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THEORETICAL STUDIES OF THE SINGLET AND TRIPLET POTENTIAL ENERGY SURFACES OF CYCLOBUTANEDIYL

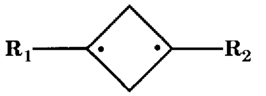
JULIANTO PRANATA AND DENNIS A. DOUGHERTY*†

Arnold and Mabel Beckman Laboratories of Chemical Synthesis‡, 164-30 California Institute of Technology, Pasadena, California 91125, USA

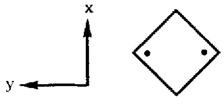
ABSTRACT

Cyclobutanediyl (2) has been studied in both its singlet and triplet states by *ab initio* electronic structure theory. The triplet, which is the ground state of the molecule, exists in both C_{2h} and C_{2v} forms which interconvert via a C_s transition state. For the singlet, only a C_{2h} form is found. It passes, via a C_s transition state, onto the C_{2v} surface on which bicyclobutane (3) is the only minimum. The ring-flipping (inversion) process in 3 includes the singlet biradical as an intermediate, and involves a novel, non-least motion path similar to one previously proposed by Gassman. Semiclassical periodic orbit theory indicates that the various minima on both the singlet and triplet surfaces can interconvert via quantum mechanical tunneling.

We recently reported the synthesis and characterization of a series of 1,3-cyclobutanediyls (**1**).[1] The cyclobutanediyls constitute the first general class of directly observable, localized 1,3-biradicals, and a variety of structures bearing both alkyl (**1-Me**, **1-CD$_3$**, **1-Et**, **1-Pr**) and unsaturated (**1-MP**, **1-EV**, **1-Ph**, **1-Vin**, **1-Vin-d$_6$**) substituents have been characterized in their triplet states by electron paramagentic resonance (EPR) spectroscopy. The spectroscopic studies on **1** provided much information on the molecular and electronic structure of these biradicals, in that zero-field splitting parameters were quantitatively correlated to the spin distributions in the molecules. In addition, the EPR spectra of some structures displayed interpretable hyperfine coupling, which showed a single, large hyperfine coupling constant with the ring methylene hydrogens.



1-Me : $R_1=R_2=CH_3$
1-CD$_3$: $R_1=R_2=CD_3$
1-Et : $R_1=R_2=CH_2CH_3$
1-Pr : $R_1=R_2=n\text{-}C_3H_7$
1-MP : $R_1=CH_3$, $R_2=Ph$
1-EV : $R_1=CH_2CH_3$, $R_2=CHCH_2$
1-Ph : $R_1=R_2=Ph$
1-Vin : $R_1=R_2=CHCH_2$
1-Vin-d$_6$: $R_1=R_2=CDCD_2$



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*Author for correspondence
†Camille and Henry Dreyfus Teacher-Scholar 1984–1989
‡Contribution number 7756

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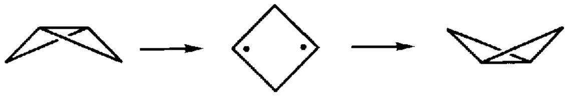
We have also studied the matrix isolation decay kinetics of **1**.[2] Structures with delocalizing substituents (**1-Vin**, **1-EV**, and **1-Ph**) exhibit normal (i.e. Arrhenius) behavior, while large deviations from such behavior are observed in the fully localized biradicals **1-Me** and **1-Et**. The latter result suggests that quantum-mechanical tunneling may be a major factor in the decay process of simple cyclobutanediyls.

In conjunction with these experimental studies, we have now undertaken a detailed theoretical investigation of the parent cyclobutanediyl, **2** (i.e. **1-H**). Structures of this type have been the subjects of several recent theoretical studies,[3–8] but these did not address several issues of special relevance to our experimental work. Ideally, of course, one would like to make a direct comparison between theory and experiment. However, the parent cyclobutanediyl **2** is the only system to date that we have been unable to observe spectroscopically, and one of the goals of the present work is to provide an explanation for this result. Theoretical studies on the substituted structures are infeasible because of their larger size and lower symmetry. Nevertheless, the experiments indicate that we can rationally explain the substituent effects as perturbations on the basic cyclobutanediyl framework, suggesting that a theoretical study of **2** would be valuable.



