J. Am. Chem. Soc. **1988**, *110*, 7575–7576

Ab Initio Calculations of the Geometries and IR Spectra of Two Derivatives of Tetramethyleneethane

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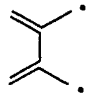
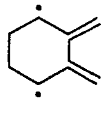
Received February 25, 1988

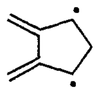
Following the observation of a triplet EPR signal for tetramethyleneethane (TME) I in 1970,[1] a conflict between experiment and theory regarding the multiplicity of the ground state of I has arisen. The ab initio calculations of Borden and Davidson[2] predict a singlet ground state, but Dowd, Chang, and Paik[3] have found that I obeys the Curie law, supporting the assignment of a triplet ground state to I. The divergence between theory and experiment might have arisen because I has a perpendicular or twisted conformation, while the early theoretical work was focused on the planar diradical.[2] However, Du and Borden[4] have recently predicted, on the basis of ab initio calculations, that I should have a singlet ground state regardless of the angle of twist about the central carbon–carbon bond; they also concluded that the singlet state adopts the perpendicular (D_{2d}) structure. At their optimized structure the singlet–triplet separation is −0.1 to 2.8 kcal/mol, depending on the level of theory applied.



I



II



III

The conflict between theory and experiment has made it desirable to prepare diradicals with unequivocal geometries. Dowd, Chang, and Paik[5] have recently demonstrated that the 2,3-dimethylenecyclohexa-1,3-diene diradical II[6] also exhibits linear Curie law behavior. It was suggested on the basis of an MM2 calculation that this ground-state triplet molecule, with four sp^2-hybridized carbon atoms in a six-membered ring, should be nearly planar.[5] However, the MM2 procedure as currently parameterized is not ideally suited for examining the question of nonplanarity of conjugated diradical systems. This motivated us to calculate the geometry of the triplet state of II as well as that of III by using the ab initio Hartree–Fock procedure.[7] Roth and co-workers[8] have concluded, on the basis of its Curie law behavior, that the planar 2,2-dimethyl-4,5-dimethylene-1,3-cyclopentadiene diradical has a triplet ground state.

The structures of both II and III were fully optimized by using the unrestricted Hartree–Fock (UHF) procedure and the 3-21G basis set.[9] The resulting structures are shown in Figure 1. The calculations yield a C_2 structure for II, with a dihedral angle of 25.0° between the planes of the allyl groups. In agreement with UHF calculations with the less flexible STO-3G basis set,[10] we found that the lowest triplet state of III is planar with C_{2v} symmetry. The structures of both II and III were shown to be true energy minima by calculating the force constants and normal mode frequencies with analytical second derivatives.

