On the Geometric Structure and Vibrational Frequencies of *o*-Benzyne. An *ab initio* Study including Electron Correlation

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The geometry of *o*-benzyne has been fully optimized using a single-pair GVB wavefunction and a 3-21G and 6-31G* basis. The geometry obtained differed significantly from that found in the absence of electron correlation, and has cumulene-like features. A consistent assignment of the experimental vibrational spectrum is made using vibrational frequencies calculated at this predicted geometry.

The geometric and electronic structure of *o*-benzyne (1,2-dehydrobenzene) (**1**) have been studied by a variety of experimental[1,2] and theoretical[3–9] methods. Experimental studies are difficult in view of the transient nature and high reactivity of this molecule, so that no direct study of its geometric structure has been carried out. For this reason the possible inference of its geometry from spectroscopic measurements has attracted interest, particularly the work by Laing and Berry,[10] who concluded from an analysis of observed matrix-infrared frequencies that an aryne-like structure (**1a**) gives a better fit than a cumulene-like structure (**1b**).

A number of semi-empirical[3–6] and *ab initio*[7–9] studies of the geometry of *o*-benzyne have been reported and in general predict no bond-length alternation. Although the diradicaloid nature of the *meta*- and *para*-isomers of benzyne have been recognized,[7] it has been assumed[7–9] that the Hartree–Fock description is adequate for the *ortho*-isomer. In this paper we investigate the effect of the possible singlet diradicaloid nature of *o*-benzyne on its predicted geometry, and we calculate the fundamental vibrational frequencies of this molecule for a comparison with the experimental data.

Calculations

It has been found[7] that at the single-determinantal (Hartree–Fock) level, calculations of *o*-benzyne yield a pair of σ-orbitals (φ_s,φ_a) which are well localized on the dehydro centres. The bonding combination (φ_s) is the highest filled σ-orbital, whilst the anti-bonding combination (φ_a) is a low-lying virtual orbital. To allow for possible singlet diradicaloid nature of the two dehydro centres a two-determinant wavefunction (ψ) is required, where relationship (1) holds. Here, both the molecular orbitals

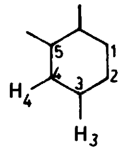
$$\psi = c_1|\ldots\ldots\varphi_s^2| + c_2|\ldots\ldots\varphi_a^2| \qquad (1)$$

and coefficients (c_1,c_2) are variationally optimized during the SCF calculation of this single-pair GVB wavefunction.[11] The geometry of *o*-benzyne was optimized, assuming the molecule was planar and possessed C_{2v} symmetry. A single-pair GVB wavefunction was employed using a 3-21G[12] and 6-31G*[13] basis, the latter having *d* polarization functions on the carbon centres. The automatic geometry optimization was carried out using analytic gradients, implemented in the program GAMESS.[14] Harmonic force constants, and associated vibrational frequencies, were calculated at this optimized geometry using the 3-21G basis and a single-pair GVB wavefunction and finite-difference method.[15] Although the reliability of the finite-difference method is generally accepted, vibrational frequencies were calculated for benzene in a 3-21G basis using both finite differences and analytic second derivatives.[16] Both methods gave frequencies identical to within 2 cm^{-1}.

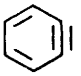
Table 1. Calculated bond lengths (Å) and angles (°) for the singlet state of *o*-benzyne

Parameter	4-31G (HF)[7]	3-21G (GVB)[a]	6-31G* (HF)[9]	6-31G* (GVB)[a]
C(1)–C(2)	1.226	1.261	1.223	1.260
C(2)–C(3)	1.389	1.382	1.382	1.383
C(3)–C(4)	1.389	1.392	1.391	1.389
C(4)–C(5)	1.420	1.403	1.410	1.404
C(3)–H(3)	1.08	1.069	1.073	1.073
C(4)–H(4)	1.08	1.072	1.076	1.076
C(1)–C(2)–C(3)	127.2	125.6	127.3	125.7
C(2)–C(3)–C(4)	110.5	112.6	110.2	112.4
C(3)–C(4)–C(5)	122.3	121.8	122.4	121.9
C(2)–C(3)–H(3)	124.8	125.2	126.9	125.3
C(3)–C(4)–H(4)	118.9	119.3	118.9	119.3
Total energy (a.u.)	−229.107 97	−228.157 80	−229.391 84	−229.436 08

[a] This paper.



(1)



(1a)

(1b)

Results and Discussion

Molecular Geometry of o-*Benzyne.*—Table 1 shows the optimized molecular geometry of *o*-benzyne computed with and without polarization functions and at the Hartree–Fock and GVB levels. The importance of allowing for diradicaloid structure in the C(1)–C(2) interaction is evident from the significant lengthening of this bond upon the inclusion of such limited electron correlation. In the 3-21G basis the values of c_1 and c_2 were 0.94 and −0.33, respectively, showing the importance of the configuration in which the anti-bonding orbital (φ_a) is doubly occupied.

