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Ab Initio Calculations of the Relative Energies of Triplet 2,4-Dimethylenecyclobutane-1,3-diyl and Singlet 2,4-Dimethylenebicyclo[1.1.0]butane

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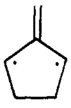
Abstract: The geometries of the triplet diradical and the closed-shell singlet, containing an additional C-C bond, have been optimized using analytical gradient techniques. Two geometries of nearly equal energy were found for the closed-shell singlet when two-configuration self-consistent-field calculations were carried out with a STO-3G basis set. Both singlet geometries have transannular bonds that are considerably longer than that computed for bicyclobutane at this level of theory, and in one structure the bridgehead carbons are significantly inverted. The effect of basis set size and configuration interaction on the relative energies of the two closed-shell singlets and the triplet diradical has been investigated. It is concluded that the combination of electron delocalization in the triplet diradical and strain in the singlet causes these states to have very similar energies.

Introduction

One method of preferentially stabilizing diradicals, relative to isomers that exist in closed-shell electronic states, is to design molecules in which the diradical forms contain considerably less strain energy than their closed-shell counterparts. This strategy has been successfully exploited by Berson and co-workers in their studies of 2-methylenecyclopentane-1,3-diyl (**1**) and its derivatives.[1]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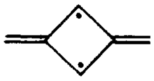
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3

Another diradical that might prove more stable than any accessible closed-shell isomer is 2,4-dimethylenecyclobutane-1,3-diyl (**2**), also known as 1,3-dimethylenecyclobutadiene (DMCBD).[2] We have previously reported the results of π-space configuration interaction (CI) calculations[3] on the planar diradical. The $^3B_{2u}$ state was found to be lowest in energy, with the lowest planar singlet (^1A_g) 23.6 kcal/mole above the triplet. However, the singlet might be significantly stabilized by transannular bond formation at nonplanar geometries and so could fall below the triplet in energy.

Given the current interest of several research groups, including our own, in synthesizing this diradical, we thought it important to provide a computational estimate of the relative stabilities of **2** and its closed-shell isomer, 2,4-dimethylenebicyclo[1.1.0]butane (**3**). In this paper we report the results of our calculations.

Procedure

At D_{2h} geometries a two-configuration self-consistent field (TCSCF) wave function is required for a zeroth order description of ^1A_g.[3] The long transannular bond in **3** also requires two configurations for its zeroth order description. Therefore, geometry optimizations at the important points on the singlet potential surface were performed with a TCSCF wave function, expanded in terms of the minimal STO-3G basis set.[4] A restricted Hartree–Fock (RHF) wave function was used for the triplet. GAMESS, an analytical gradient MCSCF program from the National Resource for Computation in Chemistry,[5] was employed to optimize structures and to compute mass-weighted hessian matrices, so that the stationary points could be characterized as minima or transition states. Additional RHF or TCSCF calculations at the stationary points were carried out with the Dunning [3s, 2p, 1d/2s][6] contraction of Huzinaga's (9s, 5p, 1d/4s)[7] basis set.

CI calculations were also performed, including all single and double excitations from RHF and TCSCF reference wave functions. The virtual orbitals were transformed to K orbitals[8] to improve CI convergence. Perturbation theory was used to select the 1500 energetically most important space orbital products (about 3000 spin-adapted configurations) from among the 7000 original space orbital products in C_{2v} symmetry. The perturbation estimate of the amount of energy associated with configurations thrown away was scaled by the ratio of the actual CI energy lowering divided by the perturbation estimate of this quantity. Over 90% of the estimated total singles and doubles correlation energy was variationally recovered. A correction was made to account for the effect of neglected quadrupole excitations.[9]

Results

Figure 1a shows the final geometry for planar ^1A_g. The four equivalent C–C ring bonds are within 0.005 Å of the full π-space CI bond lengths, while the exocyclic double bonds are, as is typically the case, 0.030 Å shorter than those optimized at the CI level.[3]

At the TCSCF STO-3G level of theory, one negative eigenvalue, with a normal mode frequency of 386i cm^{-1}, was found on diagonalization of the hessian matrix for ^1A_g. Thus, the planar singlet corresponds to a transition state at the STO-3G TCSCF level of theory. Upon following the direction of the negative eigenvalue, the stationary point shown in Figure 1b was discovered at an energy 0.0018 hartree lower than the planar singlet. This structure is labeled $^1A_1(1)$ in Table I, which gives the energies of the stationary points and the TCSCF expansion coefficients.