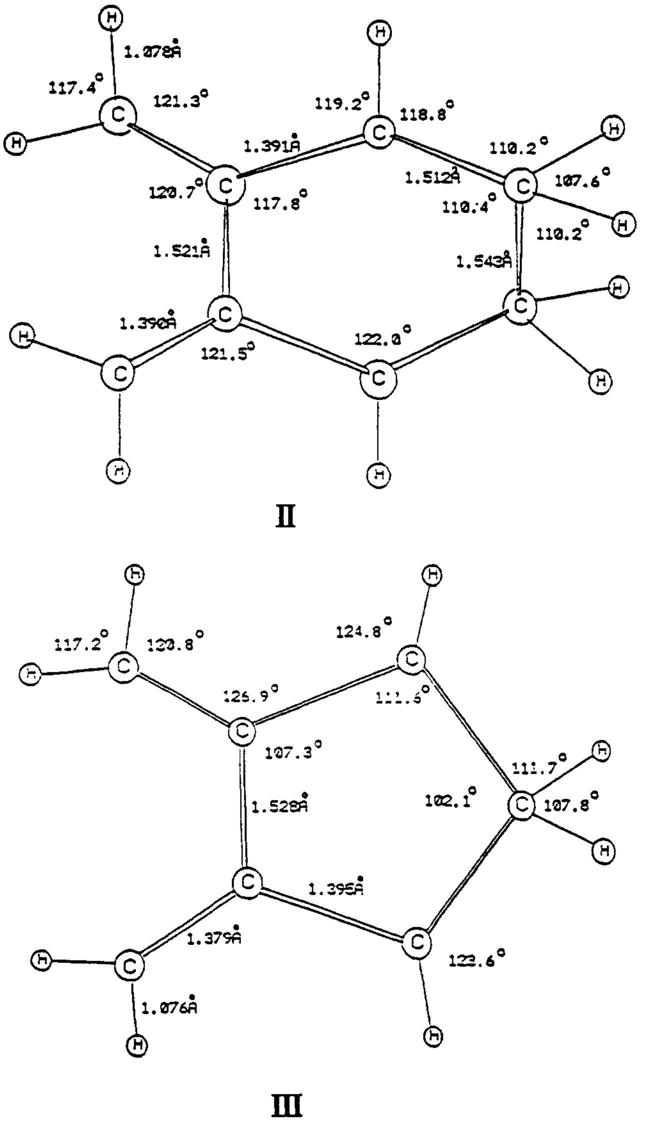


Figure 1. The optimized 3-21G geometries of the diradicals 2,3-dimethylenecyclohexa-1,3-diene (II) and 2,3-dimethylenecyclopenta-1,3-diene (III).

The normal mode frequencies, reduced by 10% to correct roughly for the deficiencies of the HF procedure and for the effects of anharmonicity, are summarized in Table I. The calculated frequencies and IR intensities of II are compared with the experimental spectrum (Figure 2) obtained by Roth et al.[6a] following irradiation at 254 nm of 5,6-dimethylene-2,3-diazabicyclo[2.2.2]oct-2-ene in an argon matrix. The bands which grew in upon irradiation were identified with those of the diradical II. Our theoretical results are in fairly good agreement with the results reported in the 600–1000-cm^{-1} region of the spectrum.[6] Likewise, we predict a strong band at 3011 cm^{-1} in agreement with experiment. We also predict eight fairly intense lines between 2933 and 2981 cm^{-1}. Although, the experimental spectrum has an intense, broad feature centered around 2930 cm^{-1}, the structure in this region was not attributed to the diradical,[6a] perhaps because this part of the C–H stretching region was not materially changed between the starting azo compound and the product. Peaks near 2820, 2880, and 3120 cm^{-1} were assigned to II; we do not predict any fundamentals within 100 cm^{-1} of these values, suggesting that these lines may be due to a species other than II. However, we

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(7) The calculations were performed with the GAUSSIAN 82 program: Binkley, J. S.; Frisch, M. J.; Raghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82 Cray COS version, Carnegie Mellon University, 1982. Sunil, K. K. and Yates, J. are also authors of the Harris VOS version of GAUSSIAN 82.

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Table I. Theoretical Frequencies and Normalized IR Intensities of II and III[a]

II			III		
symmetry	frequency (cm^{-1})	intensity	symmetry	frequency (cm^{-1})	intensity
A	3017.0	0.024	A_1	3035.6	0.043
	2975.9	0.166		2999.0	0.030
	2962.5	0.091		2958.3	0.115
	2940.7	0.229		2954.1	0.180
	2937.9	0.071		1496.7	0.043
	1493.0	0.037		1444.1	0.017
	1476.8	0.028		1360.6	0
	1386.8	0.006		1327.2	0.001
	1376.7	0.002		1165.3	0.027
	1297.8	0.022		987.4	0.007
	1204.7	0.027		870.0	0.028
	1142.6	0.012		751.9	0
	1073.6	0.002		671.4	0
	991.7	0.002		508.1	0
	960.2	0.002		296.6	0.001
	815.0	0.006	A_2	1126.4	0
	772.1	0.088		766.8	0
	693.5	0		673.6	0
	645.4	0.001		637.6	0
	630.5	0.003		141.4	0
	541.1	0.003	B_1	2980.5	0.133
	515.2	0.003		873.5	0.057
	328.0	0		768.7	1.000
	228.0	0.059		676.8	0.219
	74.6	0		555.9	0.016
B	3011.5	0.180		345.2	0.067
	2981.5	0.339		172.6	0.063
	2964.4	0.266	B_2	3030.4	0.125
	2937.4	0.175		2994.5	0.149
	2933.0	0.058		2953.2	0.064
	1479.5	0.030		1476.3	0.015
	1471.5	0.028		1345.7	0.026
	1388.6	0.009		1276.3	0.029
	1356.7	0.015		1214.0	0.028
	1246.0	0.009		1152.5	0.001
	1200.7	0.001		1001.5	0.016
	1163.1	0.003		886.5	0.021
	1039.8	0.024		579.1	0.001
	899.4	0.014		409.4	0.001
	841.5	0.020			
	772.0	1.000			
	716.7	0.052			
	605.2	0.079			
	550.1	0.017			
	457.0	0.019			
	399.5	0.002			
	312.8	0.083			
	161.8	0.014			

