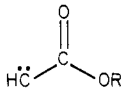
Communications to the Editor

Geometric Isomerism in Triplet Carbenes: Carbohydroxycarbene

Sir:

In a recent communication to this journal, Hutton and Roth[1] have reported several very interesting experimental observations concerning the carbomethoxycarbene and carbethoxycarbene molecules. First, they find that both carbenes have triplet ground states. This is a somewhat surprising result when one considers that although carbalkoxycarbenes have been extensively studied (following the early investigations of Doering[2]) most of their reactions appear to be characteristic of singlet carbenes. However, several exceptions to this picture were noted by Hutton and Roth (HR). Their recent EPR results[1] establish that these two triplet carbalkoxycarbenes cannot lie more than 0.01 kcal above the corresponding singlet states. The findings of HR raise the obvious question, "What are the precise singlet-triplet separations for carbenes of this type?" One of the purposes, then, of the present theoretical study was to provide a realistic estimate of this key energetic quantity.

Hutton and Roth also demonstrated that the carbalkoxycarbenes represent only the third example[3] to date of carbene geometric isomerism. That is, the hydrogen in carbene **1** may



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lie either cis or trans to the alkoxy group OR. Specifically, HR found that activation energies for the reactions of **1** were less than the barriers to isomerization. This experimental result, of course, begs the question, to be answered here, of the specific value of such isomerization barriers. Finally, the EPR spectra of HR provide direct evidence that both carbalkoxycarbenes are bent, inasmuch as a linear carbene would probably (i.e., assuming rotation about the C-O single bond is prohibited) preclude geometric isomerism. On the basis of previous experience with zero-field splitting parameters for other carbenes, HR suggest H$\ddot{C}$C angles for **1** on the order of 140°, and this question is also addressed theoretically here.

In the present research, the family of carbalkoxycarbenes has been modeled by the prototype carbohydroxycarbene H$\ddot{C}$COOH, i.e., compound **1** with R = H. This model is expected to be fairly realistic, in part because the EPR spectra of **1** for R = CH_3 and R = C_2H_5 are very similar.[1] An additional simplification was provided by assuming that the COOH fragment for all carbene electronic states considered had the precise geometrical structure found experimentally[4] for the closely related acetic acid CH_3COOH. The remaining structural optimizations were carried out at the self-consistent-field (SCF) level of theory by using the Huzinaga-Dunning double-zeta (DZ) basis set;[5] H(4s/2s), C,O-(9s5p/4s2p).

Table I. Conformational Features of the H$\ddot{C}$COOH Potential Energy Surfaces[a]

	triplet		singlet	
θ	$\phi = 0°$	$\phi = 180°$	$\phi = 0°$	$\phi = 180°$
0°	0.00 (*tt*)	7.71 (*tc*)	10.91 (*tt*)	12.18 (*tc*)
45°	2.41	9.92	4.48	10.75
90°	4.93 (*gt*)	12.84 (*gc*)	0.0 (*gt*)	11.62 (*gc*)
135°	2.70	12.35	5.42	18.74
180°	0.57 (*ct*)	11.32 (*cc*)	12.14 (*ct*)	25.53 (*cc*)

[a] The trans-trans (or *tt*, with $\theta = 0°$, $\phi = 0°$) triplet absolute energy is -226.47120 hartrees, and other singlet energies are given relative to it in kcal/mol. Similarly, the singlet gauche-trans (or *gt*, with $\theta = 90°$, $\phi = 0°$) absolute energy is -226.42336 hartrees, and other singlet energies are given in kcal/mol relative thereto.

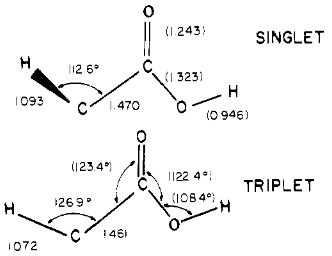
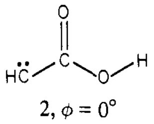
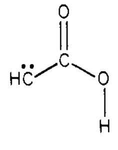


Figure 1. Predicted structures of triplet and singlet carbohydroxycarbene. For the nonplanar singlet carbene, the dihedral angle between the HCC and CCO planes is 87.8°. It should be mentioned that further geometry explorations with d functions on the carbenic C reduce the singlet CCH angle to 107°.

