direction as the displacement of the hydrogen atom (or the "outer" atom in the C≡C—H group).

As was observed for all benzene derivatives,[1,3–6] the polarity of the ring C—H bonds is C^+H^- in stretchings and C^-H^+ in both the in-plane and the out-of-oplane bendings. The stretching derivatives and, in parentheses, the corresponding values for fluorobenzene and benzonitrile, respectively, are as follows (in D/Å): ortho, −0.35 (−0.21, −0.21); meta, −0.52 (−0.42, −0.40); and para, −0.52 (−0.45, −0.40). The in-plane bending derivatives are as follows (in D/rad): ortho, 0.30 (0.31, 0.32); meta, 0.23 (0.26, 0.24); and para, 0.26 (0.23, 0.26). The out-of-plane bending derivatives are as follows (in D/rad): ortho, 0.74 (0.92, 0.76); meta, = 0.70 (0.69, 0.70); and para, 0.69 (0.72, 0.65). It can be concluded that the change in these calculated dipole derivatives with different substituents is not too large. It should be added that the dipole change in stretchings is not exactly along the CH bond and in bendings not exactly perpendicular to it; deviations up to a few degrees may occur.

Our calculated dipole gradients of the substituent stretchings are as follows: CC′, −1.1 D/Å; C′≡C, −1.4 D/Å; and CH′, +1.3 D/Å. For the CCC bending, the dipole gradient is 1.06 (in-plane) and 1.00 D/rad (out-of-plane). For the CCH bending, the dipole gradient is 1.15 (in-plane) and 1.23 D/rad (out-of-plane). The signs and the magnitudes of the above derivatives indicate the following partial changes in terms of the bond moment hypothesis both for the stretchings and the bendings: $^{\delta+}$C (ring)–$^{\delta-}$C′, $^{\delta+}$C′≡$^{\delta-}$C, and $^{\delta-}$C–$^{\delta+}$H′. The latter is a rather interesting result since it suggests that the polarity of the ≡C—H bond is C^-H^+ also in stretching, i.e., just the opposite to that of the ring CH stretchings. Thus, in this respect, the ≡CH bond in PA behaves the same way as the CH bond of acetylene.[38]

The linear bending dipole derivatives indicate that these derivatives are quite insensitive to whether the atoms move in the plane of the molecule or perpendicular to it. Furthermore, comparing these values with those of benzonitrile[6] (for which both the in-plane and out-of-plane CCN bending derivative is 1.0 D/rad), one can observe that the dipole gradient of a linear bending involving a triple bond is predicted, at this level of theory, to be fairly constant.

Quartic Centrifugal Distortion Constants. The spacing of the lines of the rotational spectra of molecules provides, in first order, the rotational constants. Theoretical calculation of these constants is straightforward from the optimized molecular geometries; for usual molecules, the measured and calculated values agree within about 1–2%. As seen in the section on geometry, the agreement for PA is even better, with errors below 0.5%. Quartic centrifugal distortion (QCD) constants represent small correction terms to these rotational constants.[39,40] Their theoretical calculation is based not only on a reasonable estimate of the true equilibrium geometry but requires, in addition, knowledge of the harmonic force field. It was demonstrated recently that quartic constants calculated from SQM force fields agree with the experimental values within about 10%,[13,14] a remarkable accuracy if the difficulties of their calculation and the small magnitude of these correction terms are both considered.[14]

The QCD constants of the asymmetric top molecule of PA calculated from its SQM force field are presented in Table VII, both in the *S*-reduction and *A*-reduction formalism, together with the available measured values. In the experimental work,[7] a symmetric top approximation was used, therefore the measured values should be compared to the calculated results obtained in the *S* reduction. The agreement is very satisfactory for both constants, D_J and D_{JK}, that were evaluated in the experimental refinement.

Conclusion

The present study has demonstrated again the great practical value of ab initio quantum chemical calculations for the interpretation of the vibrational and rotational spectra of ground-state molecules. The scaled quantum mechanical (SQM) harmonic force field of phenylacetylene, obtained from the direct calculated ab initio 4-21 values by scaling them with empirical scale factors taken over from benzene and acetylene, is probably the best harmonic force field available for this molecule. Effects of the substituent on the geometry and force field are discussed. The normal frequencies of the parent molecule, calculated from the SQM force field, support the results of the detailed experimental work of King and So[9] and also the modifications concerning the two lowest frequencies suggested by Bacon et al.[10] Calculations also confirm, with only a few exceptions, the assignments for three deuterated isotopomers (C_6H_5CCD, C_6D_5CCH, and C_6D_5CCD). Infrared intensities, together with a discussion of the dipole moment derivatives, are presented for the parent molecule. The moments of inertia calculated from the corrected equilibrium geometry and the quartic centrifugal distortion constants calculated from the SQM force field are in good agreement with the available experimental values.

Acknowledgment. Support from the Robert A. Welch Foundation is acknowledged.

Registry No. PA, 536-74-3; C_6H_5CCD, 3240-11-7; C_6D_5CCH, 25837-46-1; C_6D_5CCD, 25837-47-2.

---

(38) Wiberg, K. B.; Wendoloski, J. J. *J. Phys. Chem.* **1984**, *88*, 586.

(39) (a) Wilson, E. B., Jr.; Howard, J. B. *J. Chem. Phys.* **1936**, *4*, 260. (b) Kivelson, D.; Wilson, E. B., Jr. *J. Chem. Phys.* **1952**, *20*, 1575. (c) Kivelson, D.; Wilson, E. B., Jr. *J. Chem. Phys.* **1953**, *21*, 1229.

(40) (a) Watson, J. K. G. *J. Chem. Phys.* **1967**, *46*, 1935. (b) Watson, J. K. G. *J. Chem. Phys.* **1968**, *48*, 181.