

Periodic Errors in the Crystal Lattices of some Molecular Complexes of 4:4'-dinitrodiphenyl

BY R. W. JAMES AND D. H. SAUNDER
University of Cape Town, South Africa

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Faults in the crystal lattices of the molecular complexes of 4:4'-dinitrodiphenyl with 4-chlorodiphenyl and 4:4'-diiododiphenyl have been observed. They appear to be of a similar nature to those discussed in a previous paper (James & Saunder, 1947). The complexes of 4:4'-dinitrodiphenyl with 4-fluorodiphenyl and 4:4'-dibromodiphenyl have also been examined, but their crystal lattices show no faults. It is suggested that the interaction of dipoles, and not chemical bonding, is responsible for the stability of complexes of this type.

Introduction

In a previous paper (James & Saunder, 1947) some periodic errors which occurred in the crystal lattices of the complexes of 4:4'-dinitrodiphenyl with 4-iodo- and 4-bromodiphenyl were described. The complexes of 4:4'-dinitrodiphenyl with some other halogenated diphenyls, namely 4-chloro-, 4-fluoro-, 4:4'-diiodo-, and 4:4'-dibromodiphenyl, have since been examined and some similar effects observed.

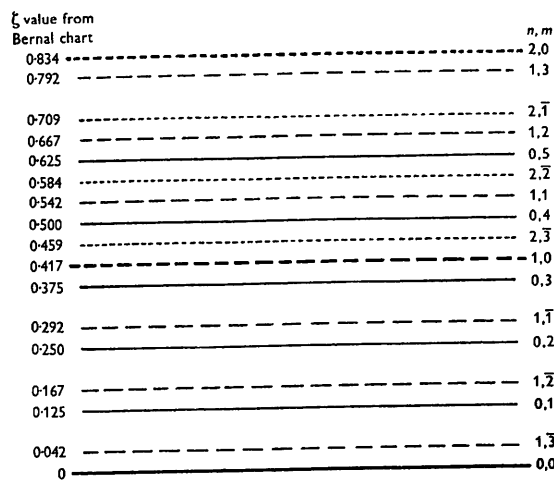
An examination (Saunder, 1946, 1947; James & Saunder, 1947) of a number of complexes formed by dinitrodiphenyl with various substituted diphenyls has shown that all these complexes conform to a definite type of structure in which the dinitrodiphenyl molecules form layers in face-centred array and lie one above the other with a spacing of about 3.7 Å. The arrangement of these molecules alone is such that a set of tubular cavities, also in face-centred array, runs through the structure. These cavities are occupied by the other component molecules, which thus lie nearly normal to the planes containing the dinitrodiphenyl molecules.

The complexes of dinitrodiphenyl with the halogenated diphenyls which have now been examined are no exception, as shown by the great similarity of photographs taken about structurally equivalent directions. Since these complexes all have external forms very similar to those of the complexes with 4-iodo- and 4-bromodiphenyl previously described, the axes have been chosen in a similar way and are as represented in Fig. 1 of the previous paper (James & Saunder, 1947); that is, the halogenated diphenyl molecules lie approximately along the *c* axis in each case, and the dinitrodiphenyl molecules lie approximately normal to this axis.

The complex with 4-chlorodiphenyl

Photographs taken with oscillations about the *c* axis show sharp and clear zero, 7th and 14th layer-lines,

but all the intermediate layer-lines show spots that are more or less diffuse, with elongations along the layer-lines (Plate 2, fig. 1). The diffuseness of the spots varies from line to line. It is also found that, as for the complex with 4-bromodiphenyl, the spacing of the diffuse layer-lines is not uniform but the lines are arranged in groups, themselves evenly spaced, about the sharp layer-lines. The departure from regularity is very plain to the eye and is shown diagrammatically in Text-fig. 1. Oscillations about the *b* axis show the elongation of the diffuse spectra to be always parallel to *b*.



