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LETTERS

The Equilibrium Structure of Benzene

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The r_e structure of benzene is revised on the basis of high-level quantum chemical calculations at the CCSD(T)/cc-pVQZ level as well a reanalysis of the experimental rotational constants using computed vibrational corrections. A least-squares fit to empirically determined B_e constants yields $r_e(CC) = 1.3914 \pm 0.0010$ Å and $r_e(CH) = 1.0802 \pm 0.0020$ Å; the latter distance is significantly shorter than the best previous estimate based on experimental data. Comparison of computed r_g and r_z distances with experiment as well as considerations of bond lengthening due to anharmonicity are consistent with the estimated r_e distance, indicating that the recommended structural parameters are very accurate.

One of the ultimate goals of structural chemistry is the determination of equilibrium molecular geometries. These structures are defined by local or global minima on the adiabatic potential energy surface and are (to a very good approximation) independent of isotopic substitution. Equilibrium structures provide the most satisfactory reference point for studying substituent effects on molecular geometries. Replacement of one group by another can have a profound effect on vibrational wavefunctions with the consequence that changes in vibrationally averaged (r_g, r_α, or r_z), effective r_0 or other (r_s) geometries attendant upon functionalization do not necessarily mirror those of the equilibrium (r_e) structure. In addition, accurate r_e structures are needed to properly calibrate the accuracy of various quantum chemical approaches.

Unfortunately, it is extremely difficult to determine accurate equilibrium geometries for polyatomic molecules. The difficulties associated with a purely experimental elucidation of r_e parameters arise mostly from imperfect knowledge of the cubic force field. Slow convergence with respect to both basis set and the treatment of electron correlation means that r_e geometries obtained by minimization of calculated energies usually are associated with unacceptably large uncertainties.

Perhaps the most pragmatic approach for the determination of r_e structures is one that combines both experimental and theoretical data. In a study of methane, Pulay, Meyer, and Boggs corrected experimental rotational constants for effects of vibration−rotation interaction and deduced an equilibrium bond length more than twenty years ago.[1] The value obtained in their study is in excellent agreement with a very recent recommendation[2] of $r_e = 1.0859_5 \pm 0.0003$ Å, attesting to the power of this procedure. Similar efforts of the same type were subsequently made by others, principally Allen,[3] Botschwina,[4] and their collaborators, and more recently by us.[5] It is now possible to routinely calculate quadratic and cubic force fields at high levels of theory. These can be combined with precisely measured rotational constants (when available) to obtain empirical esti-

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mates of the equilibrium rotational constants that are determined solely by moments of inertia of the rigid equilibrium structures. The recent development of analytic second derivative procedures[6] for methods based on coupled-cluster (CC)[7] and high-order many-body perturbation theory (MBPT)[8] together with a convenient numerical differentiation approach originally suggested by Schneider and Thiel[9] has served to greatly facilitate studies of this type, as attested by a number of recent studies.[5]

A precise equilibrium structure of benzene has not been determined. The most recent estimate of r_e distances that is based largely on experimental information is that of Pliva, Johns, and Goodman.[10] These workers inferred the values $r_e(\mathrm{CC}) = 1.3902(2)$ and $r_e(\mathrm{CH}) = 1.0862(15)$ Å by correcting ground-state rotational constants of C_6H_6, C_6D_6, and $^{13}C_6H_6$ for estimates of rotation−vibration interaction that are based on an assumed isotopic dependence. However, the CH distance that results from this procedure appears to be too long, as already pointed out in refs 18 and 19. Moreover, it is inconsistent with other experimental data, as discussed in the last paragraph of this report. While the lack of an accurate r_e structure for benzene seems surprising given its position as perhaps the most prominent prototype molecule in chemistry, it also attests to the difficulty of extracting r_e structures from experimental data.

The purpose of this work is to determine a very accurate equilibrium structure for benzene. Two separate approaches have been used to achieve this objective. In the first, precisely measured ground-state rotational constants of benzene[11] have been corrected for effects of vibration−rotation interaction using a calculated vibrational force field. The second is a purely computational approach in which the distances are obtained by straightforward energy minimization at the CC singles and doubles level[13] augmented by a perturbative treatment of triple excitations [CCSD(T)[14]] using the cc-pVQZ basis set of Dunning.[15] Previous experience suggests that this level of theory provides distances that are accurate to better than 0.003 Å,[16] so it serves as a useful consistency check for the structure obtained by the mixed experimental−theoretical procedure.

