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Ab Initio Study of Cyclobutadieno-*p*-benzoquinones: Kekulé Isomerization or Not?

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The problem of the existence of two Kekulé isomers **1a** and **1b** of cyclobutadieno-*p*-benzoquinone is addressed by the CAS(10,10)/6-31G*//GVB(2)/6-31G* and CASPT2(10,10)/ANO(3s2p1d,2s1p)//GVB(2)/6-31G* theoretical models. It is shown that the barrier separating these isomers on the Born−Oppenheimer surface practically disappears if the zero-point vibrational energies are taken into account. The angular strain and antiaromaticity of the more stable isomer **1a** are estimated by employing the appropriate homodesmic reactions. It is concluded that **1a** should be experimentally isolable, albeit in extreme conditions.

Antiaromatic cyclobutadiene (CB) belongs, together with its aromatic antipode benzene, to the most exciting organic molecules. Isolation of CB has been a tremendous synthetic challenge for decades because of its extraordinary π-electron antiaromaticity and considerable angular strain.[1−3] Brilliant preparative efforts of Pettit, Krebs, Masamune, Meier, Gomper, and others have led to CB transition-metal complexes,[4] CB flanked by large carbocycles,[5] CBs protected by large bulky groups,[6,7] and push−pull CBs.[8,9] An authoritative review article on the role of CB in the phane chemistry was provided by Gleiter and Merger[10] recently. Each of these systems extends our knowledge and deepens our understanding of the versatile chemical bonding phenomenon.

From the theoretical point of view, CB is a particularly interesting system, because it is a prototype of antiaromatic destabilization and yields insight into the nature of the intramolecular π-electron interactions. Juxtaposition of four-membered CB rings and aromatic benzene fragments in an alternating fashion by annelation leads to some unexpected molecular features.[11] The latter are the results of interplay and competition between two tendencies: an increase in the aromatic stabilization and a decrease in the antiaromatic character. Apparently, fusion of the four-membered small ring(s) to the aromatic moiety leads to significant distortions of the latter. By extention of this argument, one can anticipate formation of the CB ring if the small cyclobutene carbocycle is annelated to a large and well-localized planar π-electron system. It is intuitively clear that a π manifold of the fused large ring will provide some relief in antiaromaticity. A good candidate possessing π-bond fixation is provided by *p*-benzoquinone **1** (Figure 1), where a strong π-electron localization was confirmed by X-ray study,[12] the molecular orbital (MO) composition as revealed by photoelectron spectroscopy analysis,[13] and actual ab initio calculations.[14] Concomitantly, fusion of the cyclobutene fragment should potentially lead to two valence isomers **1a** and **1b** (Figure 1). It is plausible to assume that the antiaromatic character of the CB ring in **1a** and **1b** is lower than that of the parent four-membered free molecule, as evidenced by the ionic resonance structures shown in Scheme 1 where the degenerate structures dictated by symmetry are omitted for the sake of simplicity. The existence of the Kekulé isomers **1a** and **1b** is an open question, however, which deserves close theoretical scrutiny. The pioneering work on this topic has been performed by Schulman and Disch,[15] who considered benzocyclobutadiene and benzodicyclobutadiene. They tentatively concluded that the former molecule does not exhibit Kekulé isomerism, but the latter should exist in two valence isomeric forms. It should be pointed out, however, that Schulman and Disch did not locate the transition structure (TS) separating two benzodicyclobutadiene isomers but employed the linear synchronous transit approach instead,[15] which was not quite satisfactory. Recently, McKee et al.[16] studied inter alia **1a** and **1b** and found that they were true minima on the HF/6-31G* potential energy surface. These structures have been subsequently reoptimized at the B3LYP/6-31G* level and their (anti)aromatic properties were examined by nucleus independent chemical shift (NICS) criterion. However, conditio sine qua non for the existence of **1a** and **1b** is a barrier large enough for their separation. This problem cannot be solved by the B3LYP/6-31G* model, which corresponds to the single-determinant approach. Instead, the multireference wave functions should be used, because it is well recognized by now that both dynamic and nondynamic electron

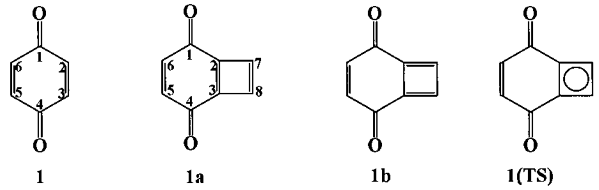

Figure 1. Schematic representation of the parent *p*-benzoquinone (**1**), cyclobutadeno-*p*-benzoquinone isomers (**1a** and **1b**), and transition structure [**1**(TS)].

