Short Communications

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Acta Cryst. (1954). **7**, 298

The space groups of nitrogen triphenyl and phosphorus triphenyl.

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(*Received* 24 *December* 1953)

The space groups and unit-cell dimensions of nitrogen triphenyl and phosphorus triphenyl were first studied by Howells (1950), but his results have been criticized by Kitajgorodskij (1951) and by Iveronova & Rojtburd (1952). Kitajgorodskij suggested that phosphorus triphenyl should be assigned to Pa instead of $P2/a$, while Iveronova & Rojtburd indicated that the space group of nitrogen triphenyl should be Cc or $C2/c$ rather than Pm.

A re-examination of these substances has been undertaken to ascertain whether these differences are the result of polymorphism or are due to errors of interpretation. Both Howells's original specimens and new supplies have been used. The space groups and unit cells have been redetermined by X-ray studies, and the monoclinic angle of nitrogen triphenyl has been redetermined by optical goniometry. The new results are set out in Table 1, where they may be compared with those published by Howells, Iveronova & Rojtburd, and Kitajgorodskij. It appears that polymorphism is not responsible for the discrepancies.

Table 1

Nitrogen triphenyl

	a (Å)	b (Å)	c (Å)	β	Z	Space group	d (g.cm.$^{-3}$) obs.	d (g.cm.$^{-3}$) calc.
Howells	22·6	11·2	11·2	90°	8	Pm	1·16	1·15
Iveronova & Rojtburd	15·6	15·8	22·1	91° 22′*	16	Cc or $C2/c$	—	1·19
Present work	$15{\cdot}7_5$	$15{\cdot}8_6$	22·3	91° 16′†	16	Cc [or $C2/c$]	1·18	$1{\cdot}17_0$
[Present work, Howells's axes	22·3	$11{\cdot}1_8$	$11{\cdot}1_8$]					

Phosphorus triphenyl

	a (Å)	b (Å)	c (Å)	β	Z	Space group	d (g.cm.$^{-3}$) obs.	d (g.cm.$^{-3}$) calc.
Howells	11·6	15·1	8·57	93°	4	$P2/a$	1·10	1·15
Iveronova & Rojtburd	8·6	14·9	11·5	93° 6′‡	4	$P,2/c$ or Pc	—	1·18
Kitajgorodskij	—	—	—	—	—	Pa	—	—
Present work	11·5	14·8	8·55	$93\pm\frac{1}{2}$°	4	$P2_1/a$	1·18	1·19

* Arzruni (1877).
† Optical determination (see Table 2).
‡ Arzruni (1885).

Nitrogen triphenyl, $N(C_6H_5)_3$

Table 2. *Nitrogen triphenyl: optical goniometry*

	Present work	Arzruni (1877)
(001) : (111)	62° 48′	62° 43′
(001) : ($\bar{1}$11)	64° 11′	64° 5′
(111) : (1$\bar{1}$1)	77° 24′	77° 28′
(111) : ($\bar{1}\bar{1}$1)	78° 53′	78° 56′
Monoclinic angle β	91° 16′	91° 22′
Axial ratios: optical	0·988 : 1 : 1·410	0·9913 : 1 : 1·4119
Axial ratios: X-ray	0·993 : 1 : 1·406	—

The crystals were grown from solutions in methanol, ethanol or ethyl acetate. The habit, interfacial angles (see Table 2) and the crystal optics agree with those recorded by Groth (1906–19). The crystals were plates or tablets with a roughly square outline and with the (001) face always conspicuous. The {111} and {$\bar{1}$11} faces were never large and rarely appeared smooth, but under the microscope exhibited ragged terracing of the (001) lamellae. By means of polarized light it was also observed that true single crystals are very rare. The lamellae appeared to be superimposed in several different orientations so that when the crystals were viewed in parallel polarized light passing normally through the plates no extinction occurred, though slight patchy 'shading' effects were observed on rotating the plane of polarization. Some very thin flakes, showing only a first-order grey, did extinguish fairly sharply parallel to a diagonal, but were much too small for X-ray work and were too thin to give a distinctive pattern in convergent polarized light. Many of these, too, had twinning blemishes. The thicker plates under convergent polarized light showed a single 'eye' of a biaxial pattern, indicative of an optic axis emerging close to the axis of the microscope. It moved by small amounts and in an abrupt fashion as the block was traversed under the objective. The other optic axis always lay on a diagonal of the (001) face well outside the field of view. The plane of the optic axes proved to be

(010). The macroscopic appearance of these crystals was indistinguishable from the true single crystals, and it was also obvious that the lamellar twinning occurred on both a macroscopic and a submicroscopic scale. Apart from this lamellar twinning, the optics suggested that other modes occurred, and this was confirmed by the very confused form of the reciprocal lattice obtained for some specimens. The best crystals still showed twinning, but this was confined to a limited type and was often such as to give unequal portions of the two twins. The present work was performed either on these or on two crystals which seemed to be almost entirely free from twinning.