All harmonic and selected cubic force constants of benzene were calculated at the level of partial fourth-order MBPT [SDQ-MBPT(4)] using the cc-pVTZ basis set.[15] In these calculations (which involve 264 basis functions), analytic second derivatives of the energy were determined analytically at both the corresponding optimized geometry ($r_{CH} = 1.0758$ Å; $r_{\mathrm{CC}} = 1.3864$ Å) and four additional points symmetrically disposed about the equilibrium structure along the two totally symmetric normal coordinates. Cubic constants $\phi_{\beta ij}$ (β represents one of the two totally symmetric coordinates) obtained from these four second derivative calculations suffice to determine vibrational corrections to the rotational constants of C_6H_6, $^{13}C_6H_6$, C_6D_6, and $^{13}C_6D_6$, although transformations amongst normal coordinate representations appropriate for the various isotopomers are also required. The set of quadratic and cubic force constants is listed in Table 2 for C_6H_6; those for the isotopically substituted benzenes are available from the authors. Using these data, empirical equilibrium rotational constants (B_e) for the four isotopomers were obtained from experimentally measured B_0 values and corrections computed according to the formulas given by Mills.[17] The equilibrium structure was then obtained by least-squares adjustment of the two independent geometrical parameters of benzene to best fit the four empirical B_e values. All relevant quantities used in the calculation are listed in Table 1. Following this procedure, the CH and CC r_e distances are found to be 1.0802 and 1.3914 Å, respectively. The maximum residual between empirical B_e values and those computed from inertia tensors of the isotopomers at the optimized geometry is 0.04 MHz, which should be compared to a value about twenty times larger (0.88 MHz) that is found when the structure is refined to best fit the uncorrected B_0 constants.

TABLE 1: Ground-State Rotational Constants, Calculated Vibrational Corrections, and Empirical Equilibrium Rotational Constants of Benzene Isotopomers (in MHz), and Summary of Internuclear Distance Data (in Å) from Both the Present and Previous Work

	rotational constants			
	C_6H_6	C_6D_6	$^{13}C_6H_6$	$^{13}C_6D_6$
B_0^a	5689.28	4707.31	5337.92	4464.37
$B_0-B_e^b$	−42.45	−32.93	−38.53	−30.23
B_e	5731.73	4740.24	5376.45	4494.60

	structural parameters			
	r_{CC}		r_{CH}	
$r_e^{Calculated}$	1.3911^c		1.0800^c	
$r_e^{Empirical}$	1.3914^b	$1.3902(2)^e$	1.0802^b	$1.0862(15)^e$
r_g	1.3988^d	$1.399(1)^f$	1.1005^d	$1.101(5)^f$
r_z	1.3964^d	$1.3976(15)^f$	1.0846^d	$1.085(1)^f$

[a] See ref 11. [b] Based on SDQ-MBPT(4)/cc-pVTZ cubic force field. [c] Optimized at CCSD(T)/cc-pVQZ level. [d] Based on CCSD(T)/cc-pVQZ geometries with vibrational corrections calculated at the SDQ-MBPT(4)/cc-pVTZ level. [e] Ref 10. [f] Ref 21.

In the second approach, the geometry of benzene was optimized at the CCSD(T)/cc-pVQZ level of theory. The energy minimization was performed numerically, using gradients obtained by double-sided differentiation of energies with respect to CH and CC distances. These calculations involved 510 basis functions and 21 occupied molecular orbitals, but only about 40 h are needed to obtain each energy on a Compaq XP-1000 workstation. Conventional techniques were employed, i.e., all integrals in the atomic orbital basis were stored on disk as well as molecular orbital integrals that carry at least one occupied index. The optimized geometry obtained in this way ($r_{CH} = 1.0800$ Å and $r_{CC} = 1.3911$ Å, which are accurate to the number of digits quoted) is in nearly perfect agreement with that derived by the empirical procedure. Based on this agreement, and the close correspondence between these structural parameters and those estimated in ref 18 via application of empirical corrections to computed internuclear distances, we believe that the structure obtained from the rotational constant analysis is the most accurate reliable structure of benzene produced to date. The values $r_e(\mathrm{CC}) = 1.3915 \pm 0.0010$ Å and $r_e(\mathrm{CH}) = 1.0800 \pm 0.0020$ Å are recommended. As an additional consistency check, force constants used to correct ground state rotational constants for vibrational effects have also been used to calculate mean internuclear distances (r_g) and distances between mean internuclear positions in the vibrational ground state (r_z) of C_6H_6 using the perturbation approach advocated by Kuchitsu.[20] These parameters have been carefully inferred from experimental data by Tamagawa et al.[21] and provide convenient benchmarks for calibrating the accuracy of our results. As seen in the last two rows of Table 1, agreement between calculated r_g and r_z distances and those of ref 21 is nearly perfect. For the CC distance, the calculated values are within the rather small ranges that are consistent with experiment. CH distances are in similarly good agreement with the experimental center-of-gravity estimates of 1.101 and 1.085 Å, respectively. The r_z comparison is somewhat more significant in the present context because of the small uncertainty assigned to the experimentally derived quantity. All in all, these comparisons fully support both our