3 **2** **3**

(1)

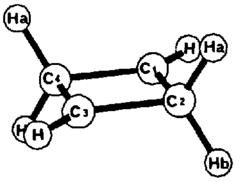
Previous theoretical studies on **2** have generally been concerned with the singlet state, which is assumed to be an intermediate or transition state in the inversion process of bicyclobutane (**3**, equation (1)).[3–5] In the present work, we have studied both the triplet and singlet potential energy surfaces of **2** in detail. In order to make meaningful comparisons between these two states, one must use for the singlet a two-configuration self-consistent field (TCSCF) wavefunction, or an equivalent generalized valence bond method (GVB (1/2)).[9] For the triplet state we use the restricted Hartree-Fock (RHF) method.[10] We have previously shown that this level of theory is both necessary and sufficient for a balanced treatment of singlet and triplet states in molecules of this sort.[8]

COMPUTATIONAL METHODS

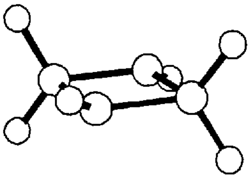
All calculations were performed using the Gaussian 86 program package.[11] As mentioned above, RHF calculations were performed for triplets and GVB (1/2) for singlets. Geometry optimizations were performed using the 3-21G basis set.[12] In most cases these are followed by single-point calculations using the 6-31G* basis set.[13] For stationary points, the geometries were completely optimized subject only to molecular symmetry constraints. The stationary points were characterized as local minima, transition states, or higher-order saddle points by performing frequency calculations to determine the number of imaginary frequencies (zero, one, or more than one, respectively). For points along a reaction pathway, one geometric parameter corresponding to the reaction coordinate was fixed, and all remaining coordinates were optimized within molecular symmetry constraints.

THE TRIPLET POTENTIAL SURFACE

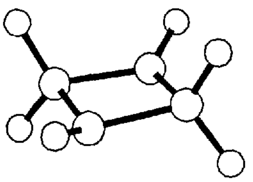
We initially optimized triplet **2** within D_{2h} symmetry constraints. However, the frequency calculation on the optimized structure (**2a**, Figure 1) revealed the presence of two imaginary



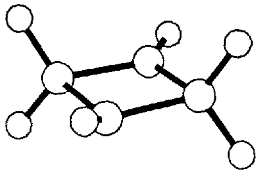
2a
D_{2h} double maximum
Energy (3-21G) 0.61
Energy (6-31G*) 1.20



2b
C_{2h} minimum
Energy (3-21G) 0.0
Energy (6-31G*) 0.0



2c
C_{2v} minimum
Energy (3-21G) 0.15
Energy (6-31G*) 0.21



2d
C_s transition state
Energy (3-21G) 0.31
Energy (6-31G*) 0.58

Figure 1. Structures and relative energies of stationary points on the triplet potential surface. Energies in kcal/mol relative to **2b** (total energy −153·962410 hartrees (3-21G) or −154·827167 hartrees (6-31G*))

frequencies. These correspond to the symmetric and antisymmetric out-of-plane bending motions (symmetries b_{1u} and b_{3g}) of the hydrogens attached to C_1 and C_3 (i.e. the radical centers). (Our choice of coordinate system places the cyclobutane ring on the xy-plane, with the CH_2 groups along the x-axis.) These distortions strongly indicated the existence of local minima having C_{2v} and C_{2h} symmetries, respectively.

Optimizations within C_{2h} and C_{2v} symmetries both led to stationary points (**2b** and **2c**, respectively) which were characterized as local minima (i.e. no imaginary frequencies). In addition, we located the transition state (C_s symmetry) for the interconversion of these two minima (**2d**). The structures and relative energies of these stationary points are shown in Figure 1, and detailed geometrical parameters are given in Table 1.

Contrary to what was assumed in our previous study,[8] these calculations indicate that triplet **2** is not planar. In both minima, H_1 (the hydrogen attached to C_1) and H_3 are substantially removed (by an angle of about 20 °) from the plane of the ring. We might also point out that these geometries are optimized with the 3-21G basis set, which is known to generally underestimate the extent of pyramidalization.[14] This is reflected in the greater energy differences between planar and non-planar forms in the 6-31G* calculations. The relative stabilities among the structures remain the same.

While the hydrogens show substantial deviations from planarity, the cyclobutane ring itself remains essentially planar. In **2b**, the ring is necessarily planar by symmetry. In **2c**, the deviation from planarity is only about 5 °. Interestingly, the ring puckers towards the *same* face of the ring as H_1 and H_3. In both structures, the planes containing the CH_2 groups remain essentially perpendicular to the ring place. This is constrained by symmetry in **2c**; in **2b** the deviation from perpendicularity is only 0·3 °.

The transition state structure (**2d**) can be seen to be intermediate in structure between **2b** and **2c** (Figure 1, Table 1). One methine hydrogen (H_1) is essentially in the plane of the ring,

Table 1. Structures of stationary points on the cyclobutanediyl potential energy surfaces[a,b]