The geometry found for the closed-shell isomer (**3**) is shown in Figure 1c. It has a rather long (1.638 Å) transannular bond compared to that in bicyclobutane (1.497 Å).[9] This structure is denoted as $^1A_1(2)$ in Table I.

In the general vicinity of the bicyclic isomer (**3**), a third stationary point on the singlet surface, $^1A_1(3)$, was discovered. As shown in Figure 1d, $^1A_1(3)$ has a very long cross ring C–C distance of 1.882 Å. The ring is less puckered than in $^1A_1(2)$, and the two bridgehead carbons are highly inverted. Convergence of the analytical gradient geometry optimization for this structure was extremely slow. Optimization was stopped when the largest component of the gradient had a value of 0.0008 hartree/bohr, which corresponded to changes in the total energy of tens of microhartrees and in the bond lengths of several thousandths of an ångström. The same convergence criterion was used for $^1A_1(2)$. Diagonalization of the hessian matrices showed both $^1A_1(2)$ and

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Table I. Total Energies (in Hartrees) at the STO-3G Stationary Points

	STO-3G				SVP[3s,2p, 1d/2s]		
state	RHF/TCSCF	c_1[a]	c_2[b]	SDQ-CI	RHF/TCSCF	c_1[a]	c_2[b]
$^3B_{2u}$	−227.7256			−228.121	−230.5783		
^1A_g	−227.7160	0.813	−0.582	−228.100	−230.5662	0.854	−0.520
$^1A_1(1)$	−227.7178	0.810	−0.586	−228.103			
$^1A_1(2)$	−227.7253	0.982	−0.187	−228.115	−230.5862	0.988	−0.154
$^1A_1(3)$	−227.7269	0.939	−0.343	−228.117	−230.5848	0.960	−0.280

[a] Coefficient of $|\ldots a_1{}^2\rangle$ in the TCSCF wave function. [b] Coefficient of $|\ldots b_1{}^2\rangle$ in the TCSCF wave function.

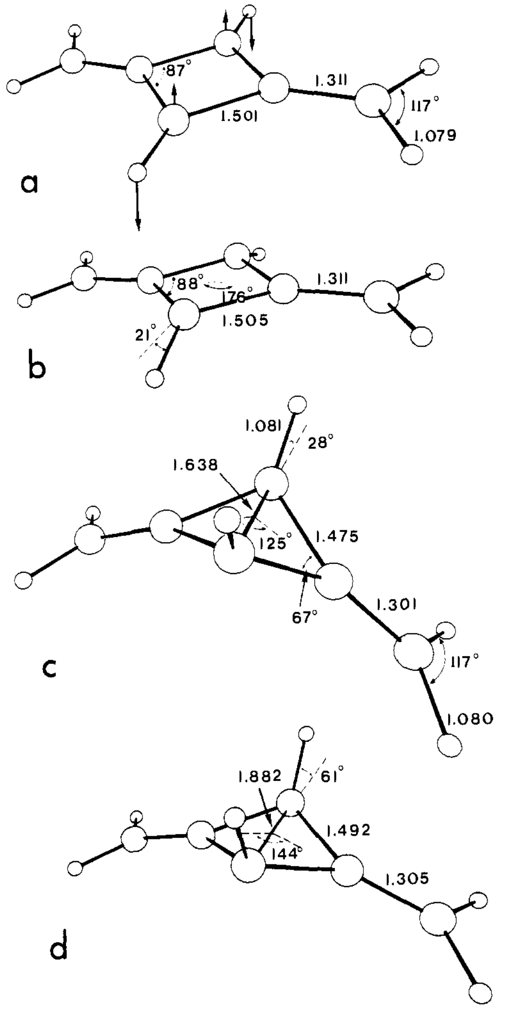

Figure 1. TCSCF STO-3G optimized geometries for (a) planar ^1A_g; (b) $^1A_1(1)$, found by following the negative eigenvalue of the hessian matrix for the planar singlet; (c) $^1A_1(2)$, the closed-shell singlet; and (d) $^1A_1(3)$, another closed-shell singlet that is nearly isoenergetic with $^1A_1(2)$.

$^1A_1(3)$ to be in regions of the potential surface where all the eigenvalues were positive.