TABLE 2: Quadratic and Cubic Force Constants (in cm^{-1}) of C_6H_6 in Dimensionless Normal Coordinates[a]

i	*j*	*k*	ϕ_{ij}	ϕ_{ijk}
1	1		1035.77	−
2	2		3255.63	−
3	3		1400.46	−
4	4		734.42	−
5	5		1031.29	−
6	6		621.07	−
7	7		3215.53	−
8	8		1684.03	−
9	9		1225.32	−
10	10		895.71	−
11	11		720.57	−
12	12		1032.20	−
13	13		3196.53	−
14	14		1314.18	−
15	15		1179.31	−
16	16		420.41	−
17	17		1015.04	−
18	18		1081.68	−
19	19		1544.68	−
20	20		3239.17	−
1	1	1	−	112.37
2	1	1	−	15.32
2	2	1	−	34.69
2	2	2	−	−804.71
3	3	1	−	21.48
3	3	2	−	164.49
4	4	1	−	-14.81
4	4	2	−	7.65
5	4	1	−	0.37
5	4	2	−	−75.38
5	5	1	−	17.97
5	5	2	−	299.68
6	6	1	−	5.36
6	6	2	−	40.56
7	6	1	−	-6.37
7	6	2	−	−10.36
7	7	1	−	27.66
7	7	2	−	−817.26
8	6	1	−	−25.26
8	6	2	−	−54.42
8	7	1	−	6.45
8	7	2	−	16.18
8	8	1	−	149.49
8	8	2	−	67.77
9	6	1	−	−17.33
9	6	2	−	79.81
9	7	1	−	3.33
9	7	2	−	−2.36
9	8	1	−	56.81
9	8	2	−	−69.30
9	9	1	−	41.62
9	9	2	−	137.45
10	10	1	−	1.79
10	10	2	−	374.33
11	11	1	−	−11.58
11	11	2	−	518.95
12	12	1	−	14.20
12	12	2	−	−10.70
13	12	1	−	−7.90
13	12	2	−	−16.23
13	13	1	−	24.11
13	13	2	−	−821.41
14	14	1	−	178.79
14	14	2	−	166.47
15	14	1	−	−113.91
15	14	2		96.47
15	15	1	−	100.87
15	15	2		109.86
16	16	1	−	−63.27
16	16	2		70.85
17	16	1	−	−9.77
17	16	2		−159.39
17	17	1	−	11.83
17	17	2	−	293.45
18	18	1		65.03
18	18	2		99.20
19	18	1	−	−53.38
19	18	2	−	85.58
19	19	1	−	69.64
19	19	2	−	101.71
20	18	1		9.55
20	18	2	−	14.06
20	19	1		−8.05
20	19	2		−30.45
20	20	1	−	32.15
20	20	2	−	−808.79

[a] The mode numbering and choice of phases is consistent with that found in ref 24. For degenerate modes (7 through 10 and 16 through 20), the constants are those corresponding to the *a* component in all cases.

recommended equilibrium structure and the associated uncertainty estimates.

Finally, we address the equilibrium structure previously estimated by Pliva, Johns, and Goodman.[10] Their CC distance is in excellent agreement with that of the present study, but there is a rather large difference in the CH distance. The accuracy of the latter can be challenged on a number of grounds. First, it is longer than the experimentally inferred r_z value. Such a shortening of a CH distance due to vibrational effects would imply that the mean displacement of the totally symmetric CH stretch normal coordinate (Q_2) is negative, clearly inconsistent with usual models of stretching anharmonicity. Second, the estimate of 1.086 Å implies an $r_g - r_e$ difference of 0.015 Å while the corresponding lengthening in methane is about 0.022 Å.[2] Such a large difference seems rather unlikely.[22]

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References and Notes

(1) Pulay, P.; Meyer, W.; Boggs, J. E. *J. Chem. Phys.* **1978**, *68*, 5077.

(2) Stanton, J. F. *Mol. Phys.* **1999**, *97*, 841.

(3) East, A. L. L.; Johnson, C. S.; Allen, W. D. *J. Chem. Phys.* **1993**, *98*, 1299; East, A. L. L.; Allen, W. D.; Klippenstein, S. J. *J. Chem. Phys.* **1995**, *102*, 8506; Allen, W. D.; East, A. L. L.; Csaszar, A. G. In *Structures and Conformations of Nonrigid Molecules*; Laane, J., Dakkouri, M., va der Vecken, B., Oberhammer, H., Eds.; Kluwer: Dordrecht, 1993; p 343.

(4) For representative studies, see: McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P.; Horn, M.; Botschwina, P. *J. Chem. Phys.* **1995**, *103*, 7820; Bartel, C.; Botschwina, P.; Bürger, H.; Guarnieri, A.; Heyl, Ä.; Huckauf, A.; Lentz, D.; Merzliak, T.; Mkdami, E. B. *Angew. Chem.* **1998**, *110*, 3036.

