The Structure of the Hydrogen Dinitrate Ion in Tetraphenylarsonium Hydrogen Dinitrate

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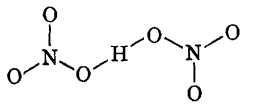
A STRUCTURE of the hydrogen dinitrate anion has recently been reported[1] where the four oxygen atoms of the two nitrate groups surround the hydrogen atom in a distorted tetrahedral arrangement. We have determined the crystal structure of tetraphenylarsonium hydrogen dinitrate and find that, in this compound, the hydrogen dinitrate anion has the structure (I) consisting of two coplanar unidentate nitrate groups linked across a centre of symmetry by a very short hydrogen bond of length 2·45 Å.

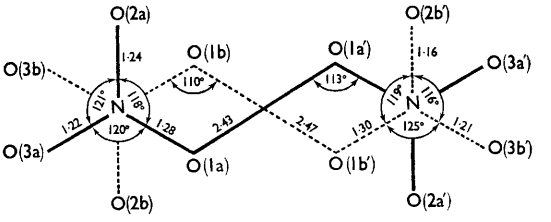


(I)

The crystals are monoclinic, with cell dimensions $a = 17{\cdot}39$, $b = 6{\cdot}91$, $c = 18{\cdot}95$ Å, $\beta = 94°$, and the density of 1·47 g. cm.$^{-3}$ indicates that there are four molecules per unit cell. Systematic absences showed the space group to be $C2/c$ or Cc, and piezo- and pyro-electric tests did not indicate any absence of a centre of symmetry. The refinement of the structure was carried out on the basis of the space group $C2/c$ to a final R value of 0·096 for 1799 independent reflections.

The arsenic atoms of the tetraphenylarsonium cations are located on the two-fold rotation axes, which relate the two pairs of phenyl groups in each tetrahedral cation. The mean dimensions in this ion, with average standard deviations in parentheses, are C–C = 1·395 (0·01) Å, C–As = 1·89 (0·01) Å, ∠ C–As–C = 109° (1°), ∠ C–C–C = 120° (1°), in good agreement with the corresponding dimensions in other tetraphenylarsonium salts.[2]

There is a disordered arrangement of the hydrogen dinitrate ions in the structure, shown in the three-dimensional Fourier maps, as in the Figure, by the appearance of two superimposed hydrogen dinitrate ions, with the plane of one rotated through 172° relative to the plane of the other. The two positions of the hydrogen dinitrate ion appear to be occupied with almost equal probability, so the least-squares refinement was carried out by assuming half an oxygen atom to be present at each oxygen position. In each of the two positions for the dinitrate ion, the two nitrate groups are coplanar and are linked to each other across the crystallographic centre of symmetry by a hydrogen bond of average length 2·45 Å. This is consistent with the Speakman 'Type A' infrared spectrum already reported for this type of compound.[3] All other methods of pairing the four half-nitrate groups give rise to structures for the dinitrate ion which have impossibly low O · · · O distances. Examination of the three-dimensional Fourier map



FIGURE

The dimensions found for the hydrogen dinitrate ion in its two alternative positions (a) *and* (b). *The average standard deviation for bond lengths is* 0·02 Å, *and for bond angles is* 2°.

shows no extra electron density which could be interpreted in terms of tetrahedral dinitrate ions. The bond lengths and angles illustrated in the Figure are almost certainly affected by the fact that the position found for the nitrogen atom is really the average of two alternative positions. In spite of this difficulty, the dimensions given by the two sets of atomic positions for the dinitrate ion are in good agreement with each other and with those previously reported for the $H_2(NO_3)_3^-$ ion.[4]

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