Do Bicyclic Forms of *m*- and *p*-Benzyne Exist?

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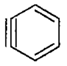
Density functional theory calculations (restricted and unrestricted B3LYP with the cc-pVDZ and cc-pVTZ basis sets) have been carried out for *m*- and *p*-benzyne. For *p*-benzyne a closed form (bicyclic **3b**) and an open form (singlet diradical **3a**) were located along with the transition structure that connects them. IRC calculations were also performed in order to ensure that the transition structure linked the two minima. Butalene (**3b**), though substantially higher in energy than the singlet diradical **3a**, might be able to be isolated at low temperature because of the relatively large activation energy predicted for its conversion into the diradical **3a**. In the case of *m*-benzyne the DFT results with the cc-pVDZ basis set also indicated that a bicyclic (**2b**) and a singlet diradical (**2a**) were minima on the potential surface. However, with the cc-pVTZ basis set only the bicyclic form **2b** was found to be a minimum. The computed IR spectrum of the bicylic form (**2b**) was found to be in good agreement with the previously reported experimental spectrum. Recent experimental evidence on the chemical reactivity of *m*-benzyne supports a bicylic structure.

Introduction

For over fifty years benzynes (didehydrobenzenes), *o*-benzyne (**1**), *m*-benzyne (**2**), and *p*-benzyne (**3**) have been recognized as reactive intermediates in a wide range of organic reactions.[1−3]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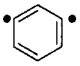
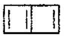

2a


2b


3a


3b

Early investigations focused on their possible existence, e.g., Roberts' classic experiment of 1956 showed by isotopic labeling that *o*-benzyne is a reactive intermediate in the "nucleophilic substitution" of halobenzenes[4] and Washburn's trapping evidence verified the existence of *m*-benzyne.[5,6] More recently the emphasis has been on low-temperature preparation of these reactive species and their characterization by infrared spectroscopy.[7] *o*-Benzyne was the first to be characterized by its generation in an argon matrix.[8] The interpretation of its infrared spectrum was greatly aided by MP2 calculations performed for *o*-benzyne and several of its isotopically labeled derivatives. The calculated (unrestricted B3LYP/6-31G*) IR spectrum of *o*-benzyne showed that it is superior to that obtained earlier with the MP2 method.[9] This result has added to the growing evidence that the DFT method is extremely useful for characterizing diradical species in spite of it being based on a single determinant.[10−15]

In 1996 *m*-benzyne was prepared in a matrix and characterized by its infrared spectrum.[16] Two years later the matrix isolation of *p*-benzyne was reported.[17] Calculated IR spectra [CCSD(T) for the former and DFT for the latter] helped in their identification, and in both cases it was concluded that the open-shell diradical had been formed (**2a** and **3a**), rather than the closed bicyclic forms (**2b** and **3b**). Here the question is addressed whether the bicyclic forms of *m*- (**2b**) and *p*-benzyne (**3b**) might possibly exist.

Computational Details

All the density functional calculations were done with the program Gaussian 98W, revision A.3,[18] using Becke's three-parameter hybrid method[19] with the Lee−Yang−Parr correlation function.[20] All structures were fully optimized, and stationary points were characterized by frequency calculations done at the same level of theory that the geometry optimizations were done. The DFT wavefunctions for the open-shell systems (**2a**, **3a** and **4**) were found to be unstable, and for these the unrestricted DFT method was employed. The reaction pathway for conversion of **3a** to **3b** via transition structure **4** was followed using the intrinsic reaction coordinate method (IRC). For following the path from **4** to **3b** "guess" was set equal to "mix,always" in order to obtain a smooth curve, since during the course of this path there is a change from an open-shell system to a closed-shell system (**3b**). Two basis sets were employed, cc-pVTZ[21] and cc-pVDZ.[22] All results quoted in the text unless otherwise noted were obtained with the cc-pVTZ basis set. The cc-pVDZ and cc-pVTZ optimized geometries, energies and vibrational frequencies are available as Supporting Information on the web.

