

of any ESR signal with our equipment.⁴ Yet, no products other than **1** and **6** were found by GLC, under conditions where a product concentration $\geq 5 \times 10^{-7}$ M could have been detected.¹⁰

An IR investigation showed the consecutive appearance of new frequencies (I, 1634 and 1648–1655 cm^{-1} ; II, 1660 cm^{-1}) upon irradiation for 30 min at 77 K and warming in the dark to 92 K, before the formation of product **6** ($\nu_{\text{CO}} = 1665 \text{ cm}^{-1}$) (Figure 3).¹¹ A three-step sequence is thus established which can be accommodated by the proposed reaction scheme. Both the long-lived ESR component and the transient IR bands I are observable only below 92 K, i.e., they may well arise from the primary metastable photoproduct(s), either **2** alone or a mixture of **2** and **4**¹² (note that the ratio $(6a + b)/6c$ is $\sim 5:1$ at 77 K). If so, then the IR band II could be due to **3** (and possibly **5**). The IR frequencies I and II are suggested to be those of the α -keto (oxallyl) radical groups, although we are not aware of appropriate reference data.

The observed D value of 0.0054 cm^{-1} is considerably smaller than any of the D values reported previously for triplet biradicals. Our assignment to the extensively delocalized biradical **2** appears acceptable, however, in light of the spread of D from 0.01 – 0.03 cm^{-1} for partly delocalized biradicals¹⁴ to 0.08 cm^{-1} for the localized 1,3-cyclopenta diyl.¹⁵

The transition from intermediate **2** to **3** when the temperature is raised to 92 K should be accompanied by the development of a new ESR spectrum which then should persist until ~ 180 K. However, no resolved signal was observed when measurements were carried out at 92 K with a flow cavity. Although it cannot be ruled out that this result was merely due to inhomogeneity caused by the nitrogen flow, the assignment of structure **3** to the species responsible to the IR band II must therefore remain tentative. Still, it appears more plausible than the alternative that the IR change between 77 and 92 K is associated with a rotation of the benzoyl group in **2** from out of conjugation into conjugation with the radical center. If this were the case, one might expect a shift to lower rather than higher IR frequency (as is observed in Figure 3). Furthermore, the benzoyl rotamers of **1** are frozen out at ca. 200 K, and oxallyl rotamers (as in **2**–**5**) are likely to have a higher barrier.

In conclusion, we note that, for the first time in di- π -methane photochemistry, direct evidence for the intervention of a biradical intermediate (or a category of biradical intermediates) and strong support for a second intermediate have been obtained. This result confirms the postulated¹⁶ stepwise mechanism for the photorearrangement of barrelenes. Furthermore, it corroborated the conclusions previously drawn¹³ from the rearrangement of independently generated biradical intermediates of the type now observed directly.

(10) Glass capillary GLC column; OV 101, 70 ft. Components $>0.05\%$ were detectable, i.e., 5×10^{-6} M at a total concentration of 10^{-2} M. A further factor of ten derives from the minimum ESR signal detectability for a 10% amplitude in the plot of Figure 2, safely assuming a maximum biradical concentration of 10^{-2} M for 100% signal amplitude.

(11) The IR experiment also reveals the striking fact that of the two rotamers of **1** which are frozen out at 77 K the major component ($\nu_{\text{CO}} = 1633 \text{ cm}^{-1}$) photoreacts preferentially while the minor component ($\nu_{\text{CO}} = 1644 \text{ cm}^{-1}$) remains largely unchanged (accounting for ca. 30% recovered **1** after 2-h irradiation at 77 K). We note that the residual IR band at around 1647 cm^{-1} (242 K) exactly corresponds to the carbonyl band of **1** under these conditions. This remarkable influence of excited-state geometry, as reflected by the ground-state conformation, on the photoreactivity at 77 K is currently under further investigation. At room temperature, a similar effect is not observed (Φ_{366} for product formation = 1.0).