SCHEME 1

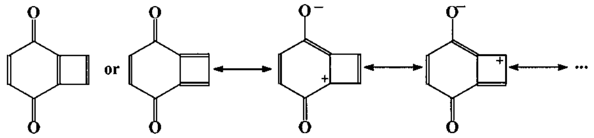

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TABLE 1: Selected Structural Parameters and Corresponding Transition-Structure Saddle Points Obtained by the GVB(2)/6-31G* and MP2(fc)/6-31G* Models of CB, 1, *1a*, and 1b

molecule	bond/angle	GVB(2)/6-31G*	MP2(fc)/6-31G*	exptl
1	C(1)−C(2)	1.490	1.480	1.477 ± 0.006[a] (1.481 ± 0.002)[b]
	C(2)═C(3)	1.344	1.349	1.322 ± 0.008 (1.344 ± 0.003)
	C(1)═O(7)	1.193	1.237	1.222 ± 0.008 (1.225 ± 0.002)
	C(2)−C(1)−C(6)	117.1°	117.6°	117.8° ± 0.6° (118.1° ± 0.3°)
CB	C(1)═C(2)	1.328	1.345	
	C(2)−C(3)	1.554	1.566	
CB(TS)	C(1)⋯C(2)	1.430		
1a	C(1)−C(2)	1.469	1.455	
	C(2)═C(3)	1.341	1.359	
	C(1)−C(6)	1.503	1.496	
	C(5)═C(6)	1.327	1.354	
	C(2)−C(7)	1.554	1.553	
	C(7)═C(8)	1.347	1.352	
	C(1)═O	1.193	1.239	
	C(1)−C(2)−C(3)	124.0°	123.9°	
	C(2)−C(1)−C(6)	112.6°	113.0°	
	C(1)−C(6)−C(5)	123.4°	123.0°	
	C(2)−C(3)−C(8)	90.1°	89.9°	
1b	C(1)−C(2)	1.464	1.453	
	C(2)−C(3)	1.529	1.545	
	C(1)−C(6)	1.502	1.492	
	C(5)═C(6)	1.336	1.365	
	C(2)═C(7)	1.347	1.360	
	C(7)−C(8)	1.571	1.547	
	C(1)═O	1.193	1.238	
	C(1)−C(2)−C(3)	122.7°	123.0°	
	C(2)−C(1)−C(6)	111.2°	110.7°	
	C(1)−C(6)−C(5)	126.2°	126.3°	
	C(2)−C(3)−C(8)	90.9°	90.1°	
1(TS)	C(1)−C(2)	1.453		
	C(2)⋯C(3)	1.464		
	C(1)−C(6)	1.505		
	C(5)═C(6)	1.352		
	C(2)⋯C(7)	1.416		
	C(7)⋯C(8)	1.419		
	C(1)═O	1.196		
	C(1)−C(2)−C(3)	123.6°		
	C(2)−C(1)−C(6)	111.5°		
	C(1)−C(6)−C(5)	124.9°		
	C(2)−C(3)−C(8)	89.1°		

[a] X-ray diffraction data are taken from ref 24. [b] Electron diffraction data are taken from ref 23.

correlation play a role of paramount importance in determining energetics of planar π systems.[17] This conclusion holds in particular in molecules involving a CB fragment.[18,19] Therefore, the problem of the valence isomerization of cyclobutadieno-*p*-benzoquinone **1a** and **1b** forms should be addressed on a more sound theoretical basis.

To test a hypothesis about Kekulé isomerism pertaining to structures **1a** and **1b**, we performed preliminary MP2(fc)/6-31G* and multiconfiguration GVB(2)/6-31G*[20] calculations by using GAUSSIAN 94[21] and GAMESS[22] programs. These two theoretical models will be abbreviated henceforth as MP2 and GVB-(2), respectively. The independent structural parameters were fully optimized at both MP2 and GVB(2) levels of the theory, and true minima on the corresponding energy surfaces have been identified by the accompanying vibrational analyses. The characteristic structural parameters of **1**, **1a** and **1b** estimated by the GVB(2) and MP2 models are presented in Table 1. Comparison of the theoretical bond distances of *p*-benzoquinone with the electron diffraction data[23] shows a high degree of compatibility. In contrast, the X-ray analysis of Trotter[24] gives C═C double bonds which are much too short. The paradigmatic CB exhibits a very strong π-electron bond localization, as evidenced by alternating short and long C−C bonds. Unfortunately, a comparison with experimental data is not possible here, because the X-ray single-bond distance varies from 1.527 to 1.600 Å, depending on the type of substituents or the size of the para-annelated large rings.[25] The same holds for the corresponding double-bond lengths which lie in the 1.344−1.441 Å range. It is instructive to compare the geometries of **1a** and **1b** with the structure of **1**. One observes that bond distances of **1a** are in harmony with the resonance effect depicted in Scheme 1. For instance, the C(1)−C(2) bond distance in **1a** is shorter than that in **1** by 0.02 Å. On the other hand, the C(7)═C(8) bond length of **1a** is longer than that in the free CB. By the same token, the localized C(5)═C(6) bond becomes even more fixed upon annelation. Analogous changes are easily found in **1b**. It is noteworthy that *p*-benzoquinone possesses some angular strain, as reflected by the C(2)−C(1)−C(6) angle, which is smaller than 120° (∼117°). This angle is additionally sharpened by fusion of the CB ring (Table 1). Hence, it appears that there is a spillover of some angular strain caused by fusion.