Results and Discussion

p-Benzyne

Butalene (**3b**) has been calculated to be a strongly antiaromatic system [resonance energy per π electron

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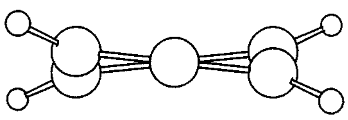
(REPE) = $-0.067\ \beta$][23] and therefore it is expected that it should be stable only at very low temperatures. The only previous ab initio calculations[24,25] on butalene were carried out at the SCF and GVB levels. This means that electron correlation effects were neglected, while it is known that they are important in highly conjugated systems. In both cases the authors suggested that butalene might very well exist. A "transition structure" was located[25] for the reaction of **3b** to **3a** by varying stepwise the C_1-C_4 distance and optimization of all other internal coordinates. However, it is known that such a procedure often does not locate the true transition structure, since it might possibly lead to "chemical hysteresis" as described by Dewar.[26]

DFT calculations (see Computational Details) were used to locate the two minima (**3a** and **3b**) as well as the transition structure that links them. Both minima were found to exist as planar (D_{2h}) structures. However, the transition structure (**4**) was found not to have D_{2h} symmetry, but rather a "twisted", nonplanar structure with D_2 symmetry.



4

The "reaction coordinate" (distance between the carbon atoms bonded only to other carbon atoms in **3a**, **3b**, and **4**) changes from 1.568 Å in butalene (**3b**) to 1.999 Å in transition structure **4** to 2.666 Å in the singlet diradical **3a**. The central C−C bond length in butalene is unusually long for a bond between two sp^2-hybridized carbon atoms, but this can be attributed to the high strain in the bicyclic structure as well as to the antiaromaticity of butalene.[23] IRC calculations were also performed to ensure that the transition structure found does link the two minima. Several points on the path are plotted in Figure 1. Note the twisting (clockwise) about the C_2 axis between **3a** and the transition structure **4**, followed by reverse twisting (counterclockwise) between **4** and butalene (**3b**).

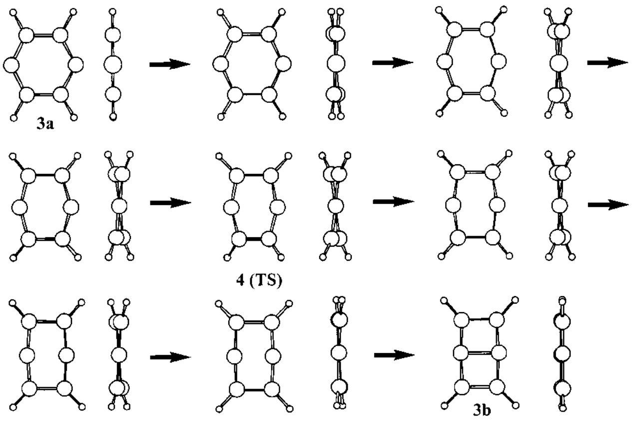


Figure 1. The IRC reaction pathway for the conversion of **3a** via transition structure **4** to butalene (**3b**)

The transition structure is computed to be 43.2 kcal/mol higher in energy than **3a** and 5.9 kcal/mol above that of butalene (**3b**). Even though the energy of butalene is computed to be 37.3 kcal/mol higher in energy than for its open-shell diradical form **3a,** it might very well be isolable at very low temperature given the relatively large activation barrier for its conversion into **3a**. In Figure 2 the computed infrared spectra of **3a**[27] and **3b** are plotted with that obtained previously from experiment.[17,28]

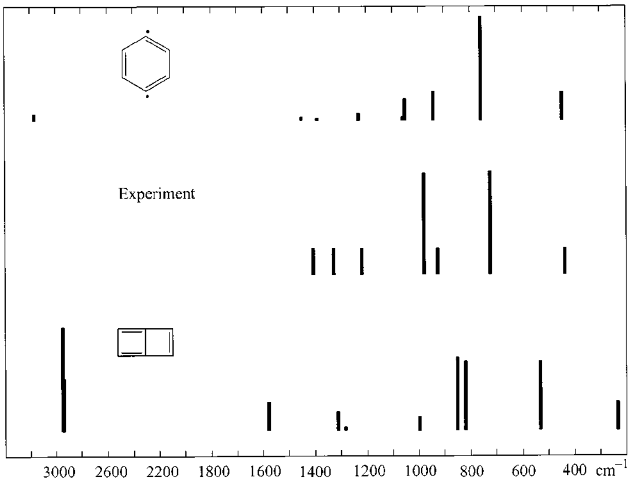
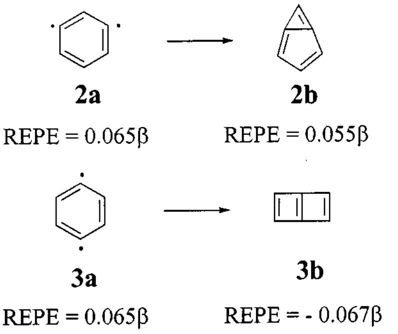