Flap angle (degree)	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**3**
$r_{C_1C_3}$	2·1017	2·1108	2·1191	2·1112	2·1030	2·1509	2·1178	1·5296
$r_{C_1C_2} = r_{C_1C_4}$	1·5354	1·5406	1·5403	1·5344	1·5403	1·5463	1·5385	1·5134
$r_{C_3C_2} = r_{C_3C_4}$	1·5354	1·5406	1·5403	1·5419	1·5403	1·5463	1·5467	1·5134
r_{C_1H}	1·0672	1·0706	1·0704	1·0674	1·6074	1·0733	1·0676	1·0616
r_{C_3H}	1·0672	1·0706	1·0704	1·0706	1·6074	1·0733	1·0707	1·0616
$r_{C_2H_a} = r_{C_4H_a}$	1·0856	1·0847	1·0857	1·0857	1·0842	1·0831	1·0842	1·0745
$r_{C_2H_b} = r_{C_4H_b}$	1·0856	1·0847	1·0837	1·0846	1·0842	1·0831	1·0836	1·0760
$C_1C_3H_3$ angle[c]	180·0	157·56	160·82	158·24	180.0	147·05	156·64	133·56
$C_3C_1H_1$ angle[c]	180·0	202·44	160·82	179·17	180·0	212·95	184·34	133·56
XC_2H_a angle = XC_4H_a angle[d]	125·48	125·42	124·60	125·06	125·27	125·16	125·08	121·48
XC_2H_b angle = XC_4H_b angle[d]	125·48	125·42	126·17	125·82	125·27	125·16	125·44	123·71
flap (C_2XC_4) angle[d,e]	180·0	180·0	185·48	183·37	180·0	180·0	181·73	119·98

[a] See Figures 1 and 3, in particular **2a** in Figure 1.

[b] Bond lengths in angstroms, angles in degrees.

[c] These angles are measured above the ring plane as drawn in Figures 1 and 3.

[d] X is a point along the C_1C_3 vector such that C_1X and C_2X are perpendicular.

[e] This angle is measured below the ring plane as drawn in Figures 1 and 3.

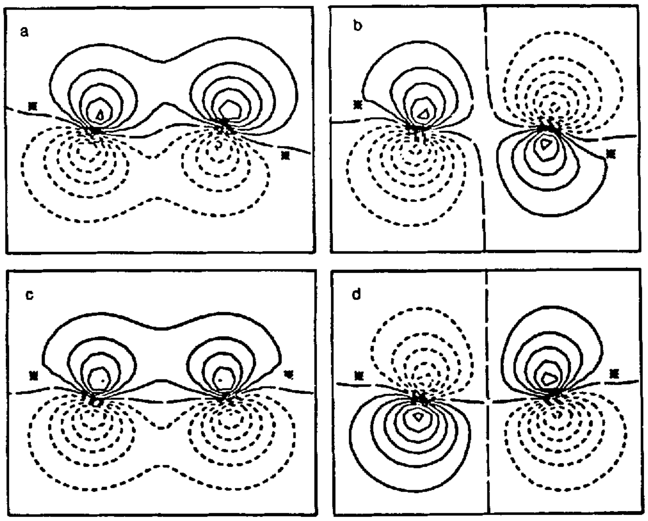


Figure 2. Contour plots of the singly occupied molecular orbitals in **2b** (*a* and *b*) and **2c** (*c* and *d*) in the $H_1C_1C_3H_3$ plane

and the single imaginary frequency in this structure corresponds to the bending motion of this hydrogen.

Figure 2 shows contour plots of the singly occupied molecular orbitals for both **2b** and **2c** in the place containing H_1C_1—C_3H_3. From the plots we estimate that the orbitals containing the radical electrons are tilted from the z-axis by about 12° in **2b** and by about 10° in **2c**. The orientations of these orbitals are important in determining the value of the EPR β-hyperfine coupling constants ($a_H{}^{\beta}$). For *planar* radical centers, these are given by the relation[15]

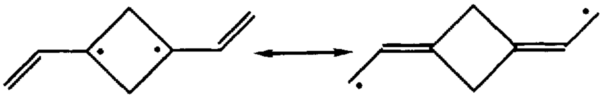
$$a_H^{\beta} = A + \rho C \cos^2 \theta \qquad (2)$$

where ρ is the electron density at the radical center; A and C are constants with typical values of 0–5 and 40–45 G, respectively; and θ is the dihedral angle between the axis of the p orbital on the α-carbon and the β C—H bond. For the pyramidalized radical centers of interest here, this equation is perhaps best considered as a semi-quantitative guideline. In **2c** we expect two hyperfine couplings since the CH_2 protons are not equivalent. However, we estimate using equation (2) that the difference between the two is of the order of 5–7 G, which is comparable to a typical intrinsic linewidth in a triplet spectrum.[1] In **2b** all the CH_2 protons are symmetry equivalent, and we expect a single hyperfine coupling constant. Attempts to apply equation (2) to **2b** produce a value for a_H^{β} in the range of 30–40 G, which is in acceptable agreement with the value of 32 G observed in the spectra of **1-CD₃**.[1] We note that simulation of this experimental spectrum required an unusually large linewidth. Possible causes of this could be a mixture of C_{2h} and C_{2v} forms, or, perhaps, tunneling (see below).

