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THE SYNTHESIS AND THE MOLECULAR STRUCTURE OF DIAMINOFUMARONITRILE

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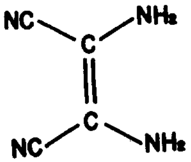
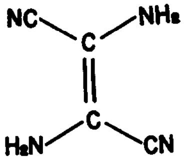
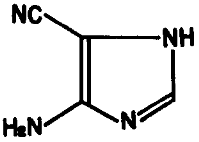
Diaminomaleonitrile (I), (1) a tetramer of hydrogen cyanide, is known to be a useful intermediate for preparing some imidazole and purine derivatives. Ferris and Orgel have reported (2) that irradiation of I at 350 mμ in an aqueous solution gives 4-amino-5-cyanoimidazole (III), and also suggested (3) intermediary formation of diaminofumaronitrile (II) through cis-trans isomerization prior to the phtochemical rearrangement. However the structural elucidation on this intermediate may not be conclusive yet.



(I)



(II)



(III)

We have reexamined the experimental condition of this photochemical rearrangement in detail, and succeeded in isolating the compound which is believed to be an intermediate of this reaction. From the structural studies by spectroscopic and X-ray diffraction methods, the compound has been proved to be II.

When a solution of I in acetonitrile was exposed to uv light filtered through pyrex glass, the absorption maximum rapidly shifted from 295.5 mμ to 304-305 mμ. Then the band due to III slowly appeared at a shorter wavelength and gradually increased in its intensity. Simultaneously, the intensity of the band at 304-305 mμ decreased. The rapid shift mentioned above apparently demonstrates the formation of II, through which the photochemical rearrangement into III may take place. From the monochromatic study, an optimum wavelength for the rearrangement from I to II, in acetonitrile, has been found to be between 270 and 320 mμ. Irradiation with the light above 320 mμ rather promoted a reverse reaction to I, in contrast with the result presented by Ferris and Orgel (2).

A solution (0.02 M) of I in acetonitrile was irradiated at 25°C for 7.5 hr in a pyrex glass vessel with uv ray ranging from 295 to 335 mμ by means of a 100 W high pressure mercury lamp equipped with a filter containing aqueous potassium chromate solution (2 mM). On evaporating the solvent under a reduced pressure the residual brown solid was sublimed under 1 mmHg at 120-150°C and the sublimate obtained was recrystallized twice from n-butanol to give 1.35 g of II: mp 169°; uv λmax (H_2O) 310 mμ (ε 8,200); ir (nujol mull), νNH (3394, 3350, 3254 and 3192 cm^{-1}), νC≡N (2243 and 2198 cm^{-1}), νC=C (1618 cm^{-1}); molecular weight, 108 (mass spectrum). Anal., Found: C, 44.47; H, 3.77; N, 51.66; Calcd for $C_4H_4N_4$: C, 44.44; H, 3.73; N, 51.83%.

The compound (II) was markedly labile in acidic or alkaline solutions, and rapidly reversed to I. Even in a neutral solution, II was gradually converted to I in the presence of activated charcoal or filter paper.

The nmr spectrum of II in acetone-d_6 shows only a single broad peak due to NH protons, and no other peaks due to CH protons. The uv absorption maximum at 310 mμ suggests the existence of some conjugate system in the molecule.

The majority of the analytical and spectroscopic information may be reasonably interpreted as the structure of diaminofumaronitrile. However, the numbers of observed ir absorption bands are contradictory to its ideal conformation of C_{2h} symmetry, according to which the expected numbers of NH stretching, C≡N stretching and C=C stretching bands should be two, one and zero, respectively.

To overcome this inconsistency, it was required to establish the structure of the compound II with certainty.

Such being the case an X-ray diffraction study has been undertaken with the crystal obtained from an acetonitrile solution. The space group of the crystal is $P2_1/c$ (monoclinic), and the unit-cell dimensions are:

a = 6.81, b = 5.69, c = 12.84 Å, β = 90.0°.

The density measured by flotation is 1.445 g/cm^3 at 22°C, which is in good agreement with the calculated value of 1.454 g/cm^3 based on the assumption of four $(HCN)_4$ molecules per unit cell.

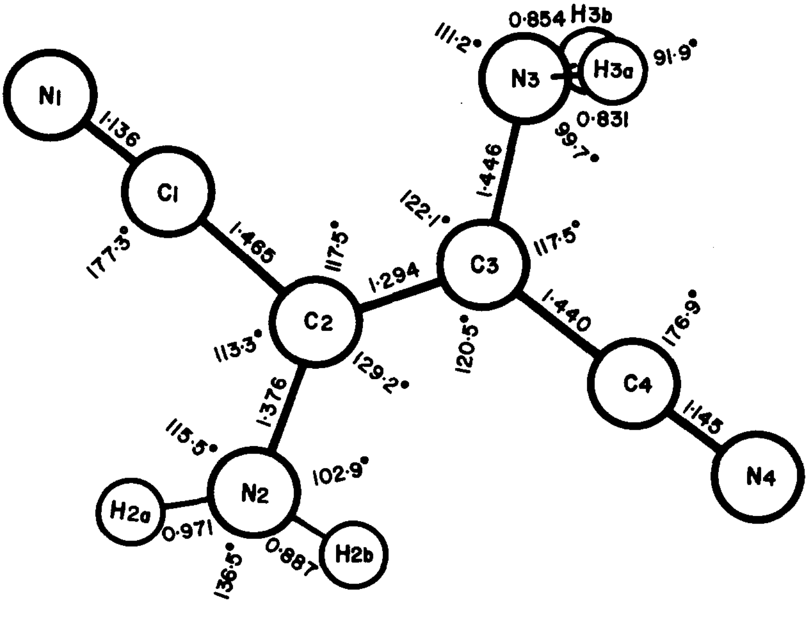


Fig. 1

The bond distances (Å) and angles. The actual conformation of the molecule in the crystal viewed down the c-axis.

The conformation of the molecule, the bond lengths and angles are shown in Fig. 1. The final R index is 7.8%, excluding the most intense reflection. The estimated standard deviations of bond lengths and bond angles involving only heavy atoms are about 0.006 Å and 0.4°, respectively.

Thus, the compound isolated from the photochemical reaction has been positively identified as diaminofumaronitrile (II). The apparent inconsistency in its ir spectrum can now be satisfactorily elucidated by the large deviation of its conformation from the ideal C_{2h} symmetry, as is seen in Fig. 1. This result strongly supports the path of the photochemical rearrangement from I to III via II.

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