Lawrence Berkeley National Laboratory

Recent Work

Title

DICYANOCARBENE: TRIPLET AND SINGLET STRUCTURES AND ENERGETICS

Permalink

<https://escholarship.org/uc/item/4vk95039>

Author

Schaefer Iii., Henry F.

Publication Date

1976-06-01

DICYANOCARBENE: TRIPLET AND SINGLET
STRUCTURES AND ENERGETICS

Robert R. Lucchese and Henry F. Schaefer III

June 1976

RECEIVED
LAWRENCE
BERKELEY LABORATORY
JUL 26 1976
LIBRARY AND
DOCUMENTS SECTION

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LBL-5168
c. 1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Dicyanocarbene: Triplet and Singlet Structures and Energetics

Robert R. Lucchese and Henry F. Schaefer III

Department of Chemistry
University of California
Berkeley, California 94720

Abstract

Dicyanocarbene $C(CN)_2$ is thought to have a linear triplet state as its electronic ground state. Here ab initio electronic structure theory has been used to test this hypothesis. A double zeta basis set (with d functions on the central carbon in some cases) was employed in conjunction with one (for the 3B_1 state) and two (1A_1 state) configuration self-consistent-field wave functions. The predicted 3B_1 structure is $r_e(CC) = 1.41 \text{ \AA}$, $r_e(CN) = 1.15 \text{ \AA}$, and $\theta(CCC) = 133^\circ$ when the CCN atoms are constrained to be collinear. Similarly for the 1A_1 state, theory predicts $r_e(CC) = 1.42 \text{ \AA}$, $r_e(CN) = 1.16 \text{ \AA}$, and $\theta(CCC) = 115^\circ$. The barriers to linearity for the triplet and singlet states are 9 and 10 kcal/mole. Exploration of the two equivalent CCN angles suggests optimum values of ~ 177 and ~ 174 for 3B_1 and 1A_1 . Finally the triplet state is estimated to lie ~ 14 kcal below the singlet state.

Dicyanocarbene $\text{C}(\text{CN})_2$ is one of the relatively few carbenes still thought to have a linear triplet ground state. The basis for this expectation is both experimental and theoretical. On the experimental side, Wasserman, Barash, and Yager¹ have reported the electron paramagnetic resonance (EPR) spectra of $\text{C}(\text{CN})_2$. In fluorolobe suspension Wasserman and co-workers determined the zero field splitting (zfs) parameters $D = 1.002$ and $E < 0.002 \text{ cm}^{-1}$, which are compatible with a linear molecule. However, in a hexafluorobenzene matrix E was found to be nonzero ($E = 0.0033 \text{ cm}^{-1}$) indicative of a slightly bent species. They concluded that the deviation of triplet dicyanocarbene from linearity is not more than $10\text{--}15^\circ$ and that this slight nonlinearity may be due to the hexafluorobenzene matrix. $\text{C}(\text{CN})_2$ has also been the subject of a careful matrix infrared spectroscopic study by Smith and Leroi.² Their vibrational analysis is consistent with that normally expected for a linear molecule and they estimate the central carbon bending frequency to be very low, $\sim 32 \text{ cm}^{-1}$.

The earliest theoretical study of dicyanocarbene was that of Hoffmann, Zeiss, and Van Dine³ using the extended Hückel method. In the same paper many other carbenes were investigated and a number of their qualitative conclusions concerning the halocarbenes have been supported by more recent ab initio studies.⁴ Hoffmann and co-workers conclude that there is no doubt that the ground state of $\text{C}(\text{CN})_2$ will be a linear triplet. This is a particularly strong statement since all but $\text{C}(\text{CN})_2$ and $\text{HC}(\text{CN})$ among the 19 carbenes are predicted to be bent molecules. They also note that the $^1\text{A}_1$ bending potential curve is the flattest of the carbenes studied. Hoffmann's determination of linearity for triplet $\text{C}(\text{CN})_2$ was supported by the research of Olsen and Burnelle⁵ using both extended Hückel and INDO methods.

The reactions of dicyanocarbenes have been studied in some detail by organic chemists.^{6,7} For example, it is known that addition of $C(CN)_2$ to olefins is largely but not completely stereospecific. Typical is the addition reaction with cis-2-butene, which yields 92% cis and 8% of the trans-cyclopropane, with C-H insertion also occurring to a small extent.⁸ However, it seems quite clear that the interpretation of such experiments would be greatly aided by reliable triplet and singlet structural and energetic data. Our feeling is that at the present time ab initio theory is better able than experiment to provide this type of reliable information.

The theoretical methods used here are relatively standard⁹ and require no detailed exposition here. Triplet dicyanocarbene has electron configuration

$$1a_1^2 1b_2^2 2a_1^2 2b_2^2 3a_1^2 4a_1^2 3b_2^2 5a_1^2 4b_2^2 6a_1^2 5b_2^2 1b_1^2 7a_1^2 1a_2^2 6b_2^2 8a_1 2b_1 \quad (1)$$

and straightforward restricted self-consistent-field (SCF) theory¹⁰ was applied. For the lowest singlet state a two-configuration SCF treatment

$$\begin{aligned} & C_1 \dots\dots 4b_2^2 5b_2^2 1b_1^2 7a_1^2 1a_2^2 6b_2^2 8a_1^2 \\ + & C_2 \dots\dots 4b_2^2 5b_2^2 1b_1^2 7a_1^2 1a_2^2 6b_2^2 2b_1^2 \end{aligned} \quad (2)$$

was adopted. The standard Dunning-Huzinaga double zeta (two contracted gaussian functions per atomic orbital) basis set¹¹ was used, designated (9s 5p/4s 2p). After geometry optimization, a set of d functions on the central carbon atom was added. For the 3B_1 and 1A_1 states the optimum values of these gaussian orbital exponents α were determined to be 0.80 and 0.62.