The question remains whether the substituted cyclobutanediyls (**1**) also adopt a C_{2h}-like structure. We have performed single point calculations (using the 3-21G basis set) on dimethylcyclobutanediyl (**1-Me**), using the geometry optimized for **2** for the ring and the optimized geometry of the t-butyl radical for the methyl groups.[16] The relative energy ordering of **1-Me** structures derived from **2a–2d** remains unchanged. The C_{2h}-like structure is of lowest energy, followed by the C_{2v}-like structure (0·23 kcal/mol higher), then the C_s-like structure

(1·08 kcal/mol), and the D_{2h}-like structure has the highest energy (2·28 kcal/mol). While these values would certainly change upon optimization, the results indicate that there are no major changes expected in the cyclobutanediyl structure upon substitution with a localized substituent.

We do expect changes when the substituent is a delocalizing group. For example, in divinylcyclobutanediyl (**1-Vin**), delocalization would provide a substantial driving force towards planarity. We assume that this delocalization energy is sufficient to overcome the small intrinsic preference for non-planarity in the cyclobutanediyl framework. We have not been able to explore this question, however, since calculations on **1-Vin** would be quite a significant undertaking, requiring the full correlation of at least six π electrons.[17]



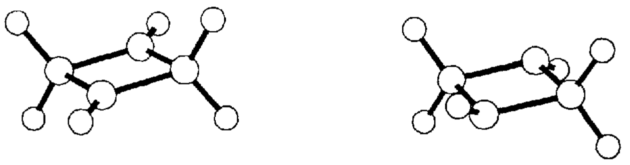
1-Vin

THE SINGLET POTENTIAL SURFACE. INVERSION PROCESS OF BICYCLOBUTANE

Singlet **2** has generally been regarded as a transition state or an intermediate in the inversion process of bicyclobutane (**3**, equation (1)). Collins and co-workers[5] have reported a single imaginary frequency for the D_{2h} structure, indicating it is a transition state. However, their calculations were done at the RHF level, a wholly inadequate level of theory for such a molecule, in that it fails to adequately treat the biradical nature of the structure. The inversion barrier they obtained (82·5 kcal/mol) was unrealistically large, further illustrating the failure of the RHF method for this type of system. Inclusion of some level of electron correlation via MP3 and CI methods did not substantially alter these results. In contrast, the barriers obtained by Schleyer and co-workers (using GVB (1/2)/3–21 G)[4] and by Gassman and co-workers (using GVB (1/2)/PRDDO)[3] were much more realistic, but somewhat too small (29·1 and 23·2 kcal/mol, respectively). While the actual barrier height has not been determined experimentally, it is known that **3** undergoes a thermal ring-opening process to give butadiene with an activation energy of 40·6 kcal/mol, rather than undergoing inversion.[18] Thus the inversion barrier has to be significantly higher than 40·6 kcal/mol, and thermochemical estimates suggest a value in the vicinity of 47 kcal/mol.[19]

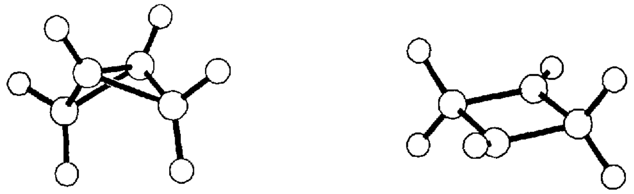
In addition to obtaining the barrier height, Gassman and co-workers also traced the inversion pathway. They did this by using the flap angle of **3** as the reaction coordinate. What they found was that the inversion process does not follow a least-motion pathway. Surprisingly, the bridgehead hydrogens initially move *inward* as the flap angle increased.[20] At a flap angle of about 150 °, the hydrogens reverse their direction of motion and move outward towards planarity. Gassman also found a shallow local minimum on the inversion pathway, corresponding to a structure with a planar cyclobutane ring but having H_1 and H_3 out of plane (C_{2v} symmetry). The structure of this minimum was not optimized, and it was postulated that the D_{2h} structure was the transition state between this shallow minimum and its inverted counterpart

In our own work we began by optimizing the D_{2h} structure (**2e**, Figure 3, Table 1). This structure is, of course, identical to Schleyer's, which was obtained at an identical level of theory, and is qualitatively similar to Gassman's. Collins' structure has an unreasonably short



2e
D_{2h} double maximum
Energy (3-21G) 0.94
Energy (6-31G*) 1.49

2f
C_{2h} minimum
Energy (3-21G) 0.0
Energy (6-31G*) 0.0



3
C_{2v} bicyclobutane
Energy (3-21G) -28.19
Energy (6-31G*) -38.42

2g
C_s transition state
Energy (3-21G) 0.66
Energy (6-31G*) 1.02

Figure 3. Structures and relative energies of stationary points on the singlet potential surface. Energies in kcal/mol relative to **2f** (total energy −153·960117 hartrees (3-21G) or −154·824840 hartrees (6-31G*))

C_1–C_3 distance (1·86 Å), which is no doubt a consequence of using RHF theory. Our frequency calculation on **2e** resulted in two imaginary frequencies, as was found for the triplet state. Optimization within C_{2h} symmetry resulted in a local minimum (**2f**), but we found no minimum with C_{2v} symmetry other than bicyclobutane. In addition, we found a transition state with C_s symmetry (**2g**).