Figure 2. The DFT (B3LYP/cc-pVTZ) IR spectra of **3a** and **3b** compared to that of experiment[17,27]

The significant difference between the spectra of **3a** and **3b** should make the identification of butalene by its IR spectrum relatively easy. We also note that as in the case of *o*-benzyne[9] the unrestricted DFT calculation reproduces the observed *p*-benzyne spectrum in an excellent fashion.

m-Benzyne

Unlike butalene, the bicyclic form of *m*-benzyne (**2b**) is computed to have a very high resonance energy per π electron (REPE = 0.055 β) which is in fact very close to that of benzene (0.065 β).[23,29] This might very well affect the stability of the bicylic form of *m*-benzyne. Consider the following two processes in which the singlet diradical, the open form of the benzyne, closes to the bicylic benzyne.



In both cases the ring closure will lead to a significant amount of angle strain which of course is offset to some extent by the formation of a σ bond. Both open forms (**2a** and **3a**) might be considered to be similar to benzene in their π stabilization or aromaticity (REPE = 0.065 β). However, ring closure of *m*-benzyne to **2b** will bring about only a slight loss of π stabilization, while ring closure of *p*-benzyne to **3b** will bring a significant decrease in π stabilization. From this simple analysis it may be predicted that it is a more probable that *m*-benzyne should exist in the bicyclic form, whereas the open-shell singlet of *p*-benzyne (**3**) might very well be favored over that of butalene. This latter point is borne out by the calculations described above.

However, previous calculations are not conclusive on what the structure(s) of *m*-benzyne is. CCSD(T) calculations[16] indicate only a single minimum for *m*-benzyne, that of the singlet diradical, while DFT calculations[30] indicate there should be two minima, with the energy of the bicylic form slightly lower than that for the singlet diradical. *m*-Benzyne was first isolated in 1996, and its structure was confirmed with the results of a CCSD(T) calculations of the IR spectrum for only the open form (**2b**); the bicyclic form was not considered, since it was not found to be a minimum on the potential surface.[16] Subsequently, the authors did mention that DFT (B3LYP/6-31G*) calculations for the bicyclic form showed, it too was a minimum on the potential surface. However, they did not consider it to be a possible structure for *m*-benzyne, since they found no bicyclic structure using CCSD(T).[30] Unfortunately, no computed DFT IR spectrum was reported for **2b**. The failure to confirm a bicyclic structure with CCSD(T) calculations should by no means rule out its existence. Indeed Cramer[14] has suggested that DFT calculations "provide very good geometries for stationary points along the Bergman and aza Bergman cyclization reaction coordinates – as good or better than much more expensive CCSD(T) geometries." It was therefore decided to pursue further the DFT calculations for *m*-benzyne, in particular to compute the DFT IR spectrum of **2b** for comparison with the observed one.

In the present investigations minima for **2a** and **2b** as well as the transition structure that links them were initially located using the cc-pVDZ basis set. The bicyclic form (**2b**) was computed to be 1.7 kcal/mol lower in energy than the open form (**2a**); however, the activation energy for conversion of **2a** to **2b** was found to be only 0.04 kcal/mol. As a consequence of this the larger cc-pVTZ basis set was employed with B3LYP and it was found that the minimum **2a** "disappeared"; that is, no minimum for the singlet diradical of *m*-benzyne was found at this level of theory. To be sure that there is indeed no minimum for the open-shell system with the cc-pVTZ basis set (this search is complicated by the fact that the open-shell system requires unrestricted DFT while the bicyclic form is correctly computed with restricted DFT), unrestricted DFT optimizations at a set of fixed distances between the two carbon atoms bearing no hydrogen atoms were carried out. The distance was varied in intervals between 2.30 Å and 1.6 Å. A plot of the energies obtained for these points vs. the C–C distance gave a curve in which there was no minimum but a slight "hump" between 2.10 Å and 2.00 Å in the otherwise smooth curve. S^2 became zero at approximately 2.00 Å.