Text-fig. 1. The complex with chlorodiphenyl. Diagrammatic representation of the position of the layer-lines as they appear on oscillation photographs about the *c* axis and using $\text{Cu } K\alpha$ radiation.

These effects may be interpreted in exactly the same way as was done for the complex with 4-bromodiphenyl. The arrangement of the diffuse layer-lines in the *c*-axis photographs is exactly that to be expected of a series of optical ghosts accompanying the sharp layer-lines, such as would appear if a set of planes of

regular spacing 3.69 Å. had been modified by a periodic error repeating in the direction of the *c* axis in a distance of 12.3 Å. The measured spacings of the layer-lines in the reciprocal-lattice space, as determined by means of a Bernal chart, and using Cu *K*α radiation, is shown diagrammatically in Text-fig. 1. The notation used in the figure has the same significance as that used in the previous paper (James & Saunder, 1947). Thus *n* is the order of the spectrum from the series of regularly spaced planes. If a periodic error is superimposed on these planes, repeating itself every *Q* planes, then ghost spectra of order $n \pm m/Q$ make their appearance. In this case the value of *Q* corresponds to $12.3/3.69 = 3.33$.

The *positions* of the layer-lines may thus be explained by supposing the regular spacing of the dinitrodiphenyl molecules, separated by 3.69 Å. along the *c* axis, to be modified by the chlorodiphenyl molecules which thus constitute a periodic 'error' repeating in a distance of 12.3 Å. This is in good agreement with the calculated length of a 4-chlorodiphenyl molecule, which is about 12.4 Å. If this hypothesis is correct, the ratio of dinitrodiphenyl to chlorodiphenyl in the complex should be 3.33 : 1. The results of chemical analysis agree with this, but could not be obtained with sufficient accuracy to provide definite confirmation.

The varying *diffuseness* of the spectra along *b* may be explained in detail on the assumption of random faults occurring in the *b* direction, exactly as assumed in the discussion of the iodo- and bromodiphenyl complexes; that is, along the *b* direction in the crystal there are supposed to be random changes in the *c* co-ordinates of the halogen molecules.

The complex with 4:4'-diiododiphenyl

In this case the *c*-axis oscillation photographs show sharp zero, 4th and 8th layer-lines, the intermediate layer-lines consisting once again of diffuse spectra elongated along *b* (Plate 2, fig. 2). The spacing of these layer-lines is, however, apparently quite regular, corresponding to a *c* cell-edge of 14.8 Å.

The position of the layer-lines may be explained on similar lines to those just discussed. The arrangement is that to be expected of the series of optical ghosts which would be produced if a set of planes (consisting of dinitrodiphenyl molecules) of spacing 3.7 Å. were modified by a periodic 'error' (the diiododiphenyl molecules) repeating in the direction of the *c* axis in a distance of 14.8 Å. This is in good agreement with the calculated length of a 4:4'-diiododiphenyl molecule which is about 15.0 Å. The ratio of dinitrodiphenyl to diiododiphenyl in this complex should then be 4 : 1 and this is in agreement with the chemical analysis.

The diffuseness of the intermediate layer-lines may again be explained by assuming that changes in the *c* co-ordinates of the halogen molecules occur in a random way along the *b* axis.

The complexes with 4-fluorodiphenyl and 4:4'-dibromodiphenyl

The oscillation photographs of both these complexes are quite normal, the spacings are regular and all the spectra are sharp. There are thus no faults in these crystal lattices.

The oscillation photographs about different axes for the complex with 4-fluorodiphenyl are very similar indeed to photographs taken about corresponding directions for the complex with 4:4'-dihydroxydiphenyl (Saunder, 1947).

Except for the fact that all the spectra are sharp the oscillation photographs for the complex with 4:4'-dibromodiphenyl are closely similar to those for the complex with diiododiphenyl.

An attempt was made to examine the complex with 4:4'-dichlorodiphenyl, but no complex could be isolated from the solvent used (acetone).