Our calculations thus indicate that singlet **2** lies in a minimum. This singlet biradical has C_{2h} symmetry, like the lowest energy structure of the corresponding triplet, and it lies in a reasonably deep well (1 kcal/mol below the C_s form at the 6-31G* level). In contrast, the parent 1,3-biradical trimethylene (**4**) does not exhibit a (computational) minimum on the singlet surface.[21] It closes without activation to cyclopropane. Apparently, ring strain is enough to induce a true well on the singlet surface of a localized 1,3-biradical.

4

Inspection of the transition state (**2g**) indicates that its single imaginary frequency corresponds to the motion of H_1. This is expected for a transition structure between a C_{2v} form (**3**) and a C_{2h} form (**2f**). We have attempted to calculate intermediate points in this reaction pathway. Starting from bicyclobutane (**3**), gradual deformation of one of the bridgehead hydrogens did not lead to the transition state structure. In fact, the flap angle decreases (from 120 to 118°) and the C_1—C_3 bond shortens (1·530 to 1·518 Å) as the hydrogen angle is deformed from 133·6° in **3** to 150°. Instead, we found a reaction pathway which did result in the breaking of the C_1—C_3 bond (and formation of a biradical) by opening up the flap angle of the ring (i.e. the same pathway proposed by Gassman and co-workers). This C_{2v} path is shown in Table 2. Unlike Gassman, however, we did not find a minimum on this reaction pathway.

Table 2. Structures obtained by deformation of the flap angle of bicyclobutane[a]

Flap angle (degree)	120[b]	130	140	150	160	170	175	180	185	190	200	210
$r_{C_1C_3}$	1·5296	1·6187	1·7948	1·8726	1·9614	2·0845	2·1143	2·1235	2·1246	2·1238	2·1173	2·0962
$r_{C_1C_2}$	1·5134	1·5088	1·5232	1·5318	1·5420	1·5512	1·5505	1·5480	1·5463	1·5457	1·5464	1·5481
C_1C_3H angle	133·56	123·42	110·32	110·83	115·90	130·92	141·07	149·95	156·19	159·95	164·80	170·38
Energy (3-12G)[c]	0	2·01	5·07	11·02	19·30	26·15	27·59	28·08	28·22	28·41	29·45	31·76
Energy (6-31G*)[c]	0	[d]	[d]	[d]	[d]	34·57	37·00	37·96	38·31	[d]	[d]	[d]

[a] Bond lengths in angstroms, bond angles in degrees, energies in kcal/mol.
[b] Structure corresponding to bicyclobutane.
[c] Relative to bicyclobutane.
[d] 6-31G* energies not calculated.

Table 3. Structures obtained by deformation of C_3C_1H angle from **2g**[a]

C_3C_1H angle	184·36[b]	175	160
$r_{C_1C_3}$	2·1178	2·1153	2·1210
$r_{C_1C_2}$	1·5385	1·5390	1·5440
$r_{C_3C_2}$	1·5467	1·5469	1·5468
C_1C_3H angle	156·64	158·37	155·71
flap angle	181·73	184·59	183·62
Energy (3-21G)[c]	28·85	28·70	28·25
Energy (6-31G*)[c]	39·45	[d]	38·40

[a] Bond lengths in angstroms, bond angles in degrees, energies in kcal/mol.
[b] Structure corresponding to **2g**.
[c] Relative to bicyclobutane.
[d] 6-31G* energy not calculated.

Instead, the energy keeps increasing as we deform the flap angle beyond 180°. We do observe a relatively flat surface in the neighborhood of 180°.

On the other hand, when we start with the C_s transition state **2g** and follow the mode corresponding to the imaginary frequency (i.e. the motion of H_1), we appear to be approaching a structure of C_{2v} symmetry (Table 3). The structures represented in the last column of Table 3 and the 185° column in Table 1 are in fact quite similar, as shown in more detail in Table 4. It appears, then, that the reaction pathway obtained by following the reaction coordinate from the transition state (**2g**) intersects that obtained by following the flap angle from **3**, the intersection point (**2h**) being the structure shown in Table 3.