Hence these results are suggestive, but not conclusive, that there exists only one form of *m*-benzyne, the π-stabilized structure **2b**. In order to support this suggestion, the IR spectrum was computed using this higher level of theory for **2b**. In Figure 3 results of these calculations are presented along with the earlier reported[16] experimental spectrum and the CCSD(T) spectrum for **2a.**

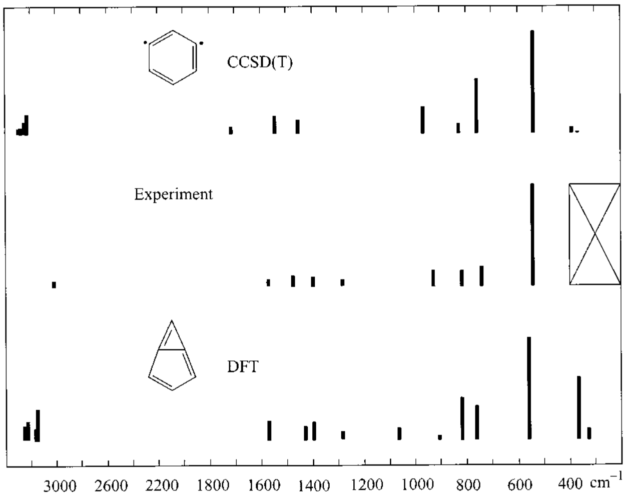
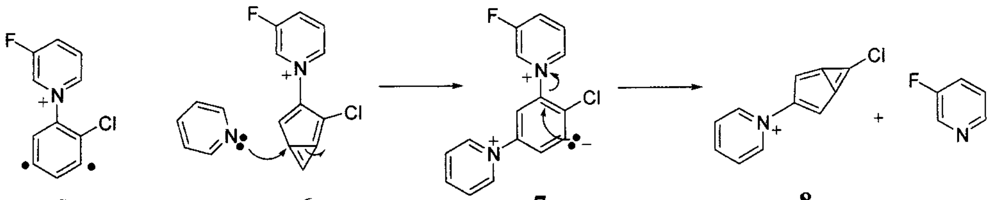


Figure 3. The computed and experimental spectra[16] of *m*-benzyne

It is seen from the figure that it is difficult to assess which calculated spectrum agrees better with that of the experiment. Both compute the strongest band to be about 550 cm^{-1}. The agreement for the CCSD(T) might be considered to be better in the region of 600–1000 cm^{-1}. At the same time note that the DFT spectrum contains four medium to weak bands in the region of 1200–1600 cm^{-1}, while the CCSD(T) contains only three bands in this region. Finally, DFT predicts a relatively strong band just below 400 cm^{-1}, whereas no intense band in this region is predicted by the CCSD(T) method. Unfortunately, the experimental spectrum for *m*-benzyne was not reported below 400 cm^{-1}. A new experimental spectrum which would include the lower frequencies might very well settle the answer to the question of what is the structure of *m*-benzyne.

Very recently two experimental reports have appeared which suggest that the structure of *m*-benzyne is the closed-shell, bicyclic tautomer **2b**, rather than the open-shell diradical **2a**. In the first report Kenttämaa studied the gas-phase chemistry of a substituted *m*-benzyne and concluded that "the *m*-benzyne is much less reactive than either the isomeric *o*-benzyne or the related monoradical. The reduced radical-type reactivity is rationalized by the strong coupling of the formally unpaired electrons in the *m*-benzyne."[31] More recently, Kenttämaa found that the substituted *m*-benzyne **5** reacts as an electrophile with pyridine, although in the mechanism he used the open-shell form of **5**, rather than its bicyclic form.[32] The following mechanism that involves the closed-shell tautomer of **5** (**6**) might better