(5) Stanton, J. F.; Gauss, J. *Int. Rev. Phys. Chem.*, in press.

(6) Gauss, J.; Stanton, J. F. *Chem. Phys. Lett.* **1997**, *276*, 70.

(7) For reviews, see: Bartlett, R. J. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; p 1047. Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer: Dordrecht, 1995; p 47. Gauss, J. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollmann, P. A., Schaefer, H. F., Schreiner, P. R., Eds.; Wiley: New York, 1998; p 615.

(8) Bartlett, R. J. *Ann. Rev. Phys. Chem.* **1981**, *32*, 359.

(9) Schneider, W.; Thiel, W. *Chem. Phys. Lett.* **1989**, *157*, 367.

(10) Pliva, J.; Johns, J. W. C; Goodman, L. *J. Mol. Spectrosc.* **1991**, *148*, 427.

(11) The rotational constant for C_6H_6 is taken from Hollenstein, H.; Piccirillo, S.; Quack, M.; Snels, M. *Mol. Phys.* **1990**, *71*, 759; that for $^{13}C_6D_6$ is from ref 10, those for $^{13}C_6H_6$ and C_6D_6 come from Pliva, J.; Johns, J. W. C.; Goodman, L. *J. Mol. Spectros.* **1990**, *140*, 214.

(12) It is interesting to note that the $r_g - r_e$ corrections obtained with the SDQ-MBPT(4)/cc-pVTZ cubic force field (0.0077 and 0.0205 Å for the CC and CH distances, respectively) compare favorably with those of Maslen et al. (0.0076 and 0.0201 Å) using a force field calculated at the self-consistent field level. See Maslen, P. E.; Handy, N. C.; Amos, R. D.; Jayatilaka, D. *J. Chem. Phys.* **1992**, *97*, 4233.

(13) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 7918.

(14) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(15) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(16) Helgaker, T.; Gauss, J.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **1997**, *106*, 6430. Halkier, A.; Jørgensen, P.; Gauss, J.; Helgaker, T. *Chem. Phys. Lett.* **1997**, *274*, 235.

(17) Mills, I. M. In *Modern Spectroscopy: Modern Research*; Rao, K. N., Matthews, C.W., Eds.; Academic Press: New York, 1972; pp 115−140.

(18) Martin, J. L. M.; Taylor, P. R.; Lee, T. J. *Chem. Phys. Lett.* **1997**, *275*, 414.

(19) Handy, N. C.; Murray, C. W.; Amos, R. D. *J. Phys. Chem.* **1993**, *97*, 4392.

(20) Kuchitsu, K. In *Accurate Molecular Structures*; Domenicano, A., Hargittai, I., Eds.; Oxford University Press: Oxford, 1992; pp 14−46. Mills, I. M. *J. Phys. Chem.* **1976**, *80*, 1187.

(21) Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Structure* **1976**, *30*, 243.

(22) The major source of the discrepancy between CH distances arises from the isotopic scaling behavior of the B_0-B_e difference that was used in ref 10. In their work, it was assumed that this difference for isotopomer i is equal to that of the normal isotopomer (β) times a scaling factor $\rho^{(i)} = (B_0{}^{(i)}/B^{(\mathrm{normal})}{}_0)^2(M^{(i)}/M^{(\mathrm{normal})})^{1/2}$, where M is the molecular weight. The value of β was varied along with CC and CH distances so as to provide the best fit to the four rotational constants. While the corresponding value of −46.15 MHz is in very good agreement with the calculated shift of −42.45 MHz, applying the same scaling procedures to the latter (yielding −30.14, −38.80, and −28.02 MHz for C_6D_6, $^{13}C_6H_6$, and $^{13}C_6D_6$, respectively) also results in a structure with long CH distances (1.3908 and 1.0850 Å). With respect to the results of this work, the good agreement between the former and poor agreement of the latter can be attributed to the fact that the isotopic scaling factors appear to quite accurate for the ^{13}C substituted isotopomers (0.914 for $C_6H_6 \rightarrow {}^{13}C_6H_6$ vs 0.908 from the calculated force field; 0.931 for $C_6D_6 \rightarrow {}^{13}C_6D_6$ vs 0.918 from the calculated force field) but considerably less adequate for the perdeuterated species (0.711 vs 0.776 for $C_6H_6 \rightarrow C_6D_6$; 0.724 vs 0.784 for $^{13}C_6H_6 \rightarrow {}^{13}C_6D_6$).

(23) Handy, N. C.; Maslen, P. E.; Amos, R. D.; Andrews, J. S; Murray, C. W.; Laming, G. J. *Chem. Phys. Lett.* **1992**, *197*, 506.

(24) Wilson, E. B. *Phys. Rev. B* **1934**, *45*, 706.