(12) The intermediate **4** is structurally similar to a triplet biradical which has been generated by diazo decomposition and shown to preferentially afford the di- π -methane product of 2,3-naphthobarrelene.¹³

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Effect of Through-Bond Interaction on Terminal Methylene Rotation in the Tetramethylene Diradical

Sir:

How the ease of terminal methylene rotation in tetramethylene (butane-1,4-diyl) depends upon the conformation about the central C–C bond remains a major unanswered question in the study of this diradical.¹ The pioneering investigation by Hoffmann and co-workers² of the potential surface for the singlet diradical revealed small barriers to terminal methylene rotation in the gauche conformation about the central C–C bond but large barriers in the trans conformation. In the latter conformation, the strong preference found for the 90,90 geometry at the terminal methylene groups (Figure 1) was traced to the stabilizing interaction between the formally nonbonding atomic orbitals (AO's) on these carbons and the orbitals of the central C–C bond. As a result of this "through-bond coupling" between the AO's on the terminal carbons in the 90,90 geometry of the trans diradical, Hoffmann's EH calculations found the 90,90 geometry to be favored over 0,90 and 0,0 by, respectively, 12.7 and 13.4 kcal/mol. From INDO calculations, Stephenson and Gibson³ obtained values of 45.0 and 46.7 kcal/mol for these energy differences.

Both of the above calculations are flawed by the use of one-configuration wave functions to represent singlet diradicals. In order to reduce the contribution of high-energy ionic terms to the wave function for a homosymmetric singlet diradical, a two-configuration wave function is required.⁴ For instance, if the closely spaced $7a_g$ and $6b_u$ molecular orbitals (MO's) at the 90,90 tetramethylene geometry are denoted as S and A, corresponding to the symmetry behavior of each with respect to the twofold axis, the wave function for the lowest singlet state takes the form of eq 1.

$${}^1A_g = c_1 | \dots A^2 \rangle - c_2 | \dots S^2 \rangle \quad (1)$$

In eq 1, $c_1 > c_2$ since A lies below S in energy. The origin of this energy difference is that the interactions in A between the AO's on the terminal carbons and the orbitals of the central C–C linkage are bonding while in S these interactions are antibonding.² Consequently, the presence of $| \dots S^2 \rangle$ in the two-configuration 1A_g wave function might be expected to reduce the net bonding between the AO's on the terminal carbons and the orbitals of the central C–C bond, thus lowering the energy difference between 90,90 and both 0,90 and 0,0.

The 90,90 geometry of *trans*-tetramethylene is a true intermediate on the STO-3G CI surface calculated by Segal for the singlet diradical.⁵ However, Segal did not compute the energies of the 0,90 and 0,0 geometries. In order to determine whether

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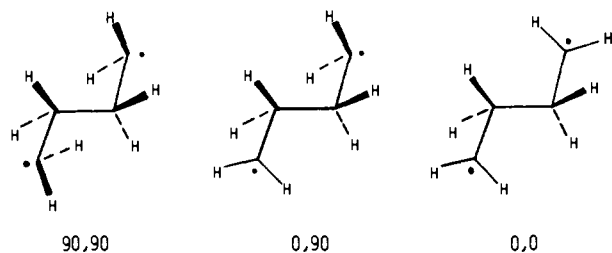


Figure 1. Three geometries at the terminal methylene groups in the trans conformation of tetramethylene.

through-bond coupling might prevent loss of stereochemistry by terminal methylene rotation in the trans diradical, we have performed ab initio calculations at all three geometries.

Calculations were carried out on the 90,90 diradical utilizing Segal's published geometry^{5,6} and the STO-3G basis set⁷ employed by him. However, instead of using a small CI among four non-optimal MO's to obtain a 1A_g wave function, we performed an MCSCF calculation that yielded a two-configuration wave function in which both the MO's and the mixing coefficients were simultaneously optimized. Thus, our 1A_g energy of -154.1728 hartrees is 0.008 hartree lower than that computed by Segal for the 90,90 geometry.

Geometries for the 0,90 and 0,0 diradicals were obtained by rigid rotations about the terminal C-C bonds from the 90,90 geometry, accompanied by depyramidalization of each methylene group rotated.⁸ A two-configuration 1A_g MCSCF wave function was again used for the 0,0 diradical, with $2a_u$ in the first configuration being replaced by $2b_g$ in the second. In the lowest singlet state at 0,90, one electron occupies a σ MO ($13a'$) and the other a π orbital ($4a''$).⁹ The open-shell RHF method of Davidson¹⁰ was used to find the wave function for this $^1A''$ state, as well as the wave functions for the lowest triplet state at all three geometries. The relative energies of the singlet and triplet states at these geometries are shown in Table I.