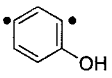


5 **6** **7** **8**

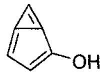
explain his observations. Here pyridine attacks the three-membered ring of **6** with formation of the intermediate **7** with subsequent formation of the *m*-benzyne **8**. The driving force for this reaction is in part due to the formation of the unusually stable bis(pyrdinium)phenide intermediate (**7**).[32]

4-Hydroxy-*m*-benzyne

The matrix isolation of 4-hydroxy-*m*-benzyne (**9**) has also been reported.[30,33] The conclusion that its structure has an open form was derived from comparison of the observed IR spectrum with spectra that were computed for the open-shell diradical with the CCSD(T) and DFT methods. Again the observed spectrum was not compared to the spectra of the bicyclic form. In Figure 4 the observed spectrum is compared with our DFT (B3LYP/cc-pVDZ) computed spectra of the bicyclic structure (**9b**) and with the previously reported CCSD(T) results performed for the open form (**9a**).



9a



9b

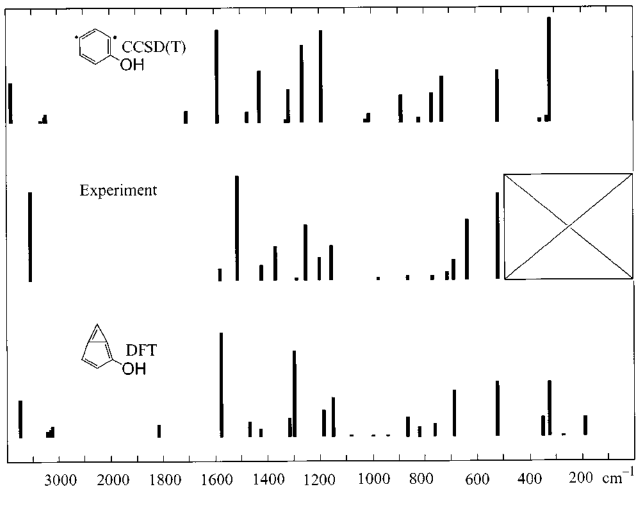


Figure 4. The computed spectra of **9a** and **9b** compared to that of experiment

It is apparent that the spectrum of the computed bicyclic structure appears to be in slightly better agreement with the observed spectrum than that for the open structure; this is especially true when the calculated relative intensities are examined. However, this agreement is not sufficiently good to conclude that this benzyne exists as a bicyclic structure rather than as an open diradical.

Conclusions

For the first time it is suggested that butalene (**3b**) is a good candidate for low-temperature isolation, since it is calculated to exist as an intermediate with a significant activation energy for its conversion into the singlet biradical **3a**. The computed spectrum of butalene (**3b**) was found to differ substantially from that of the biradical **3a** which should allow its identification by IR spectroscopy relatively easily.

The structure of *m*-benzyne has been discussed in the light of DFT calculations. It was found that DFT (B3LYP/cc-pVTZ) calculations find the optimized structure to be a closed-shell bicylic one (**2b**), in contrast to earlier CCSD(T) results that find the open-shell singlet biradical (**2a**) to be the only minimum on the potential surface. Very recently, Debbert and Cramer[34] have found the same result for *m*-benzyne (including also *m*-pyridynes) with DFT and CASSCF calculations. They noted that "absolute energies calculated at the CASPT2 level are lower for the DFT geometries than for the CAS (8,8) geometries" for a series of *m*-pyridynes. They concluded that "the ring contraction (i.e., from the open form to the bicylic form) appears to be a function of dynamical electron correlation that is included in the DFT Hamiltonian but absent in the MCSCF process." Given the recent experimental results of Kenttäsmaa, calculations by Debbert and Cramer and the results presented here, it appears that *m*-benzyne might very well exist in the bicylic form (**2b**) rather then the open-shell diradical (**2a**). However, additional experiments need to be performed, especially to obtain the IR spectrum of *m*-benzyne below 400 cm^{-1}, before the question of the structure of *m*-benzyne can be answered with certainty.

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