The energetic data are of particular interest. It appears that the valence isomer **1a** is 2.2 kcal/mol more stable than **1b** according to the MP2 model. Similarly, the GVB(2) model indicates that the **1a** Kekulé isomer is 3.4 kcal/mol lower in energy. However, the crucial question to be answered is related to the height of the energy barrier separating isomers in spe **1a** and **1b** as mentioned earlier. If the barrier on the Born−Oppenheimer surface is not large enough, then it might well disappear because of the differences in the ZPVEs (zero-point vibrational energies). In the TS, one vibrational mode corresponding to the reaction coordinate is missing, which could

TABLE 2: Molecular Energy (*E*),[a] Zero-Point Vibrational Energy (ZPVEs), and Their Δ_{TS}'s for the Ground and Transition Structures of CB, As Obtained by Utilizing the 6-31G* Basis Set

	E(GVB(2))	*E*(CAS(4,4))	*E*(CAS(10,10))	*E*(CASPT2(4,4))	ZPVE[b]
GS	−153.654 90	−153.708 06	−153.767 18	−153.745 52	37.2
TS	−153.636 24	−153.698 61	−153.756 50	−153.734 99	34.6
Δ_{TS}	11.7	5.9	6.7	6.6	−2.6

[a] Molecular energies are related to true minima or TS structure on the Born−Oppenheimer potential surface. CAS and CASPT2 calculations are executed by using GVB(2) geometries. Full specification of the CASPT2(4,4) method is CASPT2(4,4)/ANO(3s2p1d,2s1p)//GVB(2)/6-31G*. Molecular energies are in atomic units, and the remaining values are in kilocalories per mole. [b] Taken from ref 19 and based on MRCCSD calculations.

TABLE 3: Molecular Energy (*E*), Zero-Point Vibrational Energy (ZPVEs), and Their Δ_{TS}'s for the Ground and Transition Structures of 1a and 1b by the GVB(2)/6-31G*, CAS(10,10)/ANO(3s2p1d,2s1p)//GVB(2)/6-31G*, and CASPT2(10,10)/ANO(3s2p1d,2s1p)//GVB(2)/6-31G* Methods[a−c]

isomers	GVB(2)	CAS(10,10)//GVB(2)	CASPT2(10,10)//GVB(2)	ω^d	ZPVE
1a	−454.900 86	−455.086 41	−455.126 95	0.9822	46.9
1b	−454.895 46	−455.078 31	−455.119 03	0.9820	46.9
1(TS)	−454.863 69	−455.073 18	−455.114 72	0.9806	44.5
Δ_{TS}(**1a**)	23.3	8.3	7.7		−2.4
Δ_{TS}(**1b**)	19.9	3.2	2.7		−2.4
Δ_{ba}	3.4	5.1	5.0		0

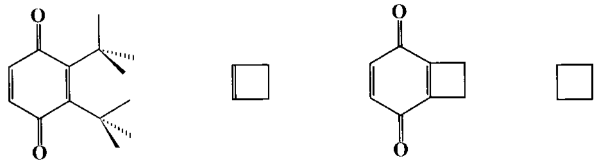
[a] GVB and CAS energies are in atomic units, and ZPVE and energy differences are in kilocalories per mole. [b] A difference in various energy contents between **1b** and **1a** is denoted by Δ_{ba}. [c] ZPVEs are estimated at the GVB(2)/6-31G* level by a scaling procedure (see text). [d] The weight of the CASSCF reference function in the first-order wave function is denoted by ω.[28,29]

flatten the barrier to such an extent that it vanishes. This seems to be the case in **1a** and **1b**, as described below.

