

# *m*-Benzyne and bicyclo[3.1.0]hexatriene – which isomer is more stable? – a quantum chemical investigation

Elfi Kraka<sup>a,\*</sup>, Josep Anglada<sup>b</sup>, Angelica Hjerpe<sup>a</sup>,  
Michael Filatov<sup>a</sup>, Dieter Cremer<sup>a</sup>

<sup>a</sup> Department of Theoretical Chemistry, Göteborg University, Box 460, Reutersgatan 2, S-41320 Göteborg, Sweden

<sup>b</sup> Departament de Química Organica Biologica, Institut d'Investigacions Químiques i Ambientals de Barcelona,  
I.I.Q.A.B.-CSIC, Jordi Girona 18, 08034-Barcelona, Catalunya, Spain

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## Abstract

Density functional theory (DFT) predicts that bicyclo[3.1.0]hexatriene (**2**) is more stable than its isomer *m*-benzyne (**1**). Hess [Eur. J. Org. Chem. (2001) 2185] has argued that experimental findings suggesting **1** can equally or even better be associated with **2**. However, high level ab initio calculations (CCSD(T), CASPT2) show that **2** does not exist and that the previously measured infrared spectrum is correctly assigned to **1**. Bond stretch isomers are possible for *p*-benzynes but not for *m*-benzynes. The electrophilic character of *m*-benzynes is in line with **1** but not with **2**. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Bond stretch isomerism is an interesting topic in structural chemistry, however unambiguous experimental examples have proven elusive because of the many difficulties in spectroscopically detecting true bond stretch isomers [1,2]. Although theoretical investigations of bond stretch isomers are easier to carry out, they can also be hampered by the fact that the bond-stretching (dissociation) process invokes multi-reference effects, that are difficult to handle quantum chemically with standard methods.

Possible candidates for bond stretch isomers are 1,4- and 1,3-didehydrobenzene (*p*- and *m*-ben-

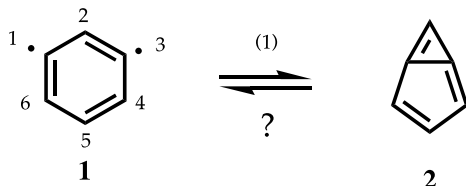
zyne), which both have been extensively studied in recent years because of their relevance in connection with enediyne antitumor drugs where in particular the former molecule was object of many investigations. Less is known about *m*-benzyne, which only recently could be directly investigated experimentally. In a pioneering paper, Sander and co-workers [3] described the isolation of *m*-benzyne in an argon matrix at low temperature and its identification by the comparison of measured and calculated infrared spectrum. According to this work, *m*-benzyne is a singlet biradical with a long C1C3-distance (2.1 Å [3]) and a slightly distorted benzene ring. Wenthold, Squires, and Lineberger measured the ultraviolet photoelectron spectra of the negative ions of the three-benzynes and were able to determine the singlet–triplet splitting of *m*-benzyne to be  $21.0 \pm 0.3$  kcal/mol [4]. Also, several substituted *m*-benzynes were experimentally in-

\* Corresponding author. Fax: +46-31-773-55-90.

E-mail address: Elfi.Kraka@theoc.gu.se (E. Kraka).

vestigated [5–9]. For example, Sander and co-workers synthesized *m*-didehydrophenol and measured its infrared spectrum under matrix isolation conditions [5–7]. Again, the properties of this derivative were determined by comparing measured with calculated infrared spectra.

Despite these experimental accomplishments, most information on *m*-benzynes is based on quantum chemical investigations, which almost exclusively suggest the biradical structure **1** to represent *m*-benzyne and its derivatives [10–15]. Kraka and Cremer [10,11] investigated the three-benzynes with various quantum chemical methods to determine their relative energies, geometries and other properties. They calculated the biradical character of **1** to be 20% [11]. Although this value indicates a relatively strong coupling of the spins of the single electrons, these authors excluded, on the basis of coupled cluster (CC) calculations, the existence of bicyclo[3.1.0]hexatriene (**2**) as a second isomer of *m*-benzyne containing a C1C3 bond [10]. Hence, a possible equilibrium (**1**) between isomers **1** and **2** was not further considered.



Recently, results of the work on *m*-benzynes [3,5–7,10–12] have been questioned by Hess [16] on the basis of the following considerations:

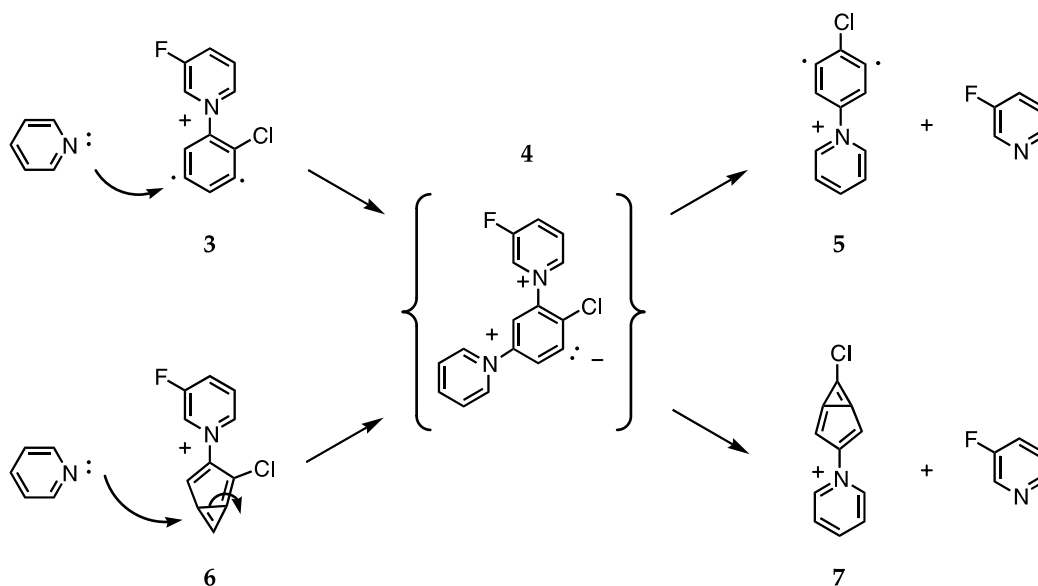
1. Density functional theory (DFT) calculations carried out with a VTZ basis set suggest that the only stable form of *m*-benzyne is the bicyclic isomer **2**.
2. The measured infrared spectrum of **1** can equally be well fitted to the calculated infrared spectrum of **2**.
3. Experimental results published by Thoen and Kenttämäa [8] on a substituted *m*-benzyne suggest that there is “a strong coupling of the formally unpaired electrons in the *m*-benzyne, which results in a reduced thermodynamic driving force and increased barrier for radical reactions”. Hence, the conclusion can be drawn that the real electronic structure of the *m*-benzyne is closer to that of isomer **2** rather than biradical **1**.

4. In a subsequent paper, Kenttämäa and co-workers [9] described the electrophilic reaction of *m*-benzyne **3** with pyridine thus yielding via a possible intermediate **4** the new *m*-benzyne **5** (see Scheme 1) [9]. Hess argued that this reaction might better be explained as a nucleophilic substitution reaction at the cyclopropene ring of the bicyclic derivative **6**, yielding again via **4** the new derivative **7** (Scheme 1).
5. Debbert and Cramer [14] published DFT calculations for *m*-pyridynes, which suggested that several of the *m*-pyridynes possess a bicyclic rather than a monocyclic structure. CASSCF calculations exclusively predicted the monocyclic structure, this however was considered as an artifact of a method lacking dynamic electron correlation [14].

In view of arguments 1–5, the question posed in the title of this Letter has to be reconsidered in particular as the DFT results for a bond-stretching problem cannot be considered to be conclusive as was also stated by Hess [16]. Although a variety of wave function theory (WFT) methods were used previously to describe the features of **1** or its derivatives [10–15], the comparison of the stabilities of **1** and **2** was not considered to be important in view of the early CC results favoring **1** [10]. Isomer **2** is a highly strained anti-Bredt compound (strain energy: ca. 90 kcal/mol), which because of its distorted (formal) methylenecyclopropene unit requires a theoretical description including several d-type and even f-type polarisation functions. Also, a balanced account of a singlet biradical possessing multi-reference character and a highly strained closed-shell system located in a flat region of the PES separated probably only by a small barrier is computationally demanding and requires a highly correlated quantum chemical method. None of the previous theoretical investigations [3,6,7, 10–16] focusing on *m*-benzynes fulfilled this requirement.

In this Letter, we compare the results of high level WFT ab initio calculations for isomers **1** and **2** with results obtained with various DFT methods to answer the following questions.

1. Are **1** and **2** possible bond stretch isomers that can co-exist under certain conditions according to the equilibrium (1)? Or does an equilibrium



Scheme 1.

- (1) not exist because only one of the two isomers is stable?
2. (2) Since DFT and CC theory obviously give contradictory answers to question (1) [10,16] it has to be clarified which of these methods can provide a reliable answer in this case. Is DFT a suitable method to describe a possible equilibrium (1) for *m*-benzyne or substituted *m*-benzynes?
3. Is it possible that any of the benzynes can exist in form of bond stretch isomers?
4. Can the reactivity observed for *m*-benzynes [8,9] better be explained invoking a bicyclic or biradical structure?
5. Do the measured infrared spectra of *m*-benzyne support structures 1 or 2 or even an equilibrium between these structures.

By answering questions 1–5, we will re-investigate the original experimental results by Sander and co-workers [3] and discuss the question whether the biradical structure 1 was really observed in the experiment.

## 2. Computational methods

The two isomers were investigated following a five-step procedure. First, exploratory calculations

were carried out using conventional single-determinant Kohn–Sham (KS) DFT with the B3LYP [17] and BLYP functionals [18,19] and the 6-31G(d,p) basis set [20]. These calculations included a stepwise scanning of the PES in the direction of the C1C3 distance (complete geometry optimizations for fixed values of the C1C3 distance in the range 1.55–2.15 Å) as well as direct minimum and saddle point searches. The internal and external stability of the restricted DFT (RDFT) solution for each structure investigated was determined employing standard procedures [21]. Vibrational frequencies were determined to characterize calculated stationary points as minimum or first order saddle point. In addition, they were used to calculate zero-point energies (ZPE) and temperature corrections to obtain enthalpies at 298 K.

In a second step, DFT–B3LYP calculations were repeated with the more reliable 6-311++G (3df,3pd) basis set [22]. The infrared spectrum for the most stable isomer was calculated and compared with the experimental spectrum. In the third step, the restricted-ensemble Kohn–Sham (REKS) method developed by Filatov and Shaik [23], which represents the total energy of a multi-configuration system as a weighted average over an

ensemble of single-determinant states, was applied. The REKS(2,2) (the active space contains the two single electrons of **1** or the electron pair forming the C1C3 bond of **2**) description includes two-configurational character to correct in this way shortcomings of single determinant KS DFT in case of structures with significant biradical character.