Inspection of **1** shows that in addition to the rotation about the C-C bond observed by HR, there is a second possible internal rotation about a single bond. This is the rotation of the OR group about the C-O single bond. Here, both conformations were initially considered. In this preliminary triplet conformational investigation, the C-C distance was fixed at 1.50 Å, the C-H distance at 1.08 Å, and the carbene H$\ddot{C}$C angle at 130°. Table I shows the potential energy as a function of θ (the angle of CH rotation about the $\ddot{C}$-C bond) for both values of the angle ϕ illustrated in **2**. Probably the most important finding in Table I is that, consistent with the experimental conclusions of HR, the trans-trans and cis-trans triplet isomers are nearly degenerate, lying only 0.57 kcal apart. The barrier separating them is rather symmetric, so the gauche-trans relative energy ($\theta = 90°$) of 4.93 kcal is probably a good estimate of the true barrier height. This barrier is significantly greater than the threefold barrier in acetic acid (0.48 kcal[6]), indicating a small amount of C-C double-bond character. Although the barrier in acetic acid for rotation about the OH bond is not known, the equilibrium structure does occur for the hydroxyl hydrogen trans to the methyl group.[6] Theoretical



2, $\phi = 0°$



2, $\phi = 180°$

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(1) R. S. Hutton and H. D. Roth, *J. Am. Chem. Soc.*, **100**, 4324 (1978).

(2) The addition reactions of carbomethoxycarbene and carbethoxycarbene with saturated hydrocarbons were first reported by W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **78**, 4947 (1956). Footnote 9 of the latter paper recalls briefly the amusing origin of the now widely used term "carbene". For other early research on carbomethoxycarbene and carbethoxycarbene, see: W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960); W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **83**, 1989 (1961).

(3) Previous examples of naphthylmethylenes: A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 129 (1965). Examples of vinylmethylenes: R. S. Hutton, M. L. Manion, H. D. Roth, and E. Wasserman, *ibid.*, **96**, 4680 (1974); O. L. Chapman, *Pure Appl. Chem.*, **40**, 511 (1974).

(4) W. Caminati, F. Scappini, and G. Corbelli, *J. Mol. Spectrosc.*, **75**, 327 (1979). The assumed structural parameters are indicated in parentheses in the figure.

(5) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); T. H. Dunning, *ibid.*, **53**, 2823 (1970).

(6) L. C. Krisher and E. Saegebarth, *J. Chem. Phys.*, **54**, 4553 (1971).

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studies[7,8] suggest an energy difference of 7-11 kcal between these acetic acid cis and trans forms, and Table I shows that for $H\ddot{C}COOH$ the analogous separation is 7.7 kcal.

With the trans-trans form established as the lowest energy triplet conformer, an optimization of the three carbene geometrical parameters was carried out at the DZ SCF level of theory, and the results are seen in Figure 1. The resulting total energy is -226.47253 hartrees, or 0.00133 hartree below the energy with the assumed triplet geometry. For the singlet state, a preliminary conformational map was obtained, assuming $r(CC) = 1.50$ Å, $r(CH) = 1.10$ Å, and $r(H\ddot{C}C) = 105°$, typical singlet carbene structural parameters.[9] These singlet conformational results are seen in Table I and show the expected[4,6-8] result (also found for the triplet state) that the hydroxyl H prefers to lie trans to the carbene carbon atom. What was not expected by us is the nonplanar equilibrium geometry predicted for the lowest singlet state. The potential well (for $\phi = 0°$) is rather symmetric with respect to the dihedral angle θ, so it is clear that the optimum angle is close to $\theta = 90°$. On the basis of this and the corresponding triplet model geometries, the singlet-triplet separation is predicted to be 30.0 kcal. Partial optimization of the singlet structure was carried out, is seen in Figure 1, and gives a total energy of -226.42480 hartrees. Comparison with the analogous triplet energy reported above provides a singlet-triplet separation of 29.9 kcal.

For the parent CH_2, the above DZ SCF approximation yields a singlet-triplet separation (E) that is ~22 kcal too large.[10] In this regard, a two-configuration SCF treatment of the singlet state is more appropriate, and this yields a DZ ΔE of 21.1 kcal for $H\ddot{C}COOH$. Addition of carbene carbon d functions reduces the singlet-triplet separation further to 11.9 kcal. Configuration interactions involving single and double excitations (19 530 configurations for the ^1A state, 6635 for the $^3A''$ state) yielded total energies of -226.63428 and -226.65360 hartrees, and hence $\Delta E = 12.1$ kcal. Finally, use of the Davidson unlinked cluster correction[11] reduced ΔE to 7.6 kcal, remarkably close to the value obtained by empirically subtracting 22 kcal from the simplest theoretical prediction of 29.9 kcal.