Selection of the appropriate theoretical tool for tackling this problem is crucial. First, it is clear that the model of choice should be a multireference approach which can describe both types of the electron correlation rather accurately. Second, it is desirable to test the model against a small characteristic system already thoroughly examined by highly sophisticated methods. This is obviously CB itself. For this purpose, we have performed GVB(2) calculations on CB followed by the complete active space CAS(4,4) and CAS(10,10) procedures employing GVB(2) geometries and the same 6-31G* basis set. Results are given in Table 2. It is important to keep in mind that the best theoretical estimate of the difference in the electronic energies of TS and the ground state (GS) is 6.4 kcal/mol, as obtained by the coupled cluster with single, double, and triple excitation (CCSDT) method.[19] The corresponding experimental estimate is 5.3 kcal/mol.[26] Perusal of the data presented in Table 2 shows that the value obtained by the GVB(2) procedure (11.7 kcal/mol) is too high. The corresponding CAS(4,4)/6-31G*//GVB(2)/6-31G* and CAS(10,10)/6-31G*//GVB(2)/6-31G* calculations give much more acceptable values of 5.9 and 6.7 kcal/mol, respectively. It is interesting and gratifying that explicit inclusion of σ electrons in the electron-correlation calculation within the CAS(10,10) framework does not significantly alter the potential barrier. Hence, one is tempted to conclude that it is sufficient to include π MO's only in the CAS calculations. It is also important to stress that the true barrier must involve the ZPVE contribution. Because the vibrational mode along the reaction coordinate is not active, it follows that the ZPVE lowers the barrier by 2.6 kcal/mol in CB, as estimated by MRCCSD computations.[19] In conclusion, one can say that the CAS(10,10)/6-31G*//GVB(2)/6-31G* theoretical model seems to be a reasonable choice for examining the valence isomerization problem of **1a** and **1b**.

However, the CAS multireference wave function describes predominantly the nondynamic part of the correlation energy.[27] It would be of considerable interest to examine the contribution of the dynamical component of the electron correlation. The latter can be conveniently described for example, by the CAS with second-order perturbation theory (CASPT2) formalism as developed by Roos et al.[28,29] In this approach, the remaining dynamic electron correlation is added by the second-order perturbation theory using a CAS self-consistent field (CASSCF) wave function as the reference state. Through use of the atomic natural orbital ANO(3s2p1d,2s1p) basis set, the barrier for the CB valence isomerization is found to be 6.6 kcal/mol (Table 2), according to CASPT2(4,4)/ANO(3s2p1d,2s1p)// GVB(2)/6-31G* single-point calculations. It appears that the dynamic correlation affects the barrier height to a very small extent, increasing it slightly by 0.7 kcal/mol. We note in passing that the B3LYP/6-31G* model grossly overestimates the CB barrier, yielding 26.3 kcal/mol by the B3LYP/6-31G*//GVB(2)/6-31G* calculations.

We are ready now to answer the question given in the title of this article. Molecular energies of GS and TS of Kekulé isomers **1a** and **1b** are summarized in Table 3 together with ZPVE values. We know already that the GVB(2) model predicts the **1a** isomer to be 3.4 kcal/mol more stable. This value seems to be too low because both CAS(10,10)/ANO(3s2p1d,2s1p)//GVB(2) /6-31G* and CASPT2(10,10)/ANO(3s2p1d,2s1p)//GVB(2)/6-31G* methods yield a Δ_{ba} of 5 kcal/mol. It is noteworthy that the dynamic correlation described by the PT2 procedure does not affect the relative stability of isomers at all. The influence of the basis set was examined at the CAS(10,10) level of theory. The difference in the total electronic energies between the Δ_{ba} of isomers is 4 kcal/mol, as obtained by the CAS(10,10)/6-31G*//GVB(2)/6-31G* calculations. Furthermore, the ZPVE contribution to Δ_{ba} is virtually zero (Table 3). Therefore, we are confident that **1a** is 5 kcal/mol more stable than **1b**. The barrier separating **1a** and **1b** is highly sensitive to electron correlation, as expected. For instance, the GVB(2) model seriously overshoots its height as evidenced by the Δ_{TS} values of **1a** and **1b** of 23.3 and 19.9 kcal/mol, respectively. The corresponding values at the B3LYP/6-31G*//GVB(2)/6-31G* level are the more realistic 13.5 and 13.1 kcal/mol, respectively, but they are still too high. The total electronic energy of TS is dramatically lowered by a full account of the nondynamic correlation as evidenced by the CAS(10,10)/ANO(3s2p1d,2s1p)//GVB(2)/6-31G* calculations, which yield a barrier of only 3.2 kcal/mol. This value additionally is decreased by 0.5 kcal/mol by explicit inclusion of the dynamic correlation as predicted by the CASPT2(10,10) level of theory (Table 3). The very modest influence of the dynamic electron