In the fourth step, geometry optimizations were repeated at the CASSCF [24] level using the 6-311+G(2df, 2p) basis set [22] and a (8, 8) active space, which comprises the six  $\pi$  electrons and the two unpaired electrons of **1** that form the 1,3-bridging bond in the case of **2**. Although the CASSCF method leads to a correct wave function in cases such as **1** and **2**, geometries obtained with this method are often not reliable because of the lack of dynamic electron correlation, which also affects relative energies. Hence, the more accurate CASPT2 method (including dynamic electron correlation) [25] was used to carry out single point CASPT2(8,8)/6-311+G(2df, 2p) calculations at DFT geometries and to determine a reliable value for the energy difference between isomers **1** and **2**.

In the last step, we applied projected CC theory at the CCSD(T) level, which includes all single (S) and double (D) excitations and adds the triple (T) excitations in a perturbative way [26]. Both the 6-31G(d, p) and the 6-311++G(3df, 3pd) basis sets were used at the CC level of theory to scan the PES explored at the DFT level of theory. These calculations were supported by many-body perturbation theory (MBPT) investigations employing the Møller–Plesset (MP) perturbation operator at second order (MP2), at third order (MP3), and at fourth order (MP4) [27]. In the latter case, all S, D, T, and quadruple (Q) excitations were included and both MP4(SDQ) and MP4(SDTQ) energies calculated [27]. For the calculations, the program systems ACES II [28], COLOGNE 2000 [29], GAMESS [30], and GAUSSIAN 98 [31] were used.

### 3. Results and discussion

Calculated energies and geometries obtained in this work are summarized in Table 1 and Fig. 1. Fig. 2 shows the PES as a function of the C1C3

Table 1

Absolute and relative energies of the *m*-benzynes biradical structure **1** and bicyclo[3.1.0]hexatriene **2** calculated with different methods and basis sets<sup>a</sup>

Method/basis	Biradical <b>1</b>		Bicyclus <b>2</b>	
	M/SP	<i>E</i>	M/SP	$\Delta E(1-2)$
B3LYP/6-31G(d, p)	M	-230.89451 (-230.81535)	M	2.6 (2.4)
B3LYP/6-311++G(3df, 3pd)	SP	-230.96520	M	2.9
BLYP/6-31G(d, p)	M	-230.80676	SP	-3.0
BLYP/6-311++G(3df, 3pd)	M	-230.88298	SP	-3.0
REKS(2,2)/6-31G(d, p)	M	-230.80805	SP	-3.8
MP2/6-31G(d, p)	M	-230.21140	SP	-7.0
MP3/6-31G(d, p)	SP	-230.28213	SP	7.9
MP4(SDQ)/6-31G(d, p)	SP	-230.20096	SP	2.1
MP4(SDTQ)/6-31G(d, p)	SP	-230.21704	SP	-9.0
CCSD(T)/6-31G(d, p)	M	-230.26811	SP	-2.8
CCSD(T)/6-311++G(3df, 3pd)	SP	-230.59656	SP	-1.0
GVB(1)/6-31G(d, p)	M	-229.42326	SP	-13.9
CASSCF(8,8)/6-31G(d)	M	-229.49880	SP	-15.5
CASPT2(8,8)/6-31G(d)	SP	-230.14562	SP	-6.5
CASSCF(8,8)/6-311+G(2df, 2p)	SP	-230.56492	SP	-12.9
CASPT2(8,8)/6-311+G(2df, 2p)	SP	-230.38811	SP	-4.7

<sup>a</sup> Absolute energies and enthalpies (in parentheses) in hartree, relative energies and enthalpies (in parentheses) in kcal/mol. M and SP denote energy minimum and single point calculation. The MBPT-MP<sub>n</sub> SP calculations for **1** were carried out at the CCSD(T)/6-31G(d, p) geometry, the CAS SP calculations for **1** at the BS-UB3LYP/6-31G(d, p) geometry, and all SP calculations for **2** at the B3LYP/6-311++G(3df, 3pd) geometry.