[a] II and III denote 2,3-dimethylenecyclohexa-1,3-diene and 2,3-dimethylenecyclopenta-1,3-diene, respectively. The intensities are normalized to the most intense peaks at 772.0 cm^{-1} (II) and 768.7 cm^{-1} (III).

cannot rule out the possibility that these lines might be due to overtones or that the UHF procedure, even with the "scaling" of the frequencies could have errors this large when applied to a diradical.

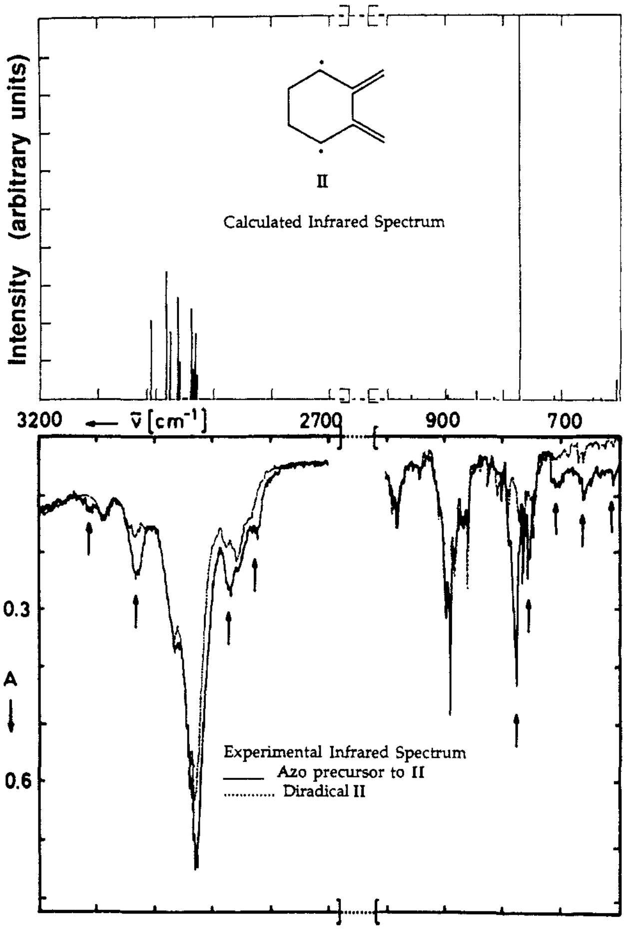

Figure 2. The calculated and experimental infrared spectra of 2,3-dimethylenecyclohexa-1,3-diene (II). The experimental spectrum is taken from ref 6a.

In conclusion, 3-21G UHF calculations predict a 25.0° deviation of the triplet diradical II from planarity. This value lies between those of tetramethyleneethane I and its five-membered ring analogue III, which are calculated to deviate by 44.9°[4] and 0° from planarity. Ab initio calculations of the normal mode vibrational frequencies were also performed, leading us to question the assignments of the structure between 2820 and 3110 cm^{-1} in the infrared spectrum.[6a]

Acknowledgment. This work was supported by grants from the National Science Foundation. The calculations were performed on the University of Pittsburgh Chemistry Department Harris H1000 minicomputer and on the Cray X-MP/48 at the Pittsburgh Supercomputing Center. The time on the Cray was provided through an award from the Center.

Supplementary Material Available: Complete tables of the calculated geometries of II and III are available upon request from the authors.