In an attempt to ascertain, at least qualitatively, the height of the barrier between $^1A_1(2)$ and $^1A_1(3)$, partial geometry optimization was performed at points along a path connecting them. The path was defined in terms of the cross ring C–C distance. The maximum along this path was less than 2 mhartrees above $^1A_1(2)$. Obviously the potential surface along the path connecting $^1A_1(2)$ and $^1A_1(3)$ is very flat.

In order to calibrate the ability of the STO-3G TCSCF wave function to yield reliable geometries for these two structures, a geometry optimization was performed on bicyclo[1.1.0]butane. The final geometry, shown in Figure 2, is in good agreement with the microwave structure[10] and with a previous SCF geometry optimization performed with a different basis set.[11] The experimental geometry parameters are $R(C_1–C_3)$ = 1.497 Å, $R(C_1–C_2)$ = 1.498 Å, HCC = 128°, and the dihedral angle between carbon atom planes is 121°. Thus, apart from the well-known tendency for the STO-3G basis to underestimate C=C bond lengths, this basis should be capable of providing a reasonable geometry for **3**.

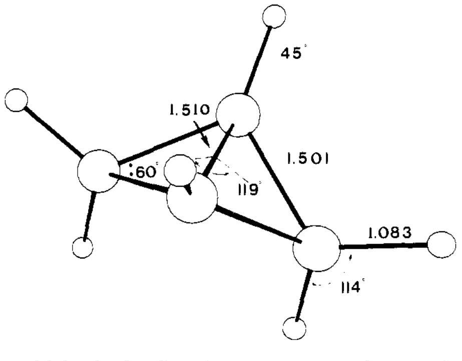

Figure 2. TCSCF STO-3G optimized geometry for bicyclobutane.

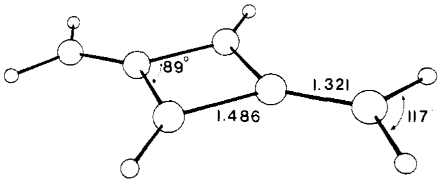

Figure 3. RHF STO-3G optimized geometry for $^3B_{2u}$.

The effect of including CI at the TCSCF optimized geometries for the singlets and at the RHF geometry for the triplet (Figure 3) is also shown in Table I. CI does not affect the small computed energy difference between $^1A_1(2)$ and $^1A_1(3)$, but it does cause the triplet to become lower in energy than either of these singlets. CI selectively stabilizes $^3B_{2u}$ by about 6 mhartrees, relative to each of the two singlets, causing $^3B_{2u}$ to lie 4 mhartrees (2.5 kcal/mol) beneath the lower of the two.

Increasing the size of the basis to the SVP level causes some rearrangement in the energy orderings. $^1A_1(2)$ now falls below the $^1A_1(3)$ structure by 0.9 kcal/mol. Since these calculations were done at the STO-3G optimized geometries, the only inference that should be drawn from them is that the potential surface, calculated with the SVP basis set, is probably also very flat.

With the SVP basis set $^1A_1(1)$ is about 8 mhartrees (5 kcal/mol) below $^3B_{2u}$. However, from the STO-3G CI results, it can be anticipated that CI with the SVP basis set should again selectively stabilize the triplet and narrow the energy difference between it and the lowest singlet.

Discussion

The results of our calculations clearly show that the planar diradical does not represent the geometry of lowest energy on the singlet potential surface. At the STO-3G level of theory with a TCSCF wave function, ^1A_g is not even a minimum on the potential surface but is, instead, a transition state for pyramidalization of two ring carbons. However, calculations of the global potential surface for trimethylenemethane have revealed that the STO-3G

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[10] Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *J. Chem. Phys.* **1969**, *50*, 1976.

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basis set is biased toward pyramidalization of radical centers;[12] with a larger basis set, ^1A_g might be found to be a true minimum. Even with STO-3G, the pyramidalized structure, $^1A_1(1)$, is only a few millihartrees lower than the planar one in energy. The coefficients in the TCSCF wave functions for the two structures are also nearly identical. In beginning these calculations, we had expected the ^1A_g state to be the transition state for interconversion of **3** with its mirror image. This clearly is not true, and the ^1A_g geometry is a relative minimum for motion along the normal coordinate leading to **3**.