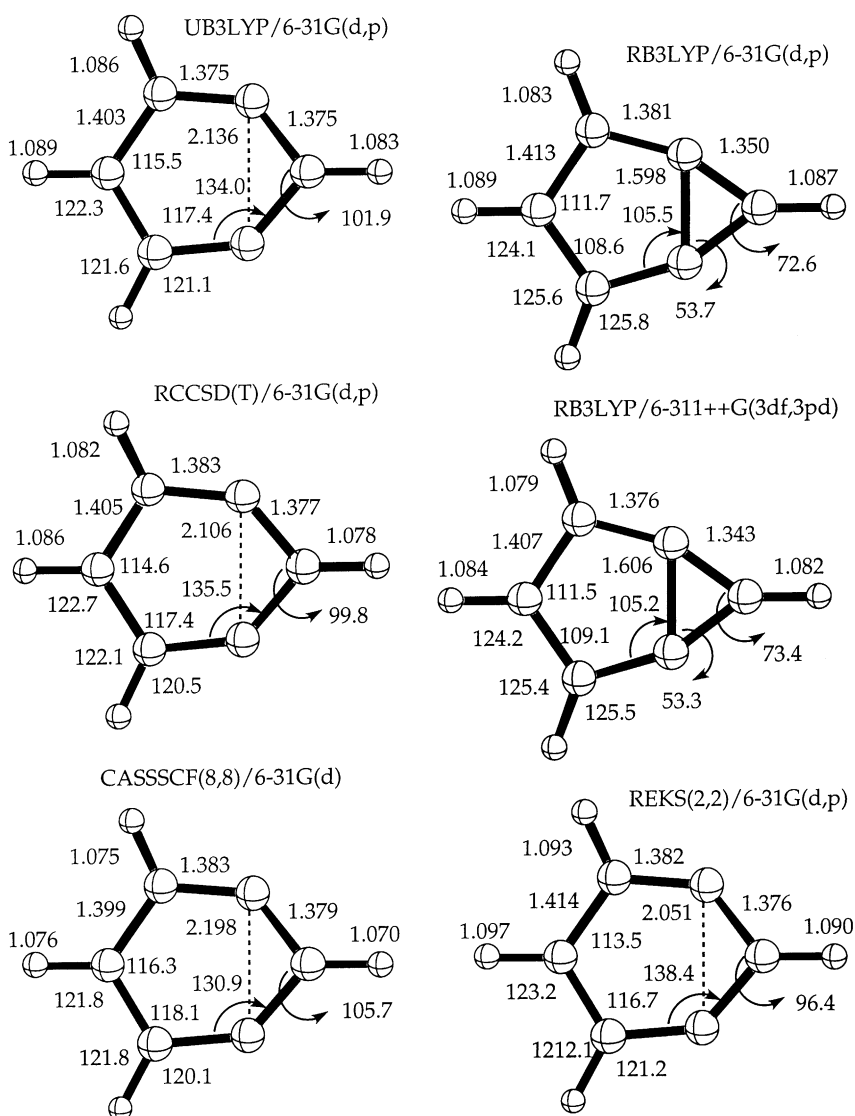


Fig. 1. Geometries of isomers **1** and **2** calculated at different levels of theory. Distances in angstrom, angles in degree.

distance where RB3LYP and UB3LYP results are compared with restricted CCSD(T) results.

At RB3LYP/6-31G(d, p), the bicyclic form rather than the open form is found to occupy the global minimum of the PES in the direction of the C1C3 distance co-ordinate. If this distance is increased stepwise, the stability analysis reveals that the RDFT description of **2** is stable up to 2.017 Å. For larger C1C3 distances, the (broken symmetry) BS-UB3LYP solution becomes more stable (Fig.

**2**), i.e., there is a branching of the RB3LYP and UB3LYP PES at this point.

At the BS-UDFT level of theory, a second minimum is found being 2.6 kcal/mol higher in energy ( $\Delta H(298) = 2.4$  kcal/mol, Table 1) than the minimum for **2** and corresponding to the open form **1** (distance C1C3: 2.136 Å, Fig. 2). However, the second minimum has little chemical relevance because the barrier separating **1** from **2** is just 0.03 kcal/mol and by this below the first vibrational

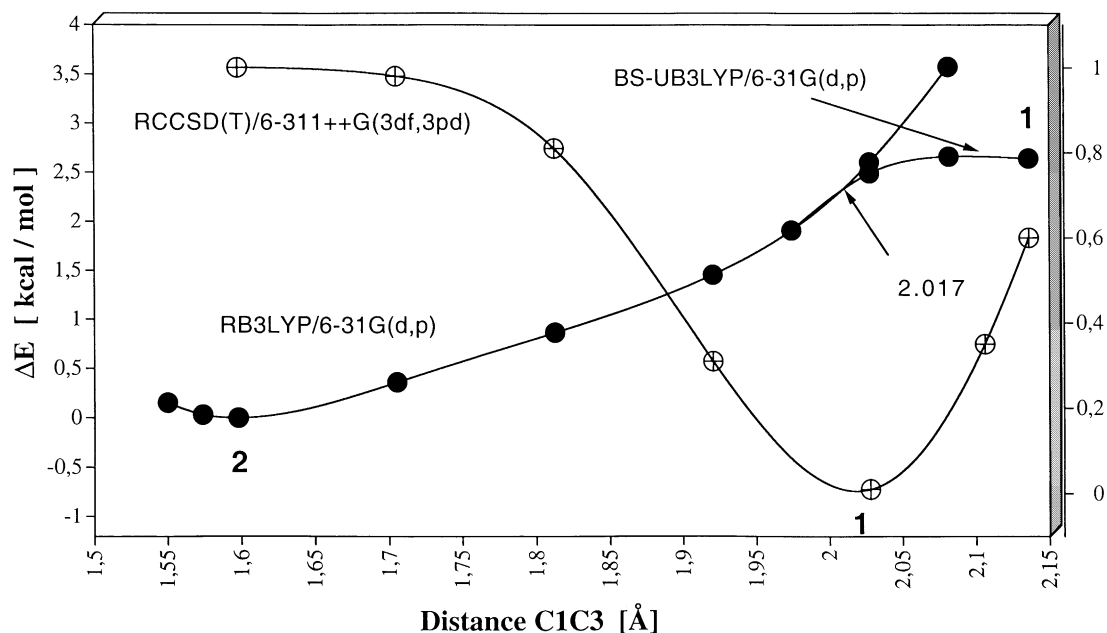


Fig. 2. Potential energy surface connecting isomers 1 and 2 calculated at different levels of theory.

level. Hence, B3LYP/6-31G(d,p) predicts the bicyclic form 2 to be the only stable form of *m*-benzyne. This result is confirmed when repeating calculations with the larger 6-311++G(3df,3pd) basis set, only that in this case a second energy minimum corresponding to the open form is no longer found despite a similar branching of the RB3LYP and UB3LYP PES. These results are in line with those of Hess [16], who used Dunning's cc-pVDZ and cc-pVTZ basis sets in connection with the B3LYP functional.