Assuming C_{2v} geometries and collinear C-C≡N arrangements the results summarized in the Table were obtained. Perhaps the most important prediction made there is that the triplet state of $C(CN)_2$ is distinctly bent. The comparable geometry optimization for linear $C(CN)_2$ yields $R(C-C) = 1.358 \text{ \AA}$, $R(C\equiv N) = 1.160 \text{ \AA}$ and a total energy fully 8.6 kcal higher. Thus there would appear to be little ambiguity concerning the prediction of triplet linearity. For elementary CH_2 the analogous theoretical procedure¹² predicts a bond angle of 130.4° , about 4° less than the accepted value¹³ of 134° . Applying a similar correction to our dicyanocarbene results would make possible a 3B_1 bond angle of 136° .

One should strike a note of caution concerning the above prediction of a bent $C(CN)_2$ triplet state. In their infrared study, Smith and Leroy note² the similarity of dicyanocarbene to the C_3O_2 and C_3 molecules, which are known to have very low vibrational bending frequencies. And previous ab initio work¹⁴ on C_3 has shown the sensitivity of the bending potential to basis set size, especially as regards d functions on the carbon atoms. However, the trend of this previous theoretical research indicates that such polarization functions favor bent geometries since only 3 (the σ and π components) of the 5 d functions contribute to the $D_{\infty h}$ SCF wave function, while all five components contribute in the case of C_{2v} symmetry. This qualitative analysis is given some support by a single computation on the geometry-optimized linear triplet state including central carbon d functions. A total energy of -222.29258 hartrees was obtained, 10.7 kcal above the comparable result at the predicted bent equilibrium geometry.

A point of particular interest to carbene chemists is the singlet-triplet separation $\Delta E(^1A_1 - ^3B_1)$. As seen in the Table ΔE is predicted to be 17.9 and

7.1 kcal/mole without and with central carbon d functions. For elementary CH_2 , the experimental ΔE value (19.5 ± 0.7 kcal)¹⁵ lies roughly halfway between the two comparable theoretical values.⁴ Thus we semi-empirically estimate the singlet-triplet separation to be ~ 14 kcal. Finally we note that the predicted dipole moments for triplet and singlet dicyanocarbene are 1.81 and 0.81 debye.

This research was supported by the National Science Foundation under Grant GP-41509X. All computations were performed on the Harris Corporation Series 100 minicomputer, supported by NSF Grant GP-39317. We thank Mr. Sanford Bustamente and Mr. Lawrence Sterna for helpful discussions.

References

1. E. Wasserman, L. Barash, and W. A. Yager, J. Am. Chem. Soc. 87, 2075 (1965).
2. W. H. Smith and G. E. Leroi, J. Chem. Phys. 45, 1784 (1966); Spectrochimica Acta 25A, 1917 (1969).
3. R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, J. Am. Chem. Soc. 90, 1485 (1968).
4. C. W. Bauschlicher, H. F. Schaefer and P. S. Bagus, "Structure and Energetics of Simple Carbenes. CH_2 , CHF, CHCl , CHBr , CF_2 , CCl_2 ", to be published.
5. J. F. Olsen and L. Burnelle, Tetrahedron 25, 5451 (1969).
6. W. Kirmse, Carbene Chemistry, second edition (Academic Press, New York, 1971).
7. M. Jones and R. A. Moss, Carbenes, Volume I (Wiley, New York, 1973).
8. E. Ciganek, J. Am. Chem. Soc. 87, 652 (1965); 88, 1979 (1966); 89, 1454 (1967).
9. H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results (Addison-Wesley, Reading, Massachusetts, 1972).
10. W. J. Hunt, P. J. Hay, and W. A. Goddard, J. Chem. Phys. 57, 738 (1972).
11. S. Huzinaga, J. Chem. Phys. 42, 1293 (1965); T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).
12. S. V. O'Neil, H. F. Schaefer and C. F. Bender, J. Chem. Phys. 55, 162 (1971).
13. R. A. Bernheim, T. Adl, H. W. Bernard, A. Songco, P. S. Wang, R. Wang, L. S. Wood, and P. S. Skell, J. Chem. Phys. 64, 2747 (1976); H. F. Schaefer, Chemistry in Britain, 11, 227 (1975).
14. D. H. Liskow, C. F. Bender, and H. F. Schaefer, J. Chem. Phys. 56, 5075 (1972). See especially the discussion on the left column of page 5080.
15. P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbst, W. C. Lineberger, W. P. Reinhardt, J. Am. Chem. Soc. 98, 0000 (1976).

Table. Theoretical predictions for triplet and singlet dicyanocarbene. Note that θ is the CCC angle.

Electronic State	$R(C-C), \text{\AA}$	$R(C\equiv N), \text{\AA}$	$\theta(\text{degrees})$	$E(\text{hartrees})$	$\Delta E(^1A_1 - ^3B_1)$ kcal/mole
3B_1					
Double Zeta Basis	1.407	1.154	132.5	-222.29571	--
With central C d functions	"	"	"	-222.30969	--
1A_1					
Double Zeta Basis	1.421	1.160	114.9	-222.26711	17.9
With central C d functions	"	"	"	-222.29842	7.1

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720