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Dicyanocarbene: Triplet and Singlet Structures and Energetics

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Abstract

Dicyanocarbene $C(CN)_2$ is thought to have a linear triplet state as its electronic ground state. Here <u>ab initio</u> 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 $r_e(CC) = 1.41$ Å, r(CN) = 1.15 Å, and $\theta(CCC) = 133°$ when the CCN atoms are constrained to be collinear. Similarly for the $^1A_1$ state, theory predicts $r_e(CC) = 1.42$ Å, $r_e(CN) = 1.16$ Å, and $\theta(CCC) = 115°$. 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 $C(CN)_2$ 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 Yager[1] have reported the electron paramagnetic resonance (EPR) spectra of $C(CN)_2$. In fluorolobe suspension Wasserman and co-workers determined the zero field spitting (zfs) parameters D = 1.002 and E < 0.002 cm^{-1}, which are compatible with a linear molecule. However, in a hexafluorobenzene matrix E was found to be nonzero (E = 0.0033 cm^{-1}) indicative of a slightly bent species. They concluded that the deviation of triplet dicyanocarbene from linearity is not more than 10-15° and that this slight nonlinearity may be due to the hexafluorobenzene matrix. $C(CN)_2$ 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, ∿ 32 cm^{-1}.

The earliest theoretical study of dicyanocarbene was that of Hoffmann, Zeiss, and Van Dine[3] 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 $C(CN)_2$ will be a linear triplet. This is a particularly strong statement since all but $C(CN)_2$ and HC(CN) among the 19 carbenes are predicted to be bent molecules. They also note that the $^1A_1$ bending potential curve is the flattest of the carbenes studied. Hoffmann's determination of linearity for triplet $C(CN)_2$ was supported by the research of Olsen and Burnelle[5] 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 standard[9] and require no detailed exposition here. Triplet dicyanocarbene has electron configuration

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

and straightforward restricted self-consistent-field (SCF) theory[10] was applied. For the lowest singlet state a two-configuration SCF treatment

$$C_1 \ldots\ldots 4b_2^2\ 5b_2^2\ 1b_1^2\ 7a_1^2\ 1a_2^2\ 6b_2^2\ 8a_1^2$$

$$+ \quad C_2 \ldots\ldots 4b_2^2\ 5b_2^2\ 1b_1^2\ 7a_1^2\ 1a_2^2\ 6b_2^2\ 2b_1^2 \qquad (2)$$

was adopted. The standard Dunning-Huzinaga double zeta (two contracted gaussian functions per atomic orbital) basis set[11] 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 Å, R(C≡N) = 1.160 Å 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 procedure[12] predicts a bond angle of 130.4°, about 4° less than the accepted value[13] 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 Leroi note[2] 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 <u>ab initio</u> work[14] 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 <u>bent</u> 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.

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

Electronic State	R(C-C), Å	R(C≡N), Å	θ(degrees)	E(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

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