The Crystal Structure of 2,4,6-Trinitrophenetole

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SINCE 2,4,6-trinitrophenetole is the parent compound of two Meisenheimer complexes, whose structures have already been determined by means of *X*-ray diffraction,[1,2] it was necessary to study the crystal structure of the parent compound.

The crystals of 2,4,6-trinitrophenetole are orthorhombic, space group $Pca2_1$, with $a = 23{\cdot}77$, $b = 7{\cdot}34$, $c = 6{\cdot}26$Å, $D_m = 1{\cdot}553$, $Z = 4$, $D_c = 1{\cdot}557$; Cu-K_α radiation was used.

The structure has been determined from a three-dimensional sharpened Patterson synthesis and Fourier transform.[3] Refinement has been carried out by the least-squares method, with anisotropic temperature factors for all the atoms, except the hydrogen atoms, which were included only in the structure-factor calculations with isotropic temperature factors. The *R*-value is 0·063 for 856 independent (non-zero) reflections ($h0l$—$h5l$ and $hk0$—$hk2$). These observations were obtained from multiple-film Weissenberg photographs by visual estimation.

The geometry of the molecule is shown in the Figure. The two nitro-groups in *ortho*-positions

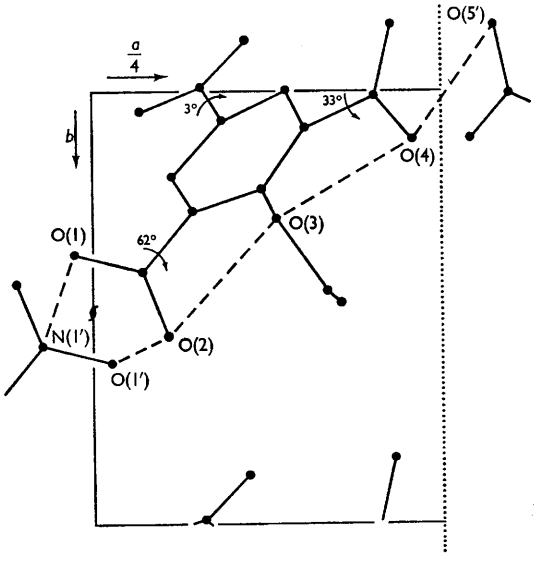

FIGURE. *Projection of the structure on* (001).

with respect to the ethoxyl group are significantly rotated out of the plane of the phenyl ring, one by 62° and one by 33°. These values are considerably higher than usual and correspond to overcrowded molecules.[4] The third nitro-group (in the *para*-position) is nearly coplanar with the phenyl ring (angle of rotation = 3°).

The plane determined by the oxygen and the two carbon atoms of the OEt group is approximately perpendicular to the phenyl ring, the angle between the two planes being 88°.

Considering only intramolecular repulsions for the isolated molecule, equal rotation of the two nitro-groups in *ortho*-positions with respect to the ethoxyl group could be expected. The observed difference in the rotation angles of these two nitro-groups can therefore be ascribed to molecular packing in the crystal. A detailed calculation of these effects, together with a complete discussion of the structure, are in preparation.

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