Both $^1A_1(2)$ and $^1A_1(3)$ lie well below the planar singlet diradical in energy. The MCSCF coefficients in the wave functions for $^1A_1(2)$ and $^1A_1(3)$ show the importance of transannular bonding in both structures, despite the long transannular bond lengths. This bond in $^1A_1(3)$ is especially interesting, since it is apparently formed between the back lobes of hybrids that point away from each other.[13] The lowest energy path along the surface connecting $^1A_1(2)$ and $^1A_1(3)$ is so flat with the STO-3G basis set and an MCSCF wave function that, if a larger basis set or a more highly correlated wave function were used, only one minimum might be found, with an optimal geometry intermediate between those of $^1A_1(2)$ and $^1A_1(3)$. Analytical gradient, geometry optimization with a SVP basis set, and an MCSCF wave function would be highly desirable but prohibitively expensive.

The relative energies of $^3B_{2u}$ and $^1A_1$ are also problematical. As discussed elsewhere,[14] the "doublet instability problem" makes the RHF geometry for $^3B_{2u}$ deviate considerably from the optimal π CI geometry. The deviation between the TCSCF geometry for $^1A_1$ and the optimal π CI geometry is smaller. Therefore, if the CI calculations in Table I were carried out at the optimal CI geometries, instead of at geometries obtained by RHF/TCSCF calculations, the triplet would be selectively stabilized. Once again, a meaningful prediction of which state lies lowest would require geometry optimizations with large basis sets and highly correlated wave functions.

In the absence of such calculations, it does seem safe to conclude, however, that the combination of electron delocalization in **2** and strain in **3** makes the triplet at least competitive in energy with the closed-shell singlet. Even if $^3B_{2u}$ lies above $^1A_1$ in energy at their equilibrium geometries, it should thus be possible experimentally to populate the triplet thermally.

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Registry No. 2, 80410-15-7; **3**, 80410-16-8.

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[13] For another example, see Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.*, **1972**, *94*, 773. It should be noted that the bridgehead carbons in the optimized structures for bicyclobutane and $^1A_1(2)$ are also inverted, but much less so than in that for $^1A_1(3)$. The angle between the C–H bond at each of these carbons and the projection of the bond onto the C–C–C plane is respectively 4, 15, and 40°. In each case the C–H bond lies on the same side of the C–C–C plane as the fourth carbon.

[14] Borden, W. T.; Feller, D.; Davidson, E. R. *Tetrahedron*, in press.

The State of Lithium Tetraphenylborate, Lithium Picrate, and Sodium Picrate Dissolved in 1,2-Dichloroethane Containing One of Several Phase-Transfer Catalysts

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Abstract: 1,2-Dichloroethane solvent containing 1 mM of either dibenzo-18-crown-6 (DBC) or triphenylphosphine oxide (TPPO) dissolves 1 equiv of lithium tetraphenylborate ($LiBPh_4$) to form 1:1 ligand–salt complexes. Conductance studies at 25 °C show the ion association constant K_A to be 1660 M^{-1} for DBC $Li^+ + BPh_4^-$ and 7400 M^{-1} for TPPO $Li^+ + BPh_4^-$. Lithium bromide, lithium picrate, and sodium picrate do not dissolve to the extent of 1 mM in solvent containing 1 equiv of crown ether. Lithium picrate does dissolve to the extent of 1 mM in solvent containing 1 equiv of either TPPO, hexamethylphosphoramide (HMPA), glyme-4, or glyme-5. Sodium picrate requires at least a tenfold excess of either TPPO, HMPA, or glyme-5 to form 1 mM solutions. Conductance and spectrophotometric studies show that the 1:1 ligand–metal picrate complexes dissociate to a very small extent and do react with additional ligand to form 2:1 and 3:1 ligand–cation complexes, decreasing the extent of ion association. Substitution of sodium for lithium in these ligand–metal picrate complexes has little or no effect on either the conductance or the UV–visible spectra of the solutions. These ligands promote charge separation in solution (as measured by conductance) in the following order: glyme-4 < glyme-5 < TPPO < HMPA < DBC.

There has been a great deal of interest in the use of neutral ligands to promote the solubility of salts in organic solvents such as methylene chloride, chloroform, and benzene in order to obtain larger concentrations of reactive ions in a nonaqueous phase.[2] Such ligands form one class of what are termed *phase transfer catalysts*.[3-5] There have been only a few reports of physicochemical studies of such systems in these relatively poor solvents; Frensdorf has reported[6] a study of the extraction of alkali metal picrates from water in methylene chloride with use of crown ethers (an extension of Pedersen's earlier work[7]) and Nae and Jagur-

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