The DFT results are obscured when the same calculations are repeated with the BLYP functional. Both BLYP/6-31G(d,p) and BLYP/6-311++G(3df,3pd) predict a *m*-benzyne structure with a C1C3 distance (2.000 and 1.991 Å). A minimum for 2 is no longer found. This result is dubious in so far as the BLYP structure is obtained at the RDFT rather than the BS-UDFT level of theory, which means that it possesses 0% biradical character and cannot correspond to structure 1. The contradiction between the B3LYP and BLYP results will be easily resolved if one compares the amount of dynamic electron correlation covered by the two functionals [32]. The

LYP correlation functional and by this also the BLYP exchange-correlation functional predict a lower bond density than that obtained with the B3LYP functional. B3LYP also uses the LYP functional but corrects dynamic electron correlation by an admixture of 19% local correlation to the non-local correlation of the LYP functional [17,32,34]. This leads to a higher bond density and a more stable electron pair bond.

By stretching a single bond from 1.6 to 2 Å the difference between the BLYP and B3LYP functional can be quantified. The latter functional predicts the single bond to be 3.5 kcal/mol more stable than the BLYP functional, which in the description of normal closed-shell molecules shows only up in slightly longer bond lengths and somewhat smaller dissociation energies. However, in the present case the PES along the C1C3 bond stretching co-ordinate is very flat so that the basic deficiency of the BLYP functional of underestimating the C1C3 bond strength leads to a bicyclic structure with an unrealistic bond length C1C3 of 2 Å and 0% of biradical character. In view of the unreliability of the BLYP functional it is appropriate to revert to the B3LYP results and to clarify

whether they can provide a reliable description of the relative stabilities of **1** and **2**.

DFT–B3LYP has been found to yield reliable results for certain multi-reference problems related to bond dissociation provided BS-UDFT is used [33,34]. For example, in the case of singlet biradicals such as *p*-benzyne or *m*-benzyne, UDFT introduces biradical character into the DFT description. The reliability of the BS-UDFT solution critically depends on the singlet–triplet splitting [34], which in the case of **1** is 21 kcal/mol [4]. Accordingly, the singlet state of **1** suffers considerably from the contamination by the triplet state and the energy of the  $^1A_1$  state is predicted to be too high at the BS-UDFT level of theory. A check with the sum formula, which provides a simple correction of BS-UDFT/B3LYP energies for singlet biradicals [33], reveals that the  $^1A_1$  state calculated at the BS-UB3LYP/6-31G(d,p) level of theory should be 4.3 kcal/mol lower in energy thus predicting isomer **1** to be at least 1.7 kcal/mol more stable than the bicyclic form **2**.

To verify this prediction, we carried out REKS(2,2)/6-31G(d,p) calculations, which cover two-configurational effects needed for a reliable account of the relative stabilities of isomers **1** and **2**. At this level of theory, biradical **1** is found to occupy the only minimum along the C1C3 co-ordinate. The bicyclic form **2** is just a transient point on the PES being at least 3.8 kcal/mol higher in energy (using its RB3LYP geometry, Table 1).

WFT methods including a sufficient amount of electron correlation exclusively predict the biradical form **1** to be the only stable form of *m*-benzyne. The calculated MBPT energy differences are –7.0 (MP2) and –9.0 kcal/mol (MP4). MP3 and to a certain degree also MP4(SDQ) are known to be close to the RHF description (RHF : +21.0; MP3 : +7.9; MP4(SDQ) : +2.0, Table 1) and therefore they are not reliable. At the restricted CCSD(T) level of theory the corresponding values are –2.8 and –1.0 kcal/mol, respectively.

GVB(1), which is identical to CASSCF(2,2), leads to a biradical structure, which is 13.9 kcal/mol more stable than a hypothetical bicyclic **2**. CASSCF(8,8) predicts the biradical to be more stable by 15.5 and 12.9 kcal/mol depending on

whether a 6-31G(d) or 6-311+G(2df,2p) basis is used. Inclusion of dynamic electron correlation at the CASPT2(8,8) level of theory corrects these values considerably yielding differences of –6.5 and –4.7 kcal/mol. A minimum for **2** is not found with any of the multi-configurational methods used in this work. Hence, we can conclude that the biradical **1** is the only stable isomer. The single determinant DFT results are clearly misleading and have to be discarded.

Although the equilibrium (**1**) does not exist, the question has to be posed whether biradical **1** carries out a large amplitude vibration involving the C1C3 co-ordinate thus effectively closing the biradical to a bicyclic structure. High-level WFT methods predict a flat PES varying just by a few kcal/mol in the relevant region. Analysis of the calculated vibrational modes [35] revealed that there is indeed a large amplitude vibration involving a stretching of the C1C3 distance, however this should deform the *m*-benzyne ring not much stronger than the benzene ring. From the shape of the PES one can deduce that contrary to benzene, the C1C3 stretching vibration will yield an  $r_z(\text{C1C3})$  distance, which should be somewhat smaller than  $r_e(\text{C1C3})$ , probably being close to 2 Å.

