Evidence from 4:4'-Dinitrodiphenyl on the Improbability of Non-Centrosymmetric Crystals Containing Centrosymmetric Molecules

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The crystal structure of 4:4'-dinitrodiphenyl has been redetermined. The 400 observed reflexions used in a least-squares analysis give an R factor of 17%. It is shown that the molecules are not planar, the benzene rings and nitro-groups being twisted in a helical fashion about the long axis of the molecule. Since such a molecule cannot have a symmetry centre, 4:4'-dinitrodiphenyl can no longer be cited as a possible example of a non-centrosymmetric crystal containing centrosymmetric molecules.

Introduction

It is common experience that centrosymmetric crystals may contain either centrosymmetric or non-centrosymmetric[†] molecules. However, the occurrence of centrosymmetric molecules in a non-centrosymmetric crystal appears to be rare, if not altogether prohibited.

From a literature survey Herbstein & Schoening (1957) found five examples which, judging on the information available, might possibly belong to this latter class. Of these, 1:2-5:6 dibenzanthracene (Iball & Robertson, 1933; Robertson & White, 1956) and 4:4'-dinitrodiphenyl $C_{12}H_8(NO_2)_2$ (van Niekerk, 1943) appeared to be the two best established examples.

Kitaigorodskii (1958) on the other hand has argued, on the basis of the theory of close packing, that centrosymmetric molecules would not be expected to crystallize in non-centrosymmetric space groups.

In order to obtain further information on this apparent anomaly, it was decided to redetermine the structure of 4:4'-dinitrodiphenyl, a structure which had been determined previously by one of us (J. N. v. N.). This structure had been derived from two electron-density projections, using intensities from a series of overlapping oscillation photographs. The β-angle of this structurally monoclinic crystal was found to be 90°, so that none of the positive axial directions could be determined unequivocally. The only systematically absent reflexions were $h0l$ with l odd, so that the space group was either Pc or $P2/c$. From purely packing considerations the space group Pc was chosen. Furthermore, to facilitate computa-

tions, the molecule was assumed to have a symmetry centre midway between the two benzene rings. This centre was taken to be slightly displaced (from a position midway between the glide planes) along the negative direction of b, since the structure would otherwise have belonged to space group $P2_1/c$.

With no computing facilities available at the time, refinement of the structure was slow and tedious and it was not carried to completion. Resolution of the atoms in the bc projection was good, with an R factor of 30% for the $0kl$ reflexions. On the ac projection the resolution was poor with an R factor of 48% for the $h0l$ reflexions. Clearly then further investigation was desirable before information from this structure could be used as evidence in the present problem.

Experimental

Although Bunn (1945) has questioned the assignment of the space group Pc, suggesting that it might be $P2_1/c$, Herbstein & Schoening (1957) have shown the crystals to be polar so that the space group Pc was fully established and needed no further confirmation. The cell dimensions, determined from oscillation and Weissenberg photographs using filtered Cu $K\alpha$ radiation, were found to be

$$a = 3\cdot76, \ b = 9\cdot58, \ c = 15\cdot50 \text{ Å}, \ \beta = 90 \pm 1°,$$

in substantial agreement with van Niekerk's results. Using the multiple film technique, the intensities of the $0kl$, $1kl$ and $2kl$ reciprocal layers were measured from equi-inclination Weissenberg photographs. Corrections were applied for spot shape, resolution, absorption and Lorentz-polarization effects. Structure factors derived from these corrected intensities were used in a least-squares refinement programme* on a Stantec Zebra computer.

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† When centrosymmetry or non-centrosymmetry is attributed to a molecule in this paper, it should be understood that this symmetry can only be demonstrated by structure analysis and will apply only to within the limits of accuracy of such an analysis.

* This programme was written by Dr J. C. Schoone of the University of Utrecht, the Netherlands, and he has kindly made it available to us.

Although the finer details of the structure are still a long way from completion (intensity measurements at low temperature are being contemplated), the main outlines of the structure are at a sufficiently advanced stage to prove beyond any doubt that the molecule is non-centrosymmetric.

