The Molecular Conformation of 2-Cyano-1,3-dimethylguanidine

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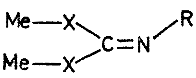
Summary The crystal structure of 2-cyano-1,3-dimethylguanidine reveals a staggered conformation with four nearly equivalent carbon–nitrogen bond lengths and a planar arrangement of the central four atoms.

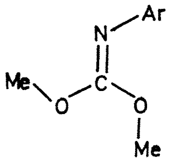
INTEREST in the mechanism of *syn–anti*-isomerization at the C=N bond has led to the synthesis and n.m.r. study of a number of compounds of the general formula (**1**).[1-3] In some of the guanidines [(**1**); X = NH or NMe, R = CN or aryl] hindered rotation about the C–N bond from the azomethine carbon has also been observed by n.m.r. techniques.[1,4] Liebfritz and Kessler[3] recently concluded from n.m.r. data that the preferred conformation of some iminocarbonates is as shown in (**2**). We report the results of the determination of the crystal structure of 2-cyano-1,3-dimethylguanidine (**3**). These results show the conformation of this guanidine to be analogous to that suggested by Liebfritz and Kessler for their iminocarbonates.

A single crystal of (**3**) was grown from an aqueous solution and found by Weissenberg photographs to crystallize in the $P2_1/n$ (C_{2h}^5, No. 14) space group, with the cell constants $a = 12{\cdot}323(1)$, $b = 8{\cdot}312(1)$, $c = 5{\cdot}834(1)$ Å and $\beta = 91{\cdot}42(1)°$. An asymmetric unit of data (1042 reflections) out to 50° in 2 θ with Mo-K_α radiation was collected using an Automated Four-Circle Picker Diffractometer. The co-ordinates of the carbon and nitrogen atoms were initially determined from an E map calculated from 115 reflections whose phases were determined by a systematic solution of

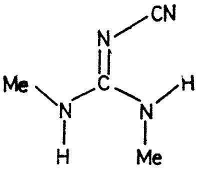


(1)

X=O, S NH, NMe
R=aryl, CN, Cl



(2)



(3)

426 highest probability Σ_2 relationships. Subsequently the eight hydrogen atoms were located by difference synthesis and the structure refined by full-matrix least-squares with a final weighted agreement index R, $(\Sigma\omega||F_0|-|F_c||)/(\Sigma\omega|F_0|)$, of 0·047.

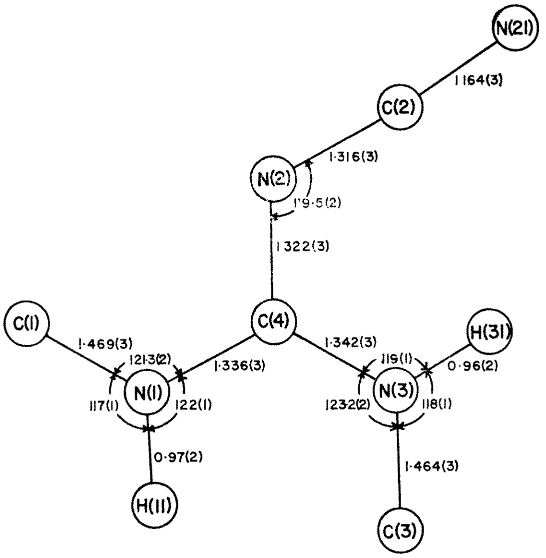


FIGURE. 2-*Cyano*-1,3-*dimethylguanidine*.

Some molecular parameters are given in the Figure. Of particular interest is the equivalence of the C(4)–N(1), C(4)–N(2), C(4)–N(3), and C(2)–N(2) bond lengths indicating a delocalized bonding system. This delocalized system is also shown by the apparent sp^2 character of N(1) and N(3) as borne out by the approximately 120° bond angles and the hydrogen atom positions. Also the molecule is nearly planar. A least-squares plane through C(4), N(1), N(2), and N(3) fits with an estimated standard deviation of 0·0003 Å, and from this plane C(1), C(3), C(2), and N(21) are removed by 0·01, 0·11, 0·16, and 0·33 Å, respectively. This planarity and delocalization must be taken into account in any discussion of the mechanism of the *syn–anti*-isomerization of *C*-iminonitriles.[1]

To obtain further information on a similar *C*-iminonitrile, we are presently determining the crystal structure of dimethyl cyanodithiocarbonate [(**1**); X = S, R = CN].

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[3] D. Leibfritz and H. Kessler, *Chem. Comm.*, 1970, 655 and refs. therein.

[4] H. Kessler, *Tetrahedron Letters*, 1968, 2041.