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Structure of the Tricyano Ion

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In a recent study, Beck *et al.* report on the formation and stability of the tricyano ion, $(CN)_3^-$ [1]. The ion was detected spectrophotometrically by extraction of a cyclohexane solution of cyanogen with an aqueous sodium cyanide solution. Beck *et al.* comment that although the cyanide ion is a pseudohalide ion, the tricyano ion cannot be regarded as an analogue of the linear trihalogenide ions. This is readily recognized since a linear tricyano ion exhibits a positive formal charge on the centrally located nitrogen atom indicating a relatively unstable structure.

$$:\overset{-}{\ddot{N}}=C=C=\overset{+}{N}=C=\overset{-}{\ddot{N}}:$$

We decided to investigate the relative stability of several possible structures of the tricyano ion using the MNDO molecular orbital method of Dewar and Thiel [2]. In addition we carried out calculations on the known isoelectronic carbonyl cyanide molecule, $(CN)_2CO$, in order to compare the calculated structure with the structure determined by microwave spectroscopy [3]. The calculations were carried out on the Prime 400 computer at Calvin College.

Results and Discussion

Calculations were carried out on carbonyl cyanide in C_{2v} symmetry. The computed and experimental structures are compared in Table I. The MNDO structure is practically identical to the experimental structure.

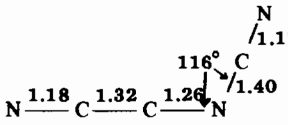
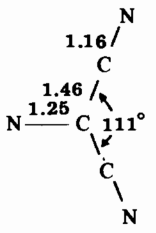
TABLE I. Computed and Experimental for Carbonyl Cyanide in C_{2v} Symmetry.

Structural Parameter	Computed	Experimental[a]
C–O	1.22 Å	1.22 Å
C–C	1.45 Å	1.45 Å
C–N	1.160 Å	1.165 Å
∠CCC	115.13°	115.32°
∠CCN	180.00°	180°

[a] Ref. 3. The CO length, CN length and CCn angle are assumed values.

Calculations were next carried out on the reactant molecules, CN^- and C_2N_2. The total energy of CN^- was found to be –333.01 eV at an optimized CN

TABLE II. Optimized Structural Parameters and Total Energy for Four Structures of the Tricyano Ion.

Structure	Spin Multiplicity	Total Energy (eV)	Structural Parameters (Å)
Linear $C_{\infty v}$	Triplet	–1001.41	$\mathrm{N}\overset{1.18}{\text{——}}\mathrm{C}\overset{1.31}{\text{——}}\mathrm{C}\overset{1.24}{\text{——}}\mathrm{N}\overset{1.27}{\text{——}}\mathrm{C}\overset{1.18}{\text{——}}\mathrm{N}$
Bent C_s	Singlet	–1002.65	
Triangular D_{3h}	Triplet	–999.80	r(CC) = 1.52 r(CN) = 1.20
C_{2v}	Singlet	–1003.25	

bond length of 1.178 Å. For linear C_2N_2, the calculated structure was r(CN) = 1.161 (1.154) Å, r(CC) = 1.378 (1.389) Å. The numbers in parentheses are the experimental result [4]. The total energy of C_2N_2 was found to be –667.93 eV.

There are many different topologies and structures possible for the tricyano ion. We optimized the geometry for four different structures: linear ($C_{\infty v}$), bent (C_s), triangular CN groups (D_{3h}); and the C_{2v} structure corresponding to the structure of carbonyl cyanide. The optimized structural parameters and total energy values are given in Table II for these structures. The results indicate that the C_{2v} structure is the most stable; the calculated structure is very similar to that of carbonyl cyanide. The bent C_s structure is second in stability, and the $C_{\infty v}$ and D_{3h} structures are least stable. The stability of the C_{2v} structure is not surprising in view of the almost universal preference for the most electropositive atoms in a covalent molecule to occupy the most central positions [5]. Correspondingly, the most stable structure of the isoelectronic butatrienedione molecule, C_4O_2, would undoubtedly be $D_{\infty h}$ with terminal oxygen atoms and a spin multiplicity of three [6]. It should be possible to test the correctness of the calculated structure of $(CN)_3^-$ by carrying out a matrix isolation reaction of cyanide ion and cyanogen using the method of Ault and Andrews [7].

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