The Crystal Structure of Hydrazine Nitroform $[N_2H_5^+C(NO_2)_3^-]$

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IN such quantitative comparisons of the nitroform $[C(NO_2)_3^-]$ and cyanoform $[C(CN)_3^-]$ anions and derivatives as the Hammett *para*-substituent constants,[1] the acid strengths,[2] the ionization behaviour,[3] the equilibrium constants,[4] and the strengths of their electron-withdrawing power in, but lack of resonance with, aromatic systems,[5] the considerable stability of the anions due to charge delocalization (*i.e.*, resonance) has usually been stressed. The greater charge-delocalization indicated in the cyanoform anion over the nitroform anion has suggested that while the cyanoform anion is probably planar, the nitroform anion may not be so. To determine the structure of the nitroform anion, and to provide bond distances and angles suitable for an analysis of the bonding in the anion, the crystal structure of hydrazine nitroform was determined in a three-dimensional single-crystal *X*-ray diffraction study with data from 1914 reflections collected by the equi-inclination method at −160°.

Hydrazine nitroform crystallizes from ethanol solution with eight molecules in a unit cell with $a = 7{\cdot}91 \pm 0{\cdot}02$, $b = 11{\cdot}77 \pm 0{\cdot}02$, $c = 13{\cdot}98 \pm 0{\cdot}02$ Å, $\beta = 104° \; 55' \pm 15'$, all at −160°, and space-group $P2_1/n$. The complete structure was solved using E maps[6] and F_0 Fourier maps.

The two independent anions (A and B) in the crystal show significant differences and the distances obtained from isotropic full-matrix least-squares refinement ($R = 0{\cdot}10$) are shown in the Figure. The anions are really propeller-shaped, with the central carbon atom and the three nitrogen atoms accurately coplanar. The dihedral angle between the plane of the N(A,1) nitro-group and the C(A,2)N(A,1)N(A;2)N(A,3) plane is 41°. For the N(A,2) and N(A,3) nitro-groups the dihedral angles are 7° and 8°. In the (B) anion the corresponding angles are 74°, 5°, and 4° respectively. The difference between the two anions is in the O(1)O(2) oxygen atoms which are displaced more from the C(B,1)N(B,1)N(B,2)N(B,3) plane in anion (B). The difference between the two symmetrically independent anions arises in the packing and hydrogen-bonding forces in the crystal structure, and not from any effect within the nitroform anion itself.

The C(A,1)–N(A,2) and C(A,1)–N(A,3) averaged distances are $1{\cdot}40 \pm 0{\cdot}02$ Å $(=3\sigma)$ and the C(A,1)–N(A,1) distance is $1{\cdot}42 \pm 0{\cdot}02$ Å. In anion (B) the corresponding distances are $1{\cdot}37 \pm 0{\cdot}02$ and $1{\cdot}46 \pm 0{\cdot}02$ Å. The parameters of the nitro-groups are comparable (N–O [average] $= 1{\cdot}23 \pm 0{\cdot}02$ Å, O–N–O $\sim 120°$) with those found in the related compound $KC(NO_2)_2CN$.[7] The N–N distances in the two hydrazine ions are $1{\cdot}44 \pm 0{\cdot}02$ and $1{\cdot}42 \pm 0{\cdot}02$ Å. Feasible indications of the hydrogen positions have been found.

The nitroform anion is thus nonplanar in the hydrazine nitroform crystal and the precise geometry is apparently dependent on the environment. The details of the structural determination

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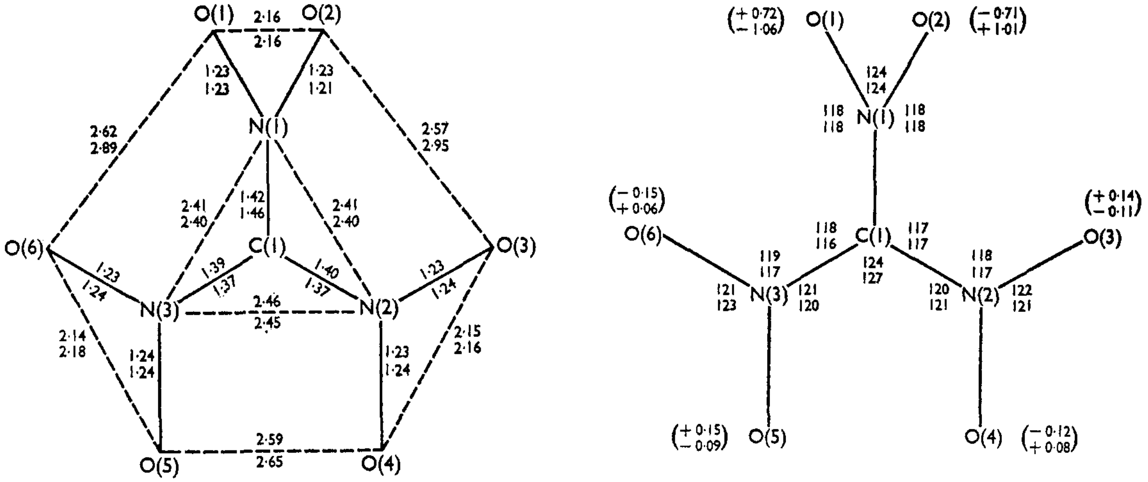

(a) (b)

FIGURE. *The structures of the nitroform anions in hydrazene nitroform. The upper numerals refer to anion* (A) *and the lower ones anion* (B). (a) *Distances in Å.* (b) *Angles* (*degrees*) *and displacements* (*Å*) *from the* C(1)–N(1)–N(2)–N(3) *plane.*

and the results of a study of the bonding will be reported later.

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