Moreover, direct theoretical studies of CH_2 at a level of theory essentially comparable to the best results reported here provide a reasonable singlet-triplet separation for methylene. Specifically, Bauschlicher and Shavitt[12] predict a separation of 12.4 kcal in this way while the most exhaustive theoretical studies[10,12,13] suggest ΔE ~11 kcal. Thus, there is independent evidence of the validity of the present theoretical treatment of singlet-triplet separations, which supports the final prediction of a gap of ~7 kcal for $H\ddot{C}COOH$. This small separation, combined with the relative nonreactivity[14] of triplet carbenes, could explain why carbalkoxycarbenes appear[2] to be singletlike on the basis of their reactions. However, a simpler explanation is that the normal course of reaction for these carbenes appears to involve generation and fast reaction of the singlet states.[15]

Carbohydroxycarbene may also be viewed in light of a number of recent studies[9,16-18] on the effects of heteroatom substitution on the singlet-triplet splitting in methylene. Bauschlicher et al.[9] and Harrison et al.[17] emphasize the stabilization of the singlet relative to the triplet state due to σ-inductive withdrawal of electrons by electronegative substituents. The inductive withdrawal of the σ electrons primarily localized on the carbenic carbon stabilizes the singlet in which this orbital is doubly occupied relative to the triplet where it is singly occupied. Baird and Taylor[16] and Feller et al.[18] have stressed the importance of considering the donation of out-of-plane lone pairs on heteroatoms such as oxygen into the empty (in the singlet) π orbital on carbon. Carbohydroxycarbene is somewhat different from simpler carbenes such as $C(OH)_2$[18] in that the optimum geometry has the HCC and CCO planes nearly orthogonal to avoid repulsion between the carbene carbon and the oxygen lone pair orbitals. The doubly occupied orbital on the carbene center is now oriented to donate electron density to the slightly positive carbonyl carbon. The empty molecular orbital on the carbenic center is now a σ-type orbital which may, in fact, accept electron density from the lone pair on oxygen. The net effect of these two interactions should be a slight stabilization of the singlet state relative to the triplet state in carbohydroxycarbene as compared to methylene.

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Assignment of the Anomalous Resonance Raman Vibrations of Bathorhodopsin

Sir:

The resonance Raman (RR) spectrum of bathorhodopsin, the primary photochemical intermediate in vision, is dominated by three intense lines near 854, 875, and 922 cm^{-1} which are unique to this intermediate (Figure 1A).[1] These lines are characteristic of the retinal chromophore conformation and must be explained by any model for the structure of bathorhodopsin.[2,3] Our previous work with methyl-deuterated and demethylbathorhodopsin analogues suggested that they are due to hydrogen out-of-plane (HOOP) wagging vibrations whose intensities are induced by small relative chain twists between ground and resonant excited states.[4] In this communication, we definitively assign the 875- and 922-cm^{-1} bathorhodopsin lines to specific HOOP modes. This assignment is based on Raman spectral shifts in analogue bathorhodopsins whose retinal chromophores are deuterated at specific positions on the polyene chain.

The synthesis of 11,12-dideuterioretinal (**6**) and 10-monodeuterioretinal (**11**) is summarized in Scheme I. The acetylenic C_{16} carbinol[5] **2** was prepared in 98% yield from β-ionone (**1**) via a Grignard. Treatment of **2** with acetic anhydride and 4-dimethylaminopyridine gave the corresponding acetate (**3**), which

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[2] For reviews, see: (a) R. H. Callender and B. Honig, *Annu. Rev. Biophys.* Bioeng., **6**, 33 (1977); (b) R. Mathies, *Chem. Biochem. Appl. Lasers*, **4**, 55 (1979).

[3] For recent models, see: (a) B. Honig, T. Ebrey, R. H. Callender, U. Dinur, and M. Ottolenghi, *Proc. Natl. Acad. Sci. U.S.A.*, **76**, 2503 (1979); (b) A. Warshel, *ibid.*, **75**, 2558 (1978); (c) A. Lewis, *ibid.*, **75**, 549 (1978); (d) K. van der Meer, J. J. C. Mulder, and J. Lugtenburg, *Photochem. Photobiol.*, **24**, 363 (1976).

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