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Robert R. Lucchese and Henry F. Schaefer III

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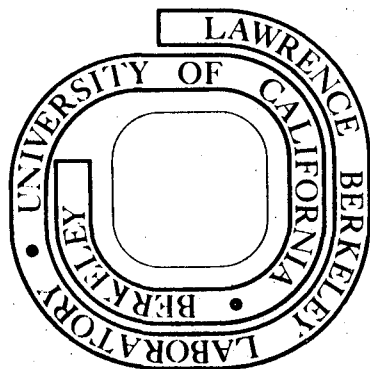
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## Dicyanocarbene: Triplet and Singlet Structures and Energetics

Robert R. Lucchese and Henry F. Schaefer III

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Berkeley, California 94720Abstract

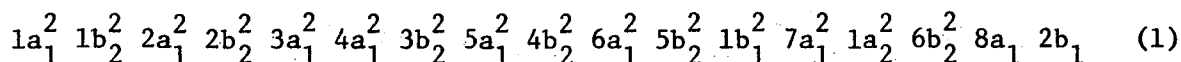
Dicyanocarbene  $C(CN)_2$  is thought to have a linear triplet state as its electronic ground state. Here ab initio electronic structure theory has been used to test this hypothesis. A double zeta basis set (with d functions on the central carbon in some cases) was employed in conjunction with one (for 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  $\sim 177$  and  $\sim 174$  for  $^3B_1$  and  $^1A_1$ . Finally the triplet state is estimated to lie  $\sim 14$  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<sup>1</sup> have reported the electron paramagnetic resonance (EPR) spectra of  $C(CN)_2$ . 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  $10-15^\circ$  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.<sup>2</sup> 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,  $\sim 32 \text{ cm}^{-1}$ .

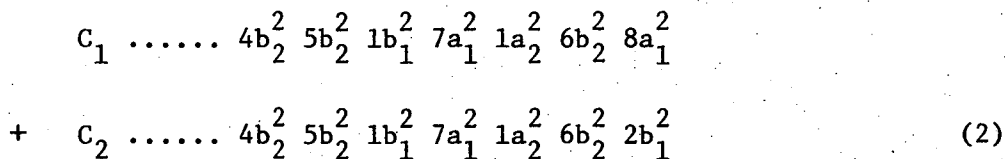
The earliest theoretical study of dicyanocarbene was that of Hoffmann, Zeiss, and Van Dine<sup>3</sup> using the extended Hückel method. In the same paper many other carbenes were investigated and a number of their qualitative conclusions concerning the halocarbenes have been supported by more recent ab initio studies.<sup>4</sup> 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<sup>5</sup> using both extended Hückel and INDO methods.

The reactions of dicyanocarbenes have been studied in some detail by organic chemists.<sup>6,7</sup> 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.<sup>8</sup> 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<sup>9</sup> and require no detailed exposition here. Triplet dicyanocarbene has electron configuration



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



was adopted. The standard Dunning-Huzinaga double zeta (two contracted gaussian functions per atomic orbital) basis set<sup>11</sup> 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  $\alpha$  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 procedure<sup>12</sup> predicts a bond angle of  $130.4^\circ$ , about  $4^\circ$  less than the accepted value<sup>13</sup> of  $134^\circ$ . Applying a similar correction to our dicyanocarbene results would make possible a  $^3B_1$  bond angle of  $136^\circ$ .

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<sup>2</sup> 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 work<sup>14</sup> 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  $\sigma$  and  $\pi$  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  $\Delta E$  is predicted to be 17.9 and

7.1 kcal/mole without and with central carbon d functions. For elementary  $\text{CH}_2$ , the experimental  $\Delta E$  value ( $19.5 \pm 0.7$  kcal)<sup>15</sup> lies roughly halfway between the two comparable theoretical values.<sup>4</sup> Thus we semi-empirically estimate the singlet-triplet separation to be  $\sim 14$  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  $\theta$  is the CCC angle.

Electronic State	R(C-C), Å	R(C≡N), Å	$\theta$ (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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