While calculated energies already exclude the existence of **2**, there is also a distinct difference in the infrared spectra of compounds **1** and **2** that suggest the existence of **1** rather than **2**. In Fig. 3, experimental and calculated infrared spectra are compared. There is reasonable agreement of the former with the CCSD(T)/6-31G(d,p) spectrum of **1** while it differs from the B3LYP/6-311++G(3df,3pd) spectrum of **2**, which possesses more infrared bands because of the stronger distortion of the benzene hexagon. We note in this connection that Hess [16] chose to assign to *m*-benzyne two weak bands of the infrared spectrum measured by Sander and co-workers [3] for the reaction mixture containing *m*-benzyne. Contrary to Hess we take the assignment of infrared bands to *m*-benzyne as suggested by the experimentalists who pointed out that “annealing of the matrix at 30–35 K (containing *m*-benzyne and other products) resulted in ... a decrease in intensity of the (infrared) absorptions assigned to (*m*-benzyne)”

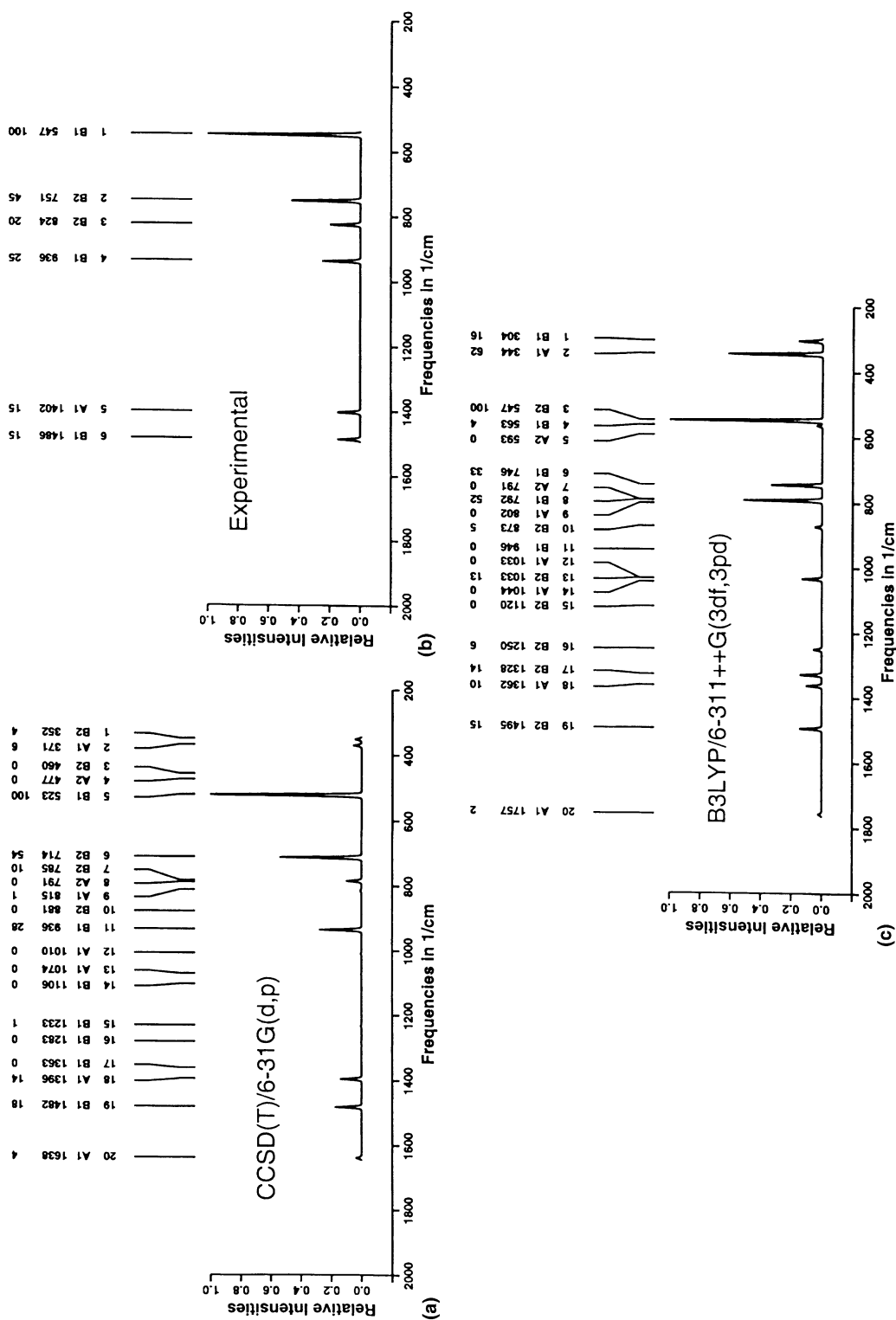


Fig. 3. CCSD(T)/6-31G(d,p) infrared spectrum of **1** (a), experimental infrared spectrum of *m*-benzene (b), and B3LYP/6-311++G(3df,3pd) infrared spectrum of **2** (c). The vibrational frequencies are scaled by a factor of 0.96. Intensities are given relative to the maximum intensity set to 100. In the case of the experimental spectrum, frequencies and intensities are taken from [3].



thus allowing the identification of those infrared absorptions belonging to *m*-benzyne [3].

The published infrared spectrum of *m*-benzyne provides sufficient evidence to assign it to **1** rather than the hypothetical bicyclic structure **2** (Fig. 3). An equilibrium (1) including a bicyclic structure can be excluded for *m*-benzyne. This conclusion, however, does not exclude that such an equilibrium may exist for substituted *m*-benzyne as has been argued by Hess [16]. To consider this argument from a more basic point of view rather than to perform extensive calculations on substituted *m*-benzyne, we recall briefly the requirements for

bond stretch isomerism [1,2]. Fig. 4a schematically gives the changes in the energies of the frontier orbitals for converting butalene (**8**) to *p*-benzyne (**9**).

