Three Dimers of Hydrogen Cyanide: Iminoacetonitrile, Aminocyanocarbene, and Azacyclopropenylidenimine; Geometry-optimized *Ab Initio* Energies

By John B. Moffat

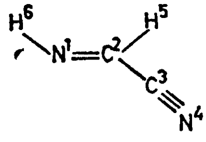
(*Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada* N2L 3G1)

Summary Geometry optimized *ab initio* molecular orbital calculations on three dimers of HCN, namely iminoacetonitrile, azacyclopropenylidenimine, and aminocyanocarbene, predict iminoacetonitrile and aminocyanocarbene to be the most stable and least stable respectively of the three dimers.

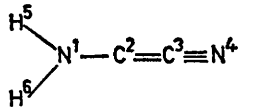
We have recently reviewed[1] the problem of the structure of the hydrogen cyanide dimer, and presented the results of some calculations involving an energy partitioning, which suggested one possible configuration to be cyclic. Subsequent to the submission of the manuscript, an interesting communication by Yang, Minard, and Matthews[2] appeared;

Table 1. Energy optimized nuclear configurations.

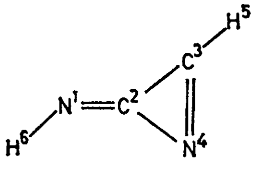
Bond lengths/Å	Iminoacetonitrile *E*	Iminoacetonitrile *Z*	Aminocyanocarbene	Azacyclo-propenylidenimine
N(1)–C(2)	1·275	1·279	1·288	1·270
C(2)–C(3)	1·470	1·475	1·318	1·413
C(2)–N(4)	—	—	—	1·452
C(3)–H(5)	—	—	—	1·083
N(1)–H(6)	1·045	1·049	1·027	1·046
C(3)–N(4)	1·157	1·157	1·193	1·312
N(1)–H(5)	—	—	1·027	—
C(2)–H(5)	1·090	1·087	—	—
Bond angles				
N(1)–C(2)–C(3)	123·9	152·2	180·0	156·1
N(1)–C(2)–N(4)	123·9	125·2	180·0	149·4
C(2)–C(3)–H(5)	—	—	—	157·1
H(6)–N(1)–C(2)	108·9	109·7	123·8	107·9
H(5)–N(1)–H(6)	—	—	112·4	—
N(1)–C(2)–H(5)	120·4	120·3	—	—



(E)-Iminoacetonitrile (I)



Aminocyanocarbene (II)



Azacyclopropenylidenimine (III)

Table 2

Total electronic energies[a] with STO-3G, STO-6G, and 6-31G basis sets and STO-3G energy-optimized nuclear configurations of Table 1.

Basis Set	Iminoacetonitrile *E*	Iminoacetonitrile *Z*	Aminocyanocarbene	Azacyclo-propenylidenimine
STO-3G	−183·371928	−183·372595	−183·273024	−183·287187
STO-6G	−185·167220	−185·167996	−185·070490	−185·084230
6-31G	−185·661382	−185·660412	−185·448129	−185·557565

[a] All energies are in hartree; 1 hartree ≡ 627·7 kcal mol^{-1}.

their semi-empirical INDO[3] calculations showed the most stable configuration to be cyclic, (III). It is well known that such methods tend to over-estimate the stability of small rings, as these authors themselves point out; accordingly, we have now performed *ab initio* S.C.F. molecular orbital calculations using the Gaussian 70 programme of Ditchfield, Hehre, and Pople[4] with standard molecular exponents.[5] In the present work three molecules were considered, iminoacetonitrile (I), aminocyanocarbene (II), and azacyclopropenylidenimine (III). Bond lengths and bond angles were optimized cyclically and independently to ±0·001 Å and ±0·1°, respectively. In all cases the core structures consisting of two carbon and two nitrogen atoms were assumed to be planar. The optimizations of geometry were performed with a minimal STO-3G basis set on an IBM 360/75 computer. However, single calculations with an STO-6G and an extended 6-31G basis set were also performed with the optimized nuclear configurations.

Table 1 shows the energy-optimized geometries for the three molecules including those for the *E* and *Z* forms of iminoacetonitrile. It may be noted that the C(2)–C(3) bond length in structure (II) is smaller than that in ethylene, providing some justification for its depiction as a double bond. Table II lists the singlet energies for the three molecules in their nuclear configurations energy-optimized with the minimal STO-3G basis, as obtained with the STO-3G, STO-6G, and 6-31G basis sets. Although it might be anticipated that the ground state is a singlet in the case of structures (I) and (III), the INDO calculations of Jameson and Yang[6] predict the triplet for (II) to be more stable than the singlet by 9 kcal mol^{-1}. With all basis sets iminoacetonitrile is predicted to be the most stable molecule and aminocyanocarbene the least stable. Of course the order of stability should be the same for both the STO-3G and the STO-6G sets but in the present work iminoacetonitrile is predicted to be more stable than azacyclopropenylidenimine by approximately 60 kcal mol^{-1} while in the work of ref. 2, the latter molecule was calculated to be the more stable by approximately 50 kcal mol^{-1}. It should be emphasized, however, that the energy-optimized nuclear configuration was obtained with the STO-3G basis and a somewhat different optimized nuclear configuration would undoubtedly be obtained with the extended set.[7]

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