2 **3** **4** **5**

Figure 2. Schematic representation of molecules appearing in homodesmic reactions (1)−(5).

correlation on the TS barrier in the CASPT2 approach can be rationalized by the fact that the multireference initial CAS state function predominates in the final CASPT2 wave function. This is illustrated by the ω values given in Table 3. It appears that 98% of the final wave function corresponds to the CAS(10,10) starting approximation of the zeroth order whereas only about 2% represents the perturbational correction. Finally, the barrier height should be corrected for the ZPVE effect, which is achieved by scaling GVB(2)/6-31G* ZPVEs in CB against the accurate MRCCSD values.[19] Through use of the linear relationship obtained in this fashion, one deduces the ZPVEs given in Table 3. It follows that the contribution of the ZPVE to the TS total energy is −2.4 kcal/mol, which is similar to the −2.6 kcal/mol found in CB. Consequently, the barrier between **1b** and **1a** drops to only 0.3 kcal/mol and thus is practically nonexistent. This conjecture is further supported by our calculations on CB, in which both CAS and CASPT2 methods overestimate the barrier of autoisomerization by at least 1 kcal/mol. Hence, we can conclude with a high degree of confidence that **1b** isomer does not exist and that cyclobutadieno-*p*-benzoquinone does not exhibit Kekulé isomerism.

It is of some interest to estimate the stability of **1a**. An illuminating insight into the (de)stabilization energies of molecules is offered by the homodesmic reactions.[30] The following reactions are used to give destabilization energies E_d in CB and fused *p*-benzoquinone **1a**

$$\mathrm{CB} + 2(\mathrm{CH_3{-}CH_3}) = 2(\textit{trans}\text{-butene-2}) + E_d(\mathrm{CB}) \quad (1)$$

$$\mathbf{1a} + 2(\mathrm{CH_3{-}CH_3}) = \mathbf{2} + \textit{trans}\text{-butene-2} + E_d(\mathbf{1a}) \quad (2)$$

where the “strain-free” reference compound **2** is depicted in Figure 2, together with cyclobutene (**3**), cyclobuteno-*p*-benzoquinone (**4**), and cyclobutane (**5**).

In addition to eqs 1 and 2, the angular strain energy E_s in eqs 3−5 is estimated by

$$\mathbf{3} + 2(\mathrm{CH_3{-}CH_3}) = \textit{trans}\text{-butene-2} + \text{butane} + E_s(3) \quad (3)$$

$$\mathbf{4} + 2(\mathrm{CH_3{-}CH_3}) = 2 + \text{butane} + E_s(4) \quad (4)$$

$$\mathbf{5} + 2(\mathrm{CH_3{-}CH_3}) = 2(\text{butane}) + E_s(5) \quad (5)$$

Because the homodesmic reactions are not very sensitive to the electron correlation, we shall use in what follows the MP2(fc)/6-31G* results. E_d(CB) and E_d(**1a**) at the MP2 level are 73.2 and 75.3 kcal/mol, respectively. These results are similar to very accurate G2 calculations on CB by Pross et al.,[31] which yield E_d(CB) = 74.2 kcal/mol. It appears that the destabilization energy of **1a** is comparable to that found in the parent CB, indicating that it may be synthesized and isolated one day, albeit in extreme conditions and by the use of protective substituent groups. It should be mentioned in this connection that cyclobutadieno-1,4-naphthoquinone already has been synthesized and characterized by Breslow et al.[32] They estimated that the antiaromatic interaction is as low as 12−16 kcal/mol, apparently because of the increased capability of the larger naphthalene moiety to relieve antiaromaticity of the four-membered ring in a rather efficient way. Finally, eqs 3 and 4 show that the strain energy of the four-membered rings is roughly 37 kcal/mol, thus being appreciably higher than the strain energy of cyclobutane E_s(**5**), which is 28 kcal/mol according to eq 5. This implies that about 50% of the destabilization energies in CB, **1a**, and **1b** arises from the Baeyer angular strain, and the remaining 50% probably is due to antiaromatic π-electron interactions. More specifically, the antiaromatic destabilization energies in **1a** and **1b** are 38 kcal/mol less an amount related to the increase in the angular strain of the *p*-benzoquinone fragment caused by annelation of the four-membered ring.

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