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THE STRUCTURE OF HCN TETRAMER

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Recently, Wadsten and Andersson[1] have proposed that the polymerisation product of hydrogen cyanide, generally regarded as the tetramer, is in fact the dimer, "iminoacetonitrile". Their evidence was obtained from a preliminary X-ray diffraction study of single crystals and from infra-red absorption measurements.

Webb, Frank and Schneider[2] had previously summarized chemical evidence for the molecular structure and presented the results of their own infra-red and ultra-violet absorption measurements and dipole moment measurements. Their deductions were that the compound is diaminomaleonitrile in the solid state and in dilute solution. Sass and Donohue[3]

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[1] T. Wadsten and S. Andersson, Acta Chem. Scand. 13, 1069 (1959).

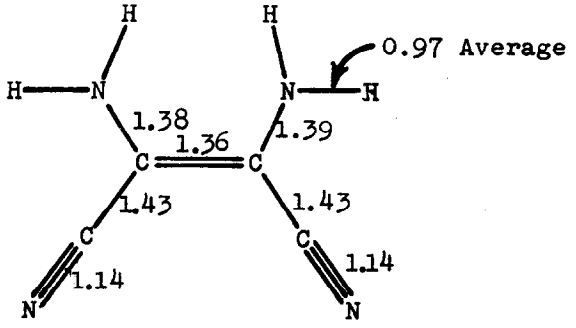
[2] R. L. Webb, S. Frank and W. C. Schneider, J. Amer. Chem. Soc. 77, 3491 (1955).

[3] R. L. Sass and J. Donohue, Acta Cryst. 10, 375 (1957).

first reported the unit cell constants and space group of the crystalline solid but did not determine the crystal structure.

We wish to report that, as a result of a detailed structure analysis of single crystals by X-ray diffraction, we have conclusive proof that the compound in question is indeed the tetramer of HCN and is diaminomaleonitrile in the solid state. The crystals used in our study were kindly supplied by Mr. J. Vaughan, Chemistry Department, University of Canterbury, New Zealand. They have the same unit cell dimensions as those examined by Sass and Donohue[3] and by Wadsten and Andersson.[1] The measured density was 1.37 g/cc.

Following a three dimensional least squares refinement of atomic parameters, in which about 900 independent X-ray reflections were considered, the positions of all the atoms are known with standard errors or 0.003 Å for carbons and nitrogens and 0.05 Å for hydrogens. The value of the reliability factor R is 0.08 for all observed reflections. The carbon nitrogen skeleton of the molecule is planar and the bond lengths are as shown in the figure below.



The crystal structure was solved by the application of Patterson superposition techniques involving the use of the Buerger minimum function[4] in three dimensions. Location of single interatomic vectors was made possible by a novel form of modification of the Patterson function as described by Jacobson, Wunderlich and Lipscomb.[5] Details of the structure analysis will be reported elsewhere.

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[4] M. J. Buerger, Vector Space. J. Wiley and Sons, New York (1959).

[5] R. A. Jacobson, J. A. Wunderlich and W. N. Lipscomb, Nature, London 184, 1719 (1959).