The previously published geometries calculated at the Hartree–Fock level in the 4-31G[7] and 6-31G*[9] bases show that the calculated structures are quite insensitive to this increase in basis size. However, a more striking change in geometry occurs upon the inclusion of the second determinant in the molecular wavefunction. At the double-zeta valence [3-21G(GVB)] level the C(1)–C(2) bond length increases by 0.035 Å and the C(4)–C(5) length decreases by 0.017 Å compared with the 4-31G (HF) results. There is naturally an associated change in the ring bond angles, leading to smaller deviations from a regular hexagonal structure than are found at the Hartree–Fock level.

Table 2. Calculated and observed vibrational frequencies (cm^{-1}) of benzene

Symmetry	Observed	Calculated	Obs./Calc.
a_{1g}	3 073	3 388	0.91
	993	1 078	0.92
a_{2g}	1 350	1 544	0.87
a_{2u}	673	785	0.86
b_{1u}	3 057	3 345	0.91
	1 010	1 148	0.88
b_{2g}	990	1 200	0.83
	707	820	0.86
b_{2u}	1 309	1 366	0.98
	1 146	1 235	0.93
e_{1g}	846	996	0.85
e_{1u}	3 064	3 374	0.91
	1 482	1 659	0.89
	1 037	1 137	0.91
e_{2g}	3 056	3 355	0.91
	1 599	1 764	0.91
	1 178	1 323	0.89
	606	698	0.87
e_{2u}	967	1 156	0.84
	398	466	0.85

Table 3. Calculated vibrational frequencies (cm^{-1}) of *o*-benzyne

	Frequency[a]		Approximate description
Symmetry	Unscaled	Scaled	of mode
a_1	3 399	3 159 (2 343)	CH Stretch
	3 369	3 130 (2 312)	CH Stretch
	1 931	1 859 (1 853)	C(1)–C(2) Stretch
	1 612	1 438 (1 316)	Ring and CH bend
	1 394	1 279 (1 201)	Ring and CH bend
	1 260	1 162 (1 015)	Ring stretch
	1 100	1 064 (844)	Ring stretch
	1 074	958 (780)	Ring stretch
	692	616 (596)	Ring bend
a_2	1 164	997 (842)	CH Bend
	1 009	868 (681)	CH bend
	762	670 (600)	Ring bend
	531	466 (427)	Ring bend
b_1	1 104	948 (776)	CH Bend
	855	736 (565)	Ring and CH bend
	464	407 (351)	Ring bend
b_2	3 394	3 154 (2 339)	CH Stretch
	3 352	3 115 (2 299)	CH Stretch
	1 653	1 549 (1 508)	Ring and CH bend
	1 570	1 449 (1 335)	Ring and CH bend
	1 364	1 253 (985)	CH Bend
	1 210	1 112 (900)	Ring and CH Bend
	1 034	927 (834)	Ring bend
	664	590 (579)	Ring bend

[a] The unscaled values refer to C_6H_4. The scaled values are for C_6H_4 and in parentheses for C_6D_4.

Table 4. Assignment of vibrational spectrum of *o*-benzyne

Frequency (cm^{-1})			
Obs.	Calc	Symmetry	Mode
468	407	b_1	Ring bend
	590	b_2	Ring bend
735	736	b_1	Ring and CH bend
849	927	b_2	Ring bend
	948	b_1	CH Bend
	958	a_1	Ring stretch
1 053 1 038	1 253	b_2	CH Bend
	1 112	b_2	Ring and CH bend
	1 279	a_1	Ring and CH bend
	1 162	a_1	Ring stretch
	1 064	a_1	Ring stretch
1 451	1 438	a_1	Ring and CH bend
1 607	1 449	b_2	Ring and CH bend
1 627	1 549	b_2	Ring and CH bend
2 085	1 859	a_1	C(1)–C(2) stretch

Thus, the five carbon–carbon bond lengths involving one or more hydrogenated carbon atoms are in the range 1.382—1.403 Å (compared to the value of 1.388 Å in benzene), and span a significantly smaller range (0.021 Å) than predicted at the Hartree–Fock level (0.031 Å). Thus, upon dehydrogenation of benzene, the delocalized structure involving the five other carbon–carbon bonds remains largely intact, with considerable triple-bond character in the C(1)–C(2) bond, with a predicted length of 1.261 Å compared with a value of 1.205 Å in acetylene. Thus, our predicted structure has some cumulene-like features, similar to structures explored by Haselbach.[3] We have focused our attention upon the GVB results using the 3-21G basis. The optimized geometry obtained with the much larger basis differs very little from that obtained from the smaller basis, although the total molecular energy is, of course, considerably lower (Table 1).