Table 4. Comparison between near-coincident structures (**2h**) from Tables 2 and 3[a]

	From Table 2	From Table 3
$r_{C_1C_3}$	2·1246	2·1210
$r_{C_1C_2}$	1·5463	1·5440
$r_{C_3C_2}$	1·5463	1·5468
r_{C_1H}	1·0716	1·0706
r_{C_3H}	1·0716	1·0717
$r_{C_2H_a}$	1·0845	1·0844
$r_{C_2H_b}$	1·0825	1·0825
C_1C_3H angle	156·19	155·71
C_3C_1H angle	156·19	160·0[c]
XC_2H_a angle[b]	124·64	124·88
XC_2H_b angle[b]	125·85	125·63
flap (C_2XC_4) angle[b]	185·0[c]	183·6

[a] Bond lengths in angstroms, bond angles in degrees.
[b] X is a point along the C_1C_3 vector such that C_1X and C_2X are perpendicular.
[c] These coordinates were constrained in the optimizations.

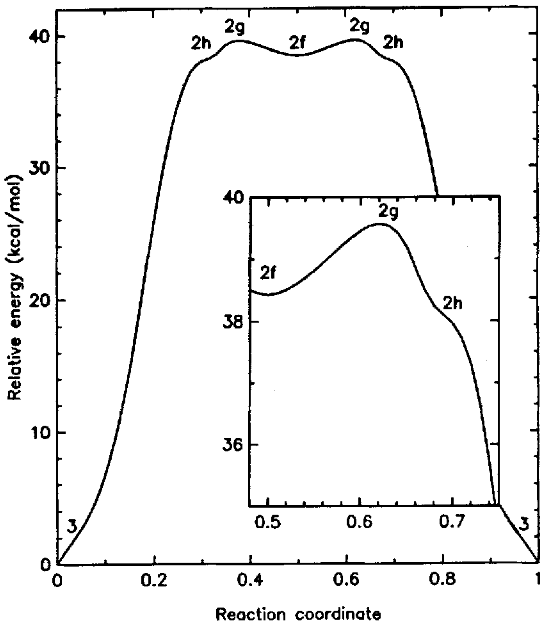


Figure 4. Reaction pathway in the singlet inversion of bicyclobutane. Insert is an expansion of the region near the transition state. Energies are at the 6-31G* level relative to bicyclobutane

Based on these observations, we propose the following pathway in the inversion of **3**. Initially, the reaction coordinate is well represented by the flap angle of **3**. This is similar to the reaction pathway proposed by Gassman, and the 'wrong way' motion of the bridgehead hydrogens is also observed here (Table 2). This pathway leads to a 'plateau' at a flap angle of about 180° (**2h**). At a flap angle near 185°, one of the hydrogens starts to move faster than the other. This leads to a C_s transition state (**2g**) and ultimately to a C_{2h} intermediate (**2f**). From this point on, the other hydrogen's motion takes over, taking the molecule past a second C_s transition state (equivalent to the first) and ending back on a C_{2v} 'plateau'. From this point on, it is a steep downhill path to inverted **3**. This is a lower energy pathway than the one obtained by staying within C_{2v} symmetry, following the flap angle. The reaction pathway is shown in Figure 4.

We note that this pathway is similar in spirit to the one proposed by Gassman and co-workers, in that it involves a change in the molecular internal coordinate which corresponds to the 'reaction coordinate'. The main difference is that in Gassman's pathway C_{2v} symmetry is maintained throughout the process, whereas we have discovered a lower energy pathway if this constraint is relaxed. We also point out that the current pathway is somewhat more fully characterized, in that we have located a true transition state based on its single imaginary frequency, and the involvement of the D_{2h} structure is ruled out on the basis of its having two imaginary frequencies.

The structures and energies we obtain for **3** and **2e** are identical to those obtained by Schleyer and co-workers,[4] since both calculations were done at the GVB (1/2)/3-21G level. By invoking a lower energy transition state, the inversion barrier is 28·85 kcal/mol at the 3-21G level. As pointed out above, this value is too small. Considerable improvement is achieved when the calculation is done at the 6-31G* level. The inversion barrier is now 39·44 kcal/mol.

This is much closer to the expected value, and we presume that the results may be improved further if the geometries were optimized at the 6-31G* level.

This is the correct inversion pathway *at this level of theory*. Some of the energy differences, though, are quite small—e.g. **2e** vs. **2g** is less than 500 cal/mol. The same is true of the geometry differences between consecutive structures along the path. Higher level theory could reverse the relative orderings of some structures, and, of course, the 'true' (i.e. experimental) inversion path could also differ from that of Figure 4. We believe, however, that the general form of this path is correct.

As in the triplet case, we expect the presence of delocalizing substituents to significantly alter the structure and energy of the biradical. In particular, 1,3-diphenyl-2,4-dicarbomethoxybicyclobutane undergoes inversion with an activation energy of 26 kcal/mol.[22] This can be rationalized by a stabilization of the transition state due to the delocalizing phenyl groups. The presence of delocalizing groups would also tend to planarize the biradical structures.