Discussion

In none of the complexes of this dinitrodiphenyl series which have been examined has there been any evidence for localized bonding between the different component molecules. It has in fact been suggested (Rapson, Saunder & Stewart, 1946) that the molecular ratios in which the components unite are determined solely by geometrical and not by chemical considerations. This is particularly striking in the case of the complex with 4-chlorodiphenyl for which the crystallographic evidence suggests a non-integral ratio of the components of 3.33 : 1.

It appears, therefore, that the stability of these complexes may be accounted for by the interaction energy due to the mutual polarization of the molecules, a conclusion reached by several workers (Briegleb, 1935, 1936; Pauling, 1939; Gibson & Loeffler, 1940; Hammick & Yule, 1940; Sutton, 1946).

These ideas are supported by the following data:

(1) The nitro group possesses one of the highest group dipole moments. In this connexion it is very significant that similar complexes are formed by nitroso compounds (Pfeiffer, 1927), quinones (Anderson, 1937), liquid SO₂ (Foote & Fleischer, 1934), aromatic acid chlorides and nitriles (Bennett & Wain, 1936). All these components contain highly polar groups. It is also of interest to note that a highly coloured complex of 4:4'-dicyanodiphenyl and benzidine has been obtained in these laboratories.

(2) Complexes of nitro compounds are only formed with unsaturated (usually aromatic) hydrocarbons or their derivatives, which contain a disperse system of electrons and so are easily polarized. It has been suggested by Sutton (1946) that the aromatic ring system may have abnormally high polarizability in the strong, highly inhomogeneous field in the neighbourhood of a dipole.

Of interest are the results of Briegleb (1935, 1936),

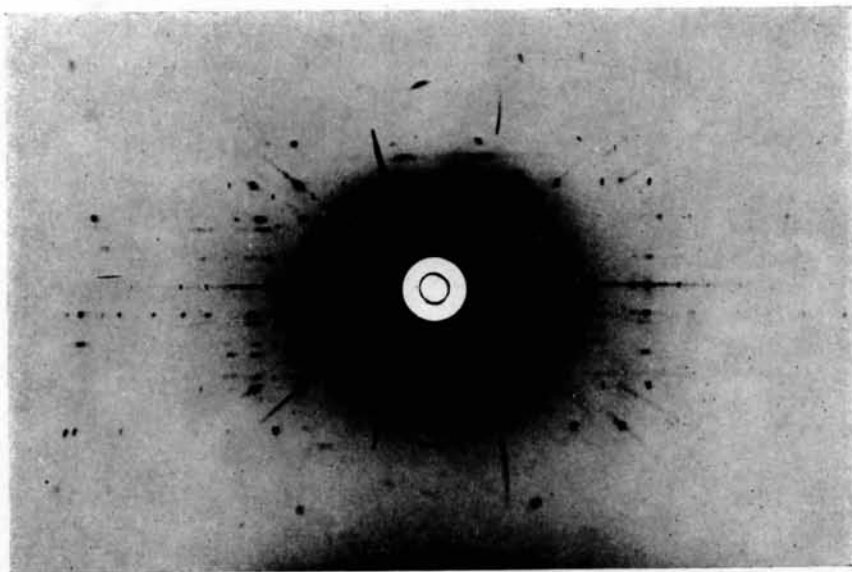


Fig. 1. The complex with chlorodiphenyl. 15° oscillation photograph about the c axis, with the rays incident initially along a^* . The blackening near the centre is due mainly to gas scattering as a result of the very long exposure required.