Description of the molecule

The somewhat idealized molecule and its orientation may be conveniently described in terms of a set of axes similar to those used by van Niekerk (Fig. 1). In order to retain a right-handed set of axes, however, we have found it necessary to reverse the positive
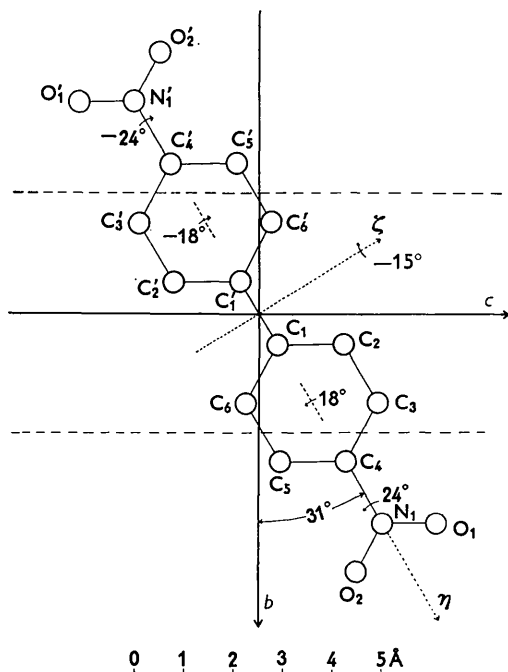

Fig. 1. The molecular orientation in 4:4'-dinitrodiphenyl.

direction of the a axis in the original determination. Also for the sake of convenience, the origin midway between the glide planes has been retained instead of choosing the origin on the glide planes as in *International Tables*.

In Fig. 1, let a, b, c be the crystallographic axes, and ξ, η, ζ be an orthogonal set of right-handed axes fixed in the molecule at the origin. For the moment, we imagine the molecular axes to coincide with the

crystallographic axes. Imagine further the molecule to be planar and linear in the sense that the positive direction of η is defined by the row of atoms $N_1' C_4' C_1' C_1 C_4 N_1$. The positive direction of ξ is normal to the plane of the molecule and the origin of the molecular axes is chosen at the midpoint of the C_1–C_1' bond.

We now rotate the molecule first through $+31°$ about $+\xi$ and then through $-15°$ about $+\zeta$. This fixes the direction of the $+\eta$ axis in the crystal. The benzene ring in the positive octant is now twisted through $+18°$ about $+\eta$, while the other benzene ring is twisted about $+\eta$ through $-18°$. The corresponding twists on the two nitro-groups are $+24°$ and $-24°$ respectively. The *bc* projection of such a molecular arrangement closely resembles the projection originally obtained by van Niekerk.

The bond lengths computed from the molecular configuration described above are entirely reasonable and, on using a calculated isotropic temperature factor of 4·0, an R factor of 17% has been obtained with the 400 recorded reflexions used during the least-squares refinement.

In this structure then, since the two benzene rings in a molecule are twisted relative to each other, the molecule cannot have a symmetry centre. This finding is contrary to the assumption made by van Niekerk when the structure was first determined and agrees with the prediction of Kitaigorodskii (1958). One of the two major examples cited in the literature of centrosymmetric molecules occurring in a non-centrosymmetric space group has therefore been eliminated and it is tempting to infer that such an occurrence is indeed impossible.

In conclusion we would like to thank Dr G. Gafner for his help and many valuable suggestions with the computational aspects of this investigation.

References

BUNN, C. W. (1945). *Chemical Crystallography*, p. 251. Oxford: University Press.
HERBSTEIN, F. H. & SCHOENING, F. R. L. (1957). *Acta Cryst.* **10**, 657.
IBALL, J. & ROBERTSON, J. M. (1933). *Nature, Lond.* **132**, 750.
KITAIGORODSKII, A. I. (1958). *Soviet Physics. Crystallography*, **3**, 393.
NIEKERK, J. N. VAN (1943). *Proc. Roy. Soc.* A, **181**, 314.
ROBERTSON, J. M. & WHITE, J. G. (1956). *J. Chem. Soc.* Part I, p. 925.