SINGLET–TRIPLET GAPS

In Table 5 we show the singlet–triplet energy differences for **2** at various geometries corresponding to minima and transition states on the triplet and singlet surfaces. For all these points, the triplet is always below the singlet in energy. The energy difference between the lowest triplet state (C_{2h}) and the lowest singlet (C_{2h}) is 1·46 kcal/mol at the 6-31G* level. We have previously shown that this substantial triplet preference in **2** is a consequence of a fortuitous balance between direct (through-space) and indirect (through-bond) overlaps of the two radical centers.[8] Both interactions are strong, but they are opposite in sign, so the net effect is that they almost completely cancel each other. The radical centers in **2** essentially have no overlap. However, the exchange repulsions between the two centers are still quite substantial, and so a triplet preference results.

Table 5. Vertical singlet–triplet gaps (kcal/mol)

Structure	S–T Gap (3-21G)	S–T Gap (6-31G*)
2b	1·80	1·78
2c	1·44	1·14
2d	1·77	1·56
2f	0·66	0·65
2g	1·79	1·64

TUNNELING IN CYCLOBUTANEDIYLS

The potential energy surfaces of **2** show several minima separated by fairly low barriers. The structures of these minima differ from each other mainly in the positions of H_1 and H_3, thus conversion from one minimum to another would involve mainly the motions of these hydrogens. Given the small mass of the moving particle and the low energy barriers involved, it seems feasible that quantum mechanical tunneling could play a major role.

The existence of C_{2h} (**2b**, **2f**) and C_{2v} (**2c**) minima instead of the more symmetrical D_{2h} structures is reminiscent of a Jahn–Teller distortion. The tunneling dynamics of Jahn–Teller distorted molecules have been studied using semiclassical periodic orbit theory.[23,24] In this method, the tunneling rate is given by

$$k = \frac{\nu_R}{\pi^2} e^{-\theta} \tag{3}$$

where ν_R is the frequency of the reactant corresponding to the reaction coordinate and θ is a barrier penetration integral. For an Eckart barrier,[25] θ is given by

$$\theta = \frac{4\pi^2[\Delta E^{\neq}_{\mathrm{eff}} - \sqrt{(E\Delta E^{\neq}_{\mathrm{eff}})}]}{h\nu_i} \tag{4}$$

where $\Delta E^{\neq}_{\mathrm{eff}}$ is the effective barrier height (i.e. the barrier height adjusted for zero-point energies of all vibrations except the reaction coordinate), ν_i is the imaginary frequency at the top of the barrier, and E is the vibrational energy of the reactant in the mode corresponding to the reaction coordinate. Equations (3) and (4) are applicable for tunneling between degenerate (symmetry equivalent) structures. Similar equations may be derived for the non-degenerate case, in which case the endothermicity of the reaction also affects the rate.

We have applied this method to calculate several tunneling rates in **2**. The results are shown in Table 6. These results certainly support our expectation that tunneling is a major factor in the interconversions among cyclobutanediyl minima.

It is also interesting to consider the possibility that tunneling is a factor in the decay of triplet **2** to **3**. Unfortunately, a direct calculation of this tunneling rate is not possible, since there is no well-defined barrier for the process. Figure 5 shows the energy diagram for singlet and triplet **2** along a portion of the singlet inversion pathway. There is an infinity of crossing points between

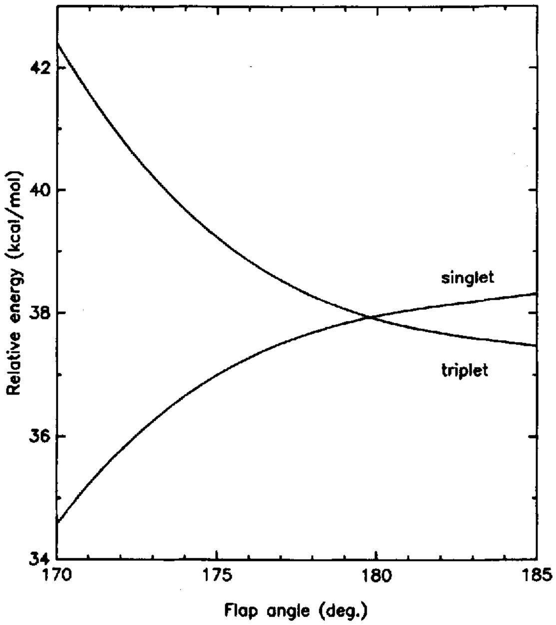


Figure 5. The crossing point between the singlet and triplet potential surfaces along the singlet inversion pathway. Energies are at the 6-31G* level relative to bicyclobutane

Table 6. Calculated tunneling rates in **2**

Reactant	TS	Product	$\Delta E_0^{\neq a}$ (kcal/mol)	$\Delta E_{\mathrm{eff}}^{\neq\, b,h}$ (kcal/mol)	ΔE_0^{c} (kcal/mol)	$\Delta E_{\mathrm{eff}}^{d,h}$ (kcal/mol)	$\nu_R^{e,h}$ (cm^{-1})	$\nu_P^{g,h}$ (cm^{-1})	$\nu_i^{f,h}$ (cm^{-1})	k (s^{-1})
2b	**2a**	**2b**	1·20	0·76	0	0	427·8	427·8	337·9*i*	$3{\cdot}2 \times 10^{12}$
2c	**2a**	**2c**	0·98	0·56	0	0	388·6	388·6	292·4*i*	$5{\cdot}0 \times 10^{12}$
2b	**2d**	**2e**	0·58	0·59	0·21	0·18	384·3	351·2	287·0*i*	$1{\cdot}5 \times 10^{12}$
2f	**2e**	**2f**	1·49	0·92	0	0	416·6	416·6	244·5*i*	$7{\cdot}9 \times 10^{12}$

[a] Original barrier height (6-31G* value).