Fixed-film and Weissenberg X-ray photographs showed them to be monoclinic (Laue symmetry $2/m$), the b axis being parallel to a diagonal of the plate. This choice of axes coincides with Groth's, and with that adopted by Iveronova & Rojtburd. The systematic absences can then be expressed as:

(hkl) absent for $(h+k)$ odd, $(h0l)$ absent for l odd,

which indicate the space groups Cc or $C2/c$. This list of absences confirms the results published by Iveronova & Rojtburd, but the new cell dimensions differ slightly from theirs. Table 1 contains a comparison of the observed and calculated densities and also compares the cell dimensions (A, B, C) given by Howells with those calculated from the present axes (a, b, c) using the transformations:—

$$\mathbf{A} \fallingdotseq \mathbf{c},\ \mathbf{B} = (\mathbf{a}+\mathbf{b}),\ \mathbf{C} = (\mathbf{a}-\mathbf{b})\,.$$

The vectorial translation **c** is slightly inclined to **A** as a result of the reorientation of axes and the re-estimation of β as 91° 16′.

The simply twinned specimens had b^* and c^* in common but two orientations of a^*. The result was readily observable on both fixed-film and Weissenberg photographs, from which a value of $91° 4' \pm 20'$ was estimated for β.

The reciprocal lattice for single crystals is not only highly pseudosymmetric in its geometry (note how closely $a:b:c$ approximates to $1:1:\sqrt{2}$ and $A:B:C$ to $2:1:1$) but oscillation photographs taken about the B, [101], and C, $[10\bar{1}]$, axes show that it possesses remarkably good approximations to transverse symmetry planes. For the multiply twinned specimen the illusion is complete; in fact, according to the mode of twinning, symmetry planes have been observed normal to a, b, B, C and also normal to $c(A)$ when the X-ray beam is parallel to a. No detailed study of these more complex modes of twinning was undertaken, nor have we attempted to reindex the powder pattern, because the indexing would not be unique. The value of β obtained by optical goniometry is to be preferred to that obtained from the X-ray photographs, and was obtained from a single crystal fragment, but as its faces were not of the best quality it is possibly not so reliable as Groth's value. The agreement is good and suggests that Arzruni (1877), whom Groth quotes, also used a true single crystal. Weissenberg photographs appear from a visual inspection to have the low dispersion of intensity and rarity of accidental absences that characterize non-centrosymmetric space groups. Cc is, therefore, somewhat more probable for this substance.

Phosphorus triphenyl, $P(C_6H_5)_3$

No difficulty was experienced in getting single crystals by recrystallization from ethanol. However, the crystals, like those used by Arzruni (1885), had faces of poor quality and were unsuitable for optical goniometry. Arzruni was, in fact, able to determine only β and the ratio $a:b$ (0·7955; the present X-ray value is 0·777), as no faces involving the ratio $c:b$ were developed. X-ray photographs indicated that the crystals were monoclinic (Laue symmetry $2/m$). The systematic absences were:

$(h0l)$ absent for h odd, $(0k0)$ absent for k odd.

The 'halving' of the $(0k0)$ axis was checked as far as $k = 14$. The space group is, therefore, uniquely determined as $P2_1/a$.

Wilson (1952) drew attention to the fact that Howells (1949) had actually observed the screw absences, but, misled by a wrong interpretation of a Patterson map, had regarded the axis as a pseudo-screw. Howells's space-group assignment was, therefore, Pa or $P2/a$, and a statistical treatment (Howells, Phillips & Rogers, 1950) had favoured $P2/a$, the centrosymmetric group. This latter choice was challenged by Kitajgorodskij (1951), who has shown (Kitajgorodskij, 1946, 1947), by a consideration of optimum packing of ellipsoids, that screws and glides are very much more likely to occur than planes of symmetry or rotation axes. Accordingly he favoured Pa and had to postulate that the structure, though strictly non-centrosymmetric, approximated sufficiently closely to centrosymmetry to give rise to a misleading statistical result. The revision of the space group to $P2_1/a$ removes Kitajgorodskij's original objection and also obviates the need for the proposal that pseudo-centrosymmetry occurs in this structure. The statistical indication was therefore correct. Although Kitajgorodskij's criticism is no longer relevant to this problem it still remains a valid criticism of statistical inferences of centrosymmetry.

The work of Iveronova & Rojtburd contains no mention of screw absences, but there can be no doubt from a comparison of all three sets of lattice vectors that the material they examined was the same as ours.

This work has been carried out using apparatus purchased with a Royal Society grant. One of us (F.M.L.) is indebted to the Department of Scientific and Industrial Research for financial assistance.

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