The  $\sigma$  MO describing the 1,4 bond of **8** is well below the corresponding  $\sigma^*$  MO. For increasing the 1,4-bond length the two orbital energies approach each other where in the normal case they should not cross in the range 1.5 (**8**)–2.7 (**9**) Å. However, in the case of **9**, through-bond interactions [2,10,11] involving vicinal  $\sigma(\text{CC})$  and  $\sigma^*(\text{CC})$  orbitals lead to a stabilization of the  $b_{1u}$ -orbital and a destabilization of the  $a_g$ -orbital so

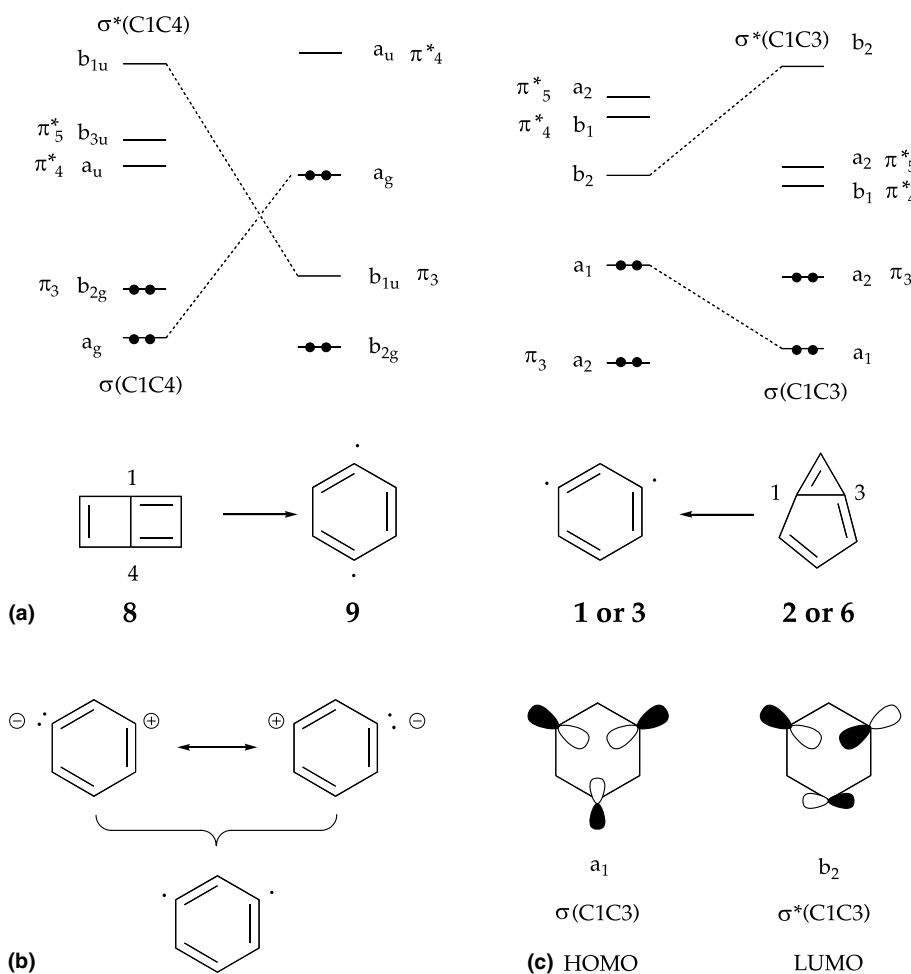


Fig. 4. (a) Frontier orbitals for the ring opening of butalene (**8**) to *p*-benzyne (**9**) and the ring opening of bicyclo[3.1.0]hexatriene (**2**) to *m*-benzyne (**1**). (b) Zwitterionic resonance structures of biradical **1**. (c) Frontier orbitals of **1**.

that the order of the orbitals is changed for **9** (Fig. 4a).

Through-bond interactions also take place in the case of *m*-benzynes, however their effect does not change the order of the  $a_1$ -symmetrical  $\sigma(\text{C1C3})$  and the  $b_2$ -symmetrical  $\sigma^*(\text{C1C3})$  orbital. In the case of **9**, breaking of the C1C4 bond formally leads to the occupation of an excited state orbital, which in the state correlation diagram corresponds to an avoided crossing of the  $^1A_g$  ground state and a doubly excited state of the same symmetry. A symmetry-induced barrier separates **8** and **9**, which accordingly can exist as true bond stretch isomers. In the case of *m*-benzynes, a symmetry-induced barrier does not exist. Also, the electron rearrangements accompanying the conversion from **2** to **1** are not so large that they could lead to an electronically induced barrier. The conversion **2**  $\rightarrow$  **1** proceeds without barrier and, therefore, bond stretch isomers cannot exist for *m*-benzynes and its derivatives.

Returning to the question whether the reaction between *m*-benzynes and pyridine proceeds via the biradical **3** or the bicyclic isomer **6** (Scheme 1), we note that the electronic structure of biradical **3** rather than that of the bicyclic isomer **6** is the driving force for the substitution reaction. Pyridine donates its electron pair to the LUMO of **3**, which is the low-lying  $b_2$ -symmetrical  $\sigma^*$  MO responsible for the electrophilic character of *m*-benzynes (see Figs. 4a and c). Occupation of the LUMO leads to an effective annihilation of bonding through-space interactions and the possibility to establish a bond to pyridine thus yielding the phenide intermediate **4**. The electrophilic nature of *m*-benzynes can also be expressed by using the zwitterionic resonance structures of biradical **1** shown in Fig. 4b.