The data in the table reveal that hyperconjugation of the AO's on the terminal carbons with the central C-C bond is favored over hyperconjugation with C-H bonds on the adjacent carbon. This result is in agreement with the findings of both Hoffmann and co-workers² and Stephenson and Gibson.³ The size of the energy change on going from 0,90 to 0,0 is also in qualitative agreement with the results of both these groups. However, in the singlet state, the energy difference between 90,90 and 0,90 is a factor of five smaller than that found by Hoffmann and co-workers and more than an order of magnitude less than that computed by Stephenson and Gibson.

Through-bond coupling in 1A_g at 90,90 nevertheless does contribute to the energy differences between this geometry and the other two. In the 90,90 1A_g MCSCF wave function, $|\dots A^2\rangle$ is found to be more than 50 kcal/mol below $|\dots S^2\rangle$, in accord with the expectations based on Hoffmann's analysis. Consequently, $|\dots A^2\rangle$ has a bigger coefficient in the MCSCF wave function than $|\dots S^2\rangle$. Thus, it can safely be inferred that through-bond coupling is responsible for making the energy increase on going from 90,90 to 0,90 more than twice as large as both the increase on going from 0,90 to 0,0 in the singlet and the

(6) The HCH bond angles at the central and terminal carbons were not given in Segal's paper. We assumed the former to be 109.5° and determined the optimal value for the latter to be 116.4° .

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(8) At the optimal 90,90 geometry determined by Segal, the terminal methylene groups are pyramidalized by 22° . We have found that simultaneous depyramidalization of both these groups at the 90,90 geometry raises the 1A_g energy by 2.76 kcal/mol and that of 3B_u by 2.32 kcal/mol.

(9) A wave function that could be used globally to calculate the complete potential surface for methylene rotation would take the form $c_1^2|\dots 16a^2\rangle - c_2^2|\dots 17a^2\rangle$. This wave function can be factored to $|\dots (c_116a + c_217a)(c_116a - c_217a)(\alpha\beta - \beta\alpha)\rangle/\sqrt{2}$, which represents one electron occupying each of two MO's. At 0,90, symmetry causes one of these MO's to be pure σ (a') and the other pure π (a'').

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Table I. Relative Energies^a (kcal/mol) of the Lowest Singlet and Triplet States at Three Geometries of *trans*-Tetramethylene

state	geometry		
	90,90	0,90	0,0
$^1A_g(^1A'')$ ^b	0	2.76	3.95
$^3B_u(^3A'')$ ^b	1.63	2.57	4.01

^a Energies are relative to -154.1728 hartrees calculated for 1A_g at 90,90. ^b Symmetry designation for this state at 0,90.

average increase on rotating one methylene group in the triplet. However, these comparisons suggest a magnitude of only about 1.5 kcal/mol for the stabilizing effect of through-bond coupling on the energy of the 1A_g state.

Despite the substantially lower energy of $|\dots A^2\rangle$ compared to $|\dots S^2\rangle$, the coefficient of 0.762 for the former is only somewhat larger than that of 0.647 for the latter in the 1A_g MCSCF wave function. This fact is responsible for the small energetic effect of through-bond coupling in the trans diradical. The large reduction in the calculated energy difference between 0,0 and 0,90 trimethylene (propane-1,3-diy) on going from EH¹¹ to multiconfigurational wave functions¹²⁻¹⁴ undoubtedly has a similar origin.

The small size of the contribution of through-bond coupling to the energy difference between 90,90 and 0,90 in the lowest singlet state of *trans*-tetramethylene¹⁵ makes this difference less than the 4.7 kcal/mol calculated by Segal for closure of the trans diradical to cyclobutane and comparable to the 2.3 kcal/mol found to be required for cleavage of the diradical to two ethylenes.⁵ Our theoretical results, taken together with Segal's, thus suggest that the trans diradical should lose stereochemistry before closing to cyclobutane and that loss of stereochemistry should also compete with ethylene formation.

Although we have not carried out calculations on the gauche diradical, the coefficients of 0.68 for $|\dots A^2\rangle$ and 0.73 for $|\dots S^2\rangle$ reported by Segal for the singlet wave function suggest that the through-space interaction that is dominant at the optimal geometry for this conformation will have even a smaller effect on the barriers to methylene rotation than does the through-bond interaction that is dominant at the optimal trans geometry. If, as expected, the barriers to methylene rotation are indeed small in the gauche conformation about the central C-C bond, in this conformation, as in the trans, loss of stereochemistry should compete with closure and cleavage. Experimentally, methylene rotation is, in fact, found to be faster than closure or cleavage in the parent tetramethylene diradical.^{1,16,17}

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