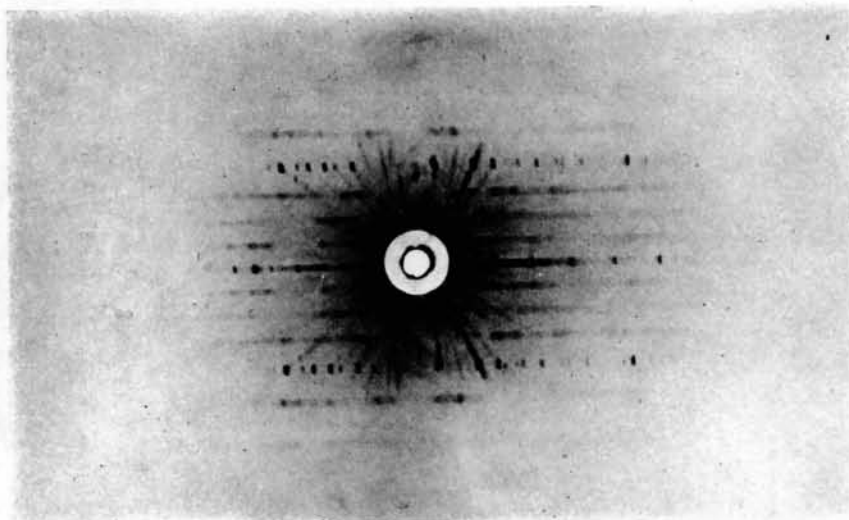


Fig. 2. The complex with diiododiphenyl. 15° oscillation photograph about the c axis, with the rays incident initially along a^* .

who found that the binding energy in complexes of *s*-trinitrobenzene with various hydrocarbons depends in a marked way on the structure of the hydrocarbon, and these binding energies are greater the greater the optical exaltation shown by the hydrocarbon. The binding energy of the complex is high if the hydrocarbon system is completely conjugated, but decreases as soon as the conjugation is interrupted.

When considering the question of the polarizability of the aromatic hydrocarbon it is interesting to note that, in general, complexes with nitro compounds are apparently more stable if electron-repelling groups are introduced into the hydrocarbon and less stable if electron-attracting groups are introduced; indeed, in the latter case it is generally impossible to isolate a crystalline complex. It is tempting to suggest that the introduction of an electron-repelling group into the hydrocarbon leads to a greater availability of electrons in the aromatic nucleus, implying a greater polarizability of the molecule. Considerable care must, however, be exercised in interpreting the effect of substituents on the stability of these complexes, since geometrical effects depending on the size of these substituents will undoubtedly be of importance in determining the approach of the molecules to one another.

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The Accurate Determination of Cell Dimensions from Single-Crystal X-ray Photographs

BY OLGA WEISZ, W. COCHRAN AND W. F. COLE

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

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The accurate determination of cell dimensions by a graphical extrapolation method from single-crystal X-ray photographs has been discussed by Farquhar & Lipson and applied by them to an orthorhombic crystal, thallium hydrogen tartrate. In the present paper an alternative method of lower accuracy but greater simplicity is described. An account is also given of the application of extrapolation methods, both graphical and analytical, to the determination of the cell dimensions of a monoclinic crystal, a heat-treated orthoclase feldspar. Procedures for determining accurate cell dimensions of orthorhombic, monoclinic and triclinic crystals are outlined.

1. Introduction

Cell dimensions may be determined approximately from measurements of layer-line separations in single-crystal rotation photographs, and accurately either with the help of a special goniometer of the Weissenberg type (Buerger, 1937) or by a graphical extrapolation method using a slightly modified ordinary goniometer (Farquhar & Lipson, 1945). In § 2 of the present paper a description is given of a new technique, based on observations of the angular setting of the crystal at which reflexion occurs, and of its application to a monoclinic orthoclase

feldspar and other crystals. In § 3 analytical and graphical extrapolation methods are applied to the same feldspar crystal and in § 4 the relative accuracies of the two methods are discussed. Finally, in § 5 a combined technique is described which has great advantages for triclinic crystals.

2. θ -Method

Theory. Both linear and angular constants are obtained from reflexions of the type (*h*00), (0*k*0), (00*l*) occurring on zero layer-line photographs. The goni-