Molecular Vibrational Frequencies of o-*Benzyne*.—The calculation of harmonic force constants from Hartree–Fock wavefunctions usually leads to values larger than those found experimentally. Only in the case of small molecules is it in general practical to include the degree of electron correlation needed to achieve close agreement with experiment. Hence scaling procedures are commonly used to interpret vibrational spectra in terms of *ab initio* wavefunctions. This has been discussed in detail by Pulay and his co-workers, an extensive study of the case of benzene being given in ref. 17. Table 2 shows a comparison between the observed and calculated [at the 3-21G(HF) level] frequencies of benzene. It can be seen that scaling factors in the range 0.8—0.9 are generally found. We would thus expect similar scaling factors to operate in the case of *o*-benzyne. However, rather than scale the frequencies, it is more appropriate, when attempting an assignment of the observed frequencies, to scale the force constants themselves, since scale factors for the different internal co-ordinates vary appreciably. We follow the procedure discussed by Pulay *et al.*[17] in their study of the force field on benzene. Empirical scale factors are introduced according to equation (2) where F'_{ij} is the

$$F'_{ij} = (x_i x_j)^{\frac{1}{2}} F_{ij} \qquad (2)$$

scaled force constant, F_{ij} is the theoretical one, and x_i, x_j are scale factors for the internal co-ordinates i and j, respectively. We have used the values of x suggested in Table 8 of ref. 17 (the special values for the off-diagonal elements were not used). Thus, the cartesian force constants given by GAMESS were transformed into the internal co-ordinate values, scaled as outlined above, and then treated by the GF matrix method. Such a procedure yielded the scaled vibrational frequencies of *o*-benzyne shown in Table 3. We also give here the predicted values for the fully deuteriated species, to aid possible future experimental work.

The experimental vibrational spectrum of *o*-benzyne[1] has given nine frequencies, and Table 4 shows our assignment of these in terms of our computational results (Table 3). The reasons for this assignment are now given.

The band at 2 085 cm^{-1} is clearly assigned to the a_1 C(1)–C(2) stretch calculated at 1 859 cm^{-1}, since the next nearest calculated frequency is 1 549 cm^{-1}. In view of our previous discussion it may seem anomalous that the unscaled calculated frequency (Table 3) is *smaller* than the experimental value. However, this mode is a strongly localized C(1)–C(2) stretch, and our wavefunction includes a substantial degree of electron correlation involving this bond. Thus, we do not expect the calculated frequency to be substantially larger than the experimental value, the latter situation being expected in the absence of correlation effects. The lowest energy vibration at 468 cm^{-1} is assigned to the b_2 and b_1 ring bend modes calculated at 590 and 407 cm^{-1}, respectively. From the calculated frequencies (Table 3) the only candidate for the observed band at 735 cm^{-1} is the b_1 CH and ring-bending mode, calculated to be at 736 cm^{-1}. We assign the observed transition at 849 cm^{-1} to the b_2 ring bending mode at 927 cm^{-1}, the b_1 CH bend at 948 cm^{-1} and to the a_1 ring stretch mode at 958 cm^{-1}. The two closely spaced transitions at 1 038 and 1 053 cm^{-1} can be associated with the five allowed CH bending and ring-stretching transitions calculated at 1 112, 1 253 (b_2) and 1 064, 1 162, 1 279 cm^{-1} (a_1). The transition at 1 451 cm^{-1} is associated with the a_1 CH and ring-bending transition at 1 438 cm^{-1}. The only calculated transitions which are close in energy to those observed at 1 607 and 1 627 cm^{-1} are the b_2 CH and ring bending vibrations at 1 449 and 1 549 cm^{-1}.

Conclusions

We have described herein the first fully optimized structure of *o*-benzyne, calculated including the most important correlation effects which allow for diradicaloid structure at the dehydro-centres. The geometry we obtain is closer to a cumulene-like structure than that found in the absence of electron correlation. We have presented a consistent assignment of the vibrational spectrum of *o*-benzyne, calculated at this predicted equilibrium geometry, although the deviations between the calculated and observed frequencies do introduce some uncertainties into the assignment. This assignment does not differ substantially from that proposed on the basis of MNDO calculations.[18]

We would stress that the transfer of force constant scaling factors from one molecule to another as carried out here may not always be appropriate, especially when the scale factors derived for a Hartree–Fock force constant matrix are applied to a force constant matrix derived from a correlated wavefunction as in the case studied in this paper.

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