[b] Effective barrier height (corrected for zero point energies of all other vibrations).

[c] Original endothermicity (6-31G* value).

[d] Effective endothermicity (corrected for zero point energies).

[e] Reactant frequency along reaction coordinate (before scaling).

[f] Imaginary frequency of barrier along reaction coordinate (before scaling).

[g] Product frequency along reaction coordinate (before scaling).

[h] All frequencies are calculated at the 3-21G level and reduced by 10% for the tunneling rate calculations.

the singlet and triplet adiabatic surfaces, but we take the crossing point shown in Figure 5 to be reasonably representative of these. This crossing point occurs at an energy of 0·75 kcal/mol above the **2c** minimum (0·9 kcal/mol above **2b**). We note that once this barrier is crossed, there is no additional barrier to form **3**. Compared to the barriers in the tunneling calculations above, the singlet–triplet crossing barrier is similar in height. Also, the process of crossing this barrier involves similar internal motions of the molecule. Thus we may conclude a similar tunneling rate may be expected, if not for the fact that the reaction is spin forbidden. The simplest way to account for this effect is to scale the barrier permeability by an appropriate factor. Data from a variety of sources indicate that simple, unimolecular processes in triplet biradicals have Arrhenius pre-exponential (*A*) terms that are smaller by factors of 10^4–10^5 compared to expectations for analogous spin-allowed reactions.[2,26] If we scale the tunneling rate by a factor of 10^{-5} to account for this spin forbiddenness, we would still obtain a rate on the order of $10^7\,s^{-1}$. This is certainly fast enough to account for the failure to observe **2** experimentally — it simply decays too fast to allow detection. Of course these calculations also suggest that, if one could prepare singlet **2**, it would tunnel out of its shallow well quite rapidly.

Note that the motions involved in the tunneling process are mainly in H_1 and H_3. Therefore, putting more massive substituents on these positions would slow down the tunneling rate, and this explains why we are able to observe the simply substituted systems such as **1-Me** and **1-Et**. For these structures, though, we still see a manifestation of (very much slower) tunneling, in that their decay rates are essentially independent of temperature. Unfortunately we do not have reliable values for the parameters necessary for a tunneling calculation on these substituted systems, especially considering that the tunneling rate calculation is quite sensitive to minor variations in the barrier height and frequencies. We do note, however, that it is possible to obtain for **1-Me** a tunneling rate for the closure reaction comparable to the experimental results (*ca.* $10^{-2}\,s^{-1}$)[2] using reasonable estimates of the barrier height (1 kcal/mol — the energy difference between the C_{2h}-like and C_s-like structure of **1-Me**) and frequencies (148 cm^{-1} for ν_R, 111i cm^{-1} for ν_i).[27] Thus, this theoretical analysis is not inconsistent with tunneling in the bond forming reaction of **1-Me**.

CONCLUSIONS

The potential energy surfaces of singlet and triplet cyclobutanediyl have been investigated using RHF and GVB (1/2) methods. No significant change was found when the calculations were performed with the 3-21G or 6-31G* basis sets.

At this level of theory, triplet cyclobutanediyl was found to be not planar. Instead, the lowest energy structure has C_{2h} symmetry, and a secondary minimum having C_{2v} symmetry was also found. The two interconvert over a small barrier through a C_s transition state, and it seems quite likely that tunneling is involved in this process.

Singlet cyclobutanediyl was found to be a true minimum having a C_{2h} structure. A quite unusual reaction pathway for the inversion process of bicyclobutane is proposed. The mechanism does not involve a planar D_{2h} transition state; instead it passes through the C_{2h} intermediate. The barrier to inversion is calculated to be 39·45 kcal/mol.

The singlet–triplet gap of cyclobutanediyl was calculated to be 1·46 kcal/mol. A crossing point between the triplet and singlet surface was located at an energy 0·75 kcal/mol above the triplet C_{2v} minimum. Crossing this barrier may involve quantum mechanical tunneling, and this would provide an explanation for our inability to observe the parent system, triplet **2**.

Quite simply, the substituted structures **1-Me** and **1-Et** are stabilized by their mass, which greatly slows the tunneling process and allows their direct detection by EPR.

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