Structure Investigation of the Free Radical Tris-*p*-Nitrophenylmethyl

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The tris-*p*-nitrophenylmethyl radical was prepared using tris-*p*-nitrophenylmethyl bromide [1] and zinc in a Wurtz' synthesis. The advantage of this method is to overcome the difficulty of growing single crystals suitable for the X-ray method. A zinc rod was kept in a solution of tris-*p*-nitrophenylmethylbromide in a mixture of benzene and some acetone. Well developed single crystals of the radical grew out on the zinc rod. The presence of the radical was controlled using electron spin resonance.

The crystal is orthorhombic with a density 1.5 g/cm^3 and four molecules in the unit cell. The space group is $Pca2_1$. The cell dimensions are, a = 11.50 Å, b = 7.80 Å and c = 18.60 Å.

The [010] Patterson projection shown in Fig. 1 showed the threefold symmetry of the molecule and gave good indications as to the orientation of the molecules in the cell. A Fourier-projection along the b-axis was successfully refined using difference syntheses and the R value for this projection at the present stage of refinement is around 13 %. A uniform isotropic temperature factor of B = 5 has been used for all atoms.

A flat model with the distances 1.5 Å from the central carbon atom to the nearest ring carbon atoms has been assumed. The plane of the ring seems to be twisted about 30° out of the plane of the molecule with the nitro group in the plane of the ring. There are so far no indications of the molecule forming an unsymmetrical propeller.

The twisting of the benzene rings out of the plane does not necessarily have to be the same for all three rings as the threefold symmetry of the molecule is not required by the crystallographic symmetry in the solid state. A threedimensional model of the cell-content shows that the proposed

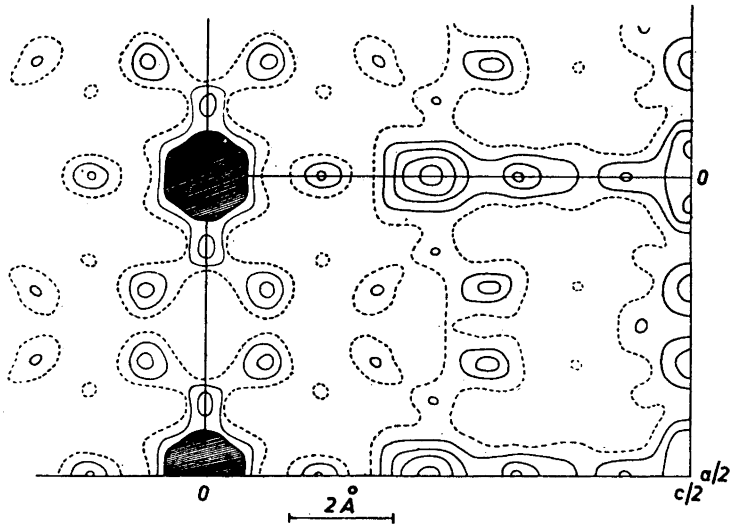

Fig. 1. The [010] Patterson projection of tris-*p*-nitrophenylmethyl.

structure is in harmony with space requirements.

A least squares refinement of the same projection resulted in an R value of around 10 %. However, because of the heavy damping the number of reflections is rather low considering the number of atomic parameters. Three-dimensional intensity data have been registered and a three-dimensional refinement of the structure is in progress.

1. Ziegler, K. and Boye, E. *Ann.* **458** (1927) 248.

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