

Short Communications

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The crystal structure of *p*-nitroaniline. By S. C. ABRAHAMS and J. M. ROBERTSON, *Chemistry Department, The University, Glasgow W. 2, Scotland*

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The structure proposed by Donohue & Trueblood (1956) for *p*-nitroaniline appears to us to be essentially correct, and it removes the peculiarity of the abnormally short intermolecular distances which arose from our earlier determination (Abrahams & Robertson, 1948).

In terms of the crystal structure as a whole, the change is not a large one; but the *y* coordinates of the atoms of two of the molecules are interchanged. Of the 245 observed structure factors, the calculated values of 185 remain unaffected by this change; of the remaining 60, the values for the 27 (*0kl*) planes with *l* odd are greatly improved, the average discrepancy dropping from 51% to 22%. This result is so striking that the new structure must be accepted as essentially correct.

A similar improvement for the 33 (*hk0*) planes with *h* odd might be expected, but this is not obtained. Using the McWeeny *f*-curve (which was not available to us in 1948) the average discrepancy for the new structure is 37%, and after nine cycles of least-squares refinement an improvement to 32% is reported. Although this is considerably better than the original structure, it can hardly be regarded as completely satisfactory. The statement by Donohue & Trueblood that the larger discrepancy for *h* odd is due entirely to the poor agreement found for (110) and (130) is scarcely correct, because if these two planes are omitted the average discrepancy for observed planes only improves to about 31%.

It seems possible that some of the *y* coordinates, taken

over from the original structure, may be too far in error for the least-squares refinement process to be effective. These coordinates were after all deduced in relation to what is now seen to be an incorrect assignment of the symmetry elements.

The example of *p*-nitroaniline, and other similar cases which have occurred recently, e.g. β -selenium (Burbank, 1952; Marsh, Pauling & McCullough, 1953), go to show that crystal-structure determinations based on two-dimensional data only must be accepted with caution. If one projection showing good resolution is available it may be refined to give quite accurate and unambiguous values for two coordinates of each atom. But if this is the case it is usually an unfortunate consequence that the data available for the other projections are rather meagre and it may be quite difficult to decide between possible alternative arrangements.

References

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 DONOHUE, J. & TRUEBLOOD, K. (1956). *Acta Cryst.* **9**, 960.
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The thermal expansion of *p*-nitroaniline. By A. R. UBBELOHDE and G. S. PARRY, *Department of Chemical Engineering, Imperial College of Science and Technology, London S.W. 7, England*

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In order to extend the thermal expansion studies of *p*-nitroaniline (McKeown, Ubbelohde & Woodward, 1951) and in order to resolve the ambiguity (pointed out previously) of interpreting the thermal expansion on a structural basis, work is in hand to evaluate the structure at low temperatures. This will permit comparison with the room-temperature structure.

Comparison of the anisotropy of thermal expansion of

p-nitroaniline with that of crystalline graphite hardly seems appropriate in view of the differences in absolute magnitude and because of the primary valence bonds which extend throughout the 0001 plane of graphite.

Reference

- MCKEOWN, P. J. A., UBBELOHDE, A. R. & WOODWARD, I. (1951). *Acta Cryst.* **4**, 391.