Azacyclopropenylidenimine: a Low Energy Dimer of Hydrogen Cyanide

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Summary INDO calculations for the ground state energies of various proposed structures for hydrogen cyanide dimer suggest that azacyclopropenylidenimine is more stable than either iminoacetonitrile or aminocyanocarbene.

The intriguing question of the structure of hydrogen cyanide dimer is of particular interest in chemical evolution studies because of the role the dimer may play in base-catalysed polymerization reactions leading to the synthesis of heteropolypeptides from hydrogen cyanide and water.[1,2] While hydrogen-bonded dimers and polymers of HCN have been well characterized,[3] no dimer formed by covalent bonding has so far been isolated directly from hydrogen cyanide.† Several semi-empirical quantum mechanical studies have therefore been made to determine the relative energies and electronic structures of various configurations and conformations for iminoacetonitrile, aminocyanocarbene,[1,2] and other possible forms of the dimer. EHT calculations by Loew and Chang[6,7] predict that aminocyanocarbene is a singlet (II) higher in energy than iminoacetonitrile (I) by 76 kcal mol^{-1}. Using the more rigorous INDO approach of Pople and Beveridge,[8] Jameson and Yang[9] obtained values relative to (I) of 65 kcal mol^{-1} for (II) and 63 kcal mol^{-1} for the vinylidenedi-imine structure (IV). They further showed that triplet aminocyanocarbene (III)—lower in energy than (II) by 9 kcal mol^{-1}—is photochemically accessible from (I). We report here the results from similar INDO calculations for yet another possible form of HCN dimer, the ($4n + 2$) Hückel heteroaromatic system azacyclopropenylidenimine (V).

Assuming (V) to be planar, and starting with estimated values of the bond lengths $r_{\mathrm{C=N}}$(*exo*), $r_{\mathrm{C-N}}$, $r_{\mathrm{C-C}}$, and $r_{\mathrm{C=N}}$(*endo*), the method of steepest descent (0·01 Å grid) was used to locate the neighbourhood of each minimum. Actual minima found by differentiation of Newton's interpolative formula for energy *versus* each of the four parameters were 1·2895, 1·4104, 1·4047, and 1·3411 Å respectively, leading to a total electronic energy for (V) of $-37{\cdot}181476$ au (1 au molecule^{-1} = 627 kcal mol^{-1}. The corresponding triplet (VI) was found to be much higher in energy, as expected.

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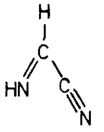
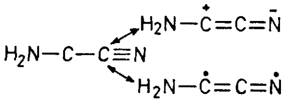
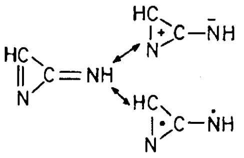
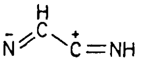
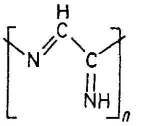
† However, a yellow species believed to be aminocyanocarbene—a postulated structure for the dimer—has been trapped in a frozen matrix at $-196°$ following photochemical decomposition either of diaminomaleonitrile[4] (the stable tetramer of hydrogen cyanide), or of the *p*-toluenesulphonylhydrazone salts of 1-cyanoformamide.[5]

Structure		Energy (au molecule^{-1})	Relative energy (kcal mol^{-1})
	(I)	-37·107329	0
	(II)	-37·003447	+65
	(III)	-37·017427	+56
HN=C=C=NH	(IV)	-37·006146	+63
	(V)	-37·181476	-46
	(VI)	-37·055676	+32
	(VII)		
	(VIII)		

Azacyclopropenylidenimine (V) is thus more stable than (I) by 46 kcal mol^{-1} and has the lowest energy of any structure so far considered for HCN dimer.‡

Several pathways are conceivable for the base-catalysed formation of (V) from HCN. The simplest is nucleophilic addition of cyanide ion to HCN followed by intramolecular cyclization and protonation. Another possible route would be *via* hydrogen isocyanide, HNC.§ Although negligible amounts of HNC are present in HCN at normal temperatures,[10] continuous generation of the reactive isomer seems possible in the presence of base following protonation of ambident cyanide ions. Carbenoid addition of HNC to HCN would then give (V) *via* the dipolar intermediate (VII).¶ Anionic polymerization of (V) into (VIII) would be expected, followed by further reactions of (VIII) with hydrogen cyanide to yield polyaminomalononitrile and then heteropolyamidines that would be converted into heteropolypeptides by water.[2,11] Clearly, investigation of the chemistry of (V) and more stable azacyclopropenylidenimines that might be formed by interactions of isonitriles with nitriles should give additional insight into ionic, radical, or photochemical mechanisms for hydrogen cyanide polymerization.

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‡ INDO calculations tend to underestimate the effect of ring strain on small-ring compounds, so that (V) probably has a slightly higher energy than these results indicate.

§ Interestingly, HNC has been tentatively identified in interstellar space,[12] suggesting that in isolation this elusive species may have a considerable lifetime. Since HCN is one of the commoner extraterrestrial molecules it would not be surprising if interstellar azacyclopropenylidenimine were also to be detected.

¶ The predicted carbenoid addition of HNC to HCN to give (VII) and (V) is analogous to the formation of cyclopropenylidenimine[13] intermediates that has been proposed for reactions involving the addition of isocyanides to substituted acetylenes.

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