Formation of **4** would not be possible if the reaction would involve bicyclic **6** because the LUMO of **6** corresponds to the  $\pi_4^*$  MO (Fig. 4a), which, if occupied by the electron lone pair of pyridine, would direct the reaction into a nucleophilic substitution at positions 2 or 5, which is not observed in the experiment. Hence, the observed reaction can only be explained invoking biradical **3** rather than bicyclic isomer **6**.

In conclusion, there is no theoretical evidence justifying the existence of the *m*-benzynes isomer **2**.

Bond stretch isomerism is possible only for *p*-benzynes (as correctly pointed out by Hess [16]), however not for *m*-benzynes. The previous investigation of Sander and co-workers [3] correctly characterized *m*-benzynes to possess the biradical structure **1**. There is a large amplitude vibration of the ring implying a  $r_z$  value probably somewhat shorter than the  $r_e$  value for the 1,3 distance. The PES is flat along the C1C3 coordinate, however there are still 4.7 kcal/mol (CASPT2 results) needed to recouple the electrons to a closed-shell singlet electron pair required for the formation of a 1,3 CC bond.

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### References

- [1] W.-D. Stohrer, R. Hoffmann, J. Am. Chem. Soc. 94 (1972) 779; W.-D. Stohrer, R. Hoffmann, J. Am. Chem. Soc. 94 (1972) 1661.
- [2] T.A. Albright, J.K. Burdett, M.H. Whangbo, Orbital Interactions in Chemistry, Wiley, New York, 1985.
- [3] R. Marquardt, W. Sander, E. Kraka, Angew. Chem. Int. Ed. Engl. 35 (1996) 746.
- [4] P.G. Wenthold, R.R. Squires, W.C. Lineberger, J. Am. Chem. Soc. 120 (1998) 5279.
- [5] W. Sander, Acc. Chem. Res. 32 (1999) 669.
- [6] G. Bucher, W. Sander, E. Kraka, Angew. Chem. 104 (1992) 1225; Angew. Chem. Int. Ed. Engl. 31 (1992) 1230.
- [7] W. Sander, G. Bucher, H. Wandel, E. Kraka, D. Cremer, W. Sheldrick, J. Am. Chem. Soc. 119 (1997) 10660.
- [8] K.K. Thoen, H.I. Kenttämaa, J. Am. Chem. Soc. 121 (1999) 800.
- [9] E.D. Nelson, A. Artau, J.M. Price, H.I. Kenttämaa, J. Am. Chem. Soc. 122 (2000) 8781.
- [10] E. Kraka, D. Cremer, Chem. Phys. Lett. 216 (1993) 333.

- [11] E. Kraka, D. Cremer, *J. Am. Chem. Soc.* 116 (1994) 4929.
- [12] E. Kraka, D. Cremer, G. Bucher, H. Wandel, W. Sander, *Chem. Phys. Lett.* 268 (1997) 313.
- [13] C.J. Cramer, J.J. Nash, R. Squires, *Chem. Phys. Lett.* 277 (1997) 311.
- [14] S.L. Debbert, C.J. Cramer, *Int. J. Mass Spectrom.* 201 (2000) 1.
- [15] W.T.G. Johnson, C.J. Cramer, *J. Am. Chem. Soc.* 123 (2001) 923.
- [16] B.A. Hess Jr., *Eur. J. Org. Chem.* (2001) 2185.
- [17] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [18] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [19] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [20] P.C. Hariharan, J.A. Pople, *Theor. Chim. Acta* 28 (1973) 213.
- [21] R. Bauernschmitt, R. Ahlrichs, *J. Chem. Phys.* 104 (1996) 9047.
- [22] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, *J. Chem. Phys.* 72 (1980) 650.
- [23] M. Filatov, S. Shaik, *Chem. Phys. Lett.* 304 (1999) 429.
- [24] B.O. Roos, *Adv. Chem. Phys.* 69 (1987) 399.
- [25] K. Anderson, P.A. Malmqvist, B.O. Roos, *J. Chem. Phys.* 96 (1992) 1218.
- [26] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* 157 (1989) 479.
- [27] D. Cremer, in: P.v.R. Schleyer, N.L. Allinger, T. Clark, J. Gasteiger, P.A. Kollman, H.F. Schaefer III, P.R. Schreiner (Eds.), *Encyclopedia of Computational Chemistry*, vol. 3, Wiley, Chichester, UK, 1998, p. 1706.
- [28] J.F. Stanton, J. Gauss, J.D. Watts, W.J. Lauderdale, R.J. Bartlett, ACES II, Quantum Theory Project, University of Florida, 1992.
- [29] E. Kraka, J. Gräfenstein, J. Gauss, Y. He, F. Reichel, L. Olsson, Z. Konkoli, Z. He., D. Cremer, COLOGNE 2000, Göteborg University, Göteborg, 2000.
- [30] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, J.H. Jensen, S. Koseki, M.S. Gordon, K.A. Nguyen, T.L. Windus, S.T. Elbert, *QCPE Bull.* 10 (1990) 52.
- [31] M.J. Frisch et al., in: *GAUSSIAN 98*, Revision A.3, Gaussian Inc, Pittsburgh, PA, 1998.
- [32] Y. He, J. Gräfenstein, E. Kraka, D. Cremer, *Mol. Phys.* 98 (2000) 1639.
- [33] J. Gräfenstein, A.M. Hjerpe, E. Kraka, D. Cremer, *J. Phys. Chem. A* 104 (2000) 1748.
- [34] J. Gräfenstein, E. Kraka, M. Filatov, D. Cremer, *Int. J. Mol. Science*, submitted.
- [35] Z. Konkoli, D. Cremer, *Int. J. Quantum Chem.* 67 (1998) 1.