

Table 2.* Table 3 contains the bond lengths and angles with their e.s.d.'s. The bond distances and angles of the title compound are in very good agreement with those of *N*-(4-nitrobenzylidene)-4-dimethylaminoaniline (Nakai, Shiro, Ezumi, Sakata & Kubota, 1976). In both compounds the bond distances C(1)–C(7) and N(1)–C(8) are shortened and N(1)–C(7) lengthened in comparison with those of *N*-benzylideneaniline (1.496, 1.460 and 1.237 Å respectively) (Bürgi & Dunitz, 1970). This trend is attributed to the quinoid resonance forms that result in intramolecular charge transfer among the electron-donating methoxy or dimethylamino groups and the strong electron-withdrawing nitro group. The same effect is responsible for the shortening of the bond length of the nitro group to the phenyl ring. In the absence of electron-donating substituents this bond is about 1.48 Å (Mak & Trotter, 1965).

The quinoid resonance forms noted above result in near planarity of the molecule. The dihedral angle between the phenyl ring and the plane through C(1), C(7), N(1) and C(8) is 3.2 (2)°, whilst that between the phenyl and pyridine rings is 19.6 (2)°. This twist of the pyridine ring around the N(1)–C(8) bond and the deformation of N(1)–C(8)–C(9) to 126.1 (1)° minimizes the interaction between H(C7) and H(C9)

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43980 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1987). C43, 1795–1798

Structure of Tris(diphenylphosphino)amine

BY JOCHEN ELLERMANN AND EBERHARD KÖCK

Institut für Anorganische Chemie der Universität Erlangen–Nürnberg, Egerlandstrasse 1, D-8520 Erlangen, Federal Republic of Germany

AND HELMUTH ZIMMERMANN* AND MARTIN GOMM

Institut für Angewandte Physik, Lehrstuhl für Kristallographie der Universität Erlangen–Nürnberg, Bismarckstrasse 10, D-8520 Erlangen, Federal Republic of Germany

(Received 16 March 1987; accepted 21 April 1987)

Abstract. C₃₆H₃₀NP₃, *M_r* = 569.57, monoclinic, *I*2/a (standard space group *C*2/c), *a* = 20.005 (4), *b* = 11.350 (2), *c* = 26.313 (11) Å, β = 92.86 (2)°, *V* = 5967 (7) Å³, *Z* = 8, *D_x* = 1.27 g cm⁻³, λ(Mo Kα) =

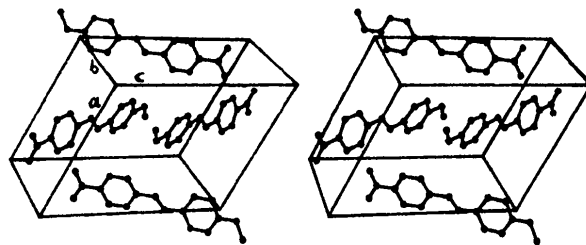


Fig. 2. Stereoscopic view of the molecular packing as viewed down the *b* axis (ORTEP; Johnson, 1965).

(Moustakali-Mavridis, Hadjoudis & Mavridis, 1980; Nakai *et al.*, 1976).

The packing diagram is shown in Fig. 2. Intermolecular contacts are normal van der Waals interactions. The distance between adjacent molecular planes related by inversion centres is 3.53 (2) Å.

References

- BÜRGI, H.-B. & DUNITZ, J. D. (1970). *Helv. Chim. Acta*, **53**, 1747–1769.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–147. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 MAK, T. C. W. & TROTTER, J. (1965). *Acta Cryst.* **18**, 68–74.
 MOUSTAKALI-MAVRIDIS, I., HADJODIS, E. & MAVRIDIS, A. (1980). *Acta Cryst.* **B36**, 1126–1130.
 NAKAI, H., SHIRO, M., EZUMI, K., SAKATA, S. & KUBOTA, T. (1976). *Acta Cryst.* **B32**, 1827–1833.
 SHELDRIK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

0.70926 Å, μ = 2.19 cm⁻¹, *F*(000) = 2384, room temperature; final *R* = 0.057 for 4432 reflections (including 20 unobserveds). The central N atom is surrounded by three P atoms in an almost planar trigonal arrangement. The mean N–P distance is 1.740 Å and the mean P–N–P angle is 119.2°. The phenyl rings

* Author for correspondence.

attached to the P atoms are located above and below the NP_3 plane. In the crystal the molecules are held together by van der Waals forces (nearest intermolecular contact: $\text{H}\cdots\text{H}$ 2.44 Å).

Introduction. The title compound $\text{N}[\text{P}(\text{C}_6\text{H}_5)_2]_3$ was synthesized for the first time by Ellermann & Wend

Table 1. *Atom coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^2$)

$$U_{\text{eq}} = (1/6\pi^2) \sum_i \sum_j \beta_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j)$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
P(1)	-52 (1)	-281 (1)	1503 (1)	4.3
P(2)	224 (1)	2146 (1)	1927 (1)	4.2
P(3)	-88 (1)	1822 (1)	812 (1)	4.4
N	106 (1)	1206 (1)	1408 (1)	4.0
C(11)	-871 (1)	-505 (1)	1167 (1)	4.5
C(12)	-1428 (1)	-94 (2)	1401 (1)	6.4
C(13)	-2065 (1)	-230 (2)	1178 (1)	7.2
C(14)	-2149 (1)	-811 (2)	726 (1)	7.2
C(15)	-1610 (1)	-1240 (2)	492 (1)	7.8
C(16)	-970 (1)	-1081 (2)	709 (1)	6.5
C(21)	494 (1)	-1074 (2)	1085 (1)	4.5
C(22)	485 (1)	-2292 (2)	1136 (1)	6.7
C(23)	872 (1)	-2998 (2)	840 (1)	7.5
C(24)	1282 (1)	-2520 (2)	502 (1)	6.7
C(25)	1309 (1)	-1317 (2)	456 (1)	7.5
C(26)	914 (1)	-602 (2)	746 (1)	6.5
C(31)	-432 (1)	1725 (1)	2353 (1)	4.3
C(32)	-987 (1)	2457 (2)	2352 (1)	5.8
C(33)	-1521 (1)	2194 (2)	2645 (1)	7.2
C(34)	-1513 (1)	1195 (2)	2939 (1)	7.1
C(35)	-964 (1)	462 (2)	2949 (1)	5.9
C(36)	-428 (1)	728 (2)	2661 (1)	4.9
C(41)	974 (1)	1622 (1)	2278 (1)	4.0
C(42)	1401 (1)	738 (2)	2132 (1)	5.3
C(43)	2009 (1)	552 (2)	2398 (1)	5.8
C(44)	2194 (1)	1229 (2)	2810 (1)	5.9
C(45)	1773 (1)	2096 (2)	2965 (1)	6.2
C(46)	1172 (1)	2292 (2)	2699 (1)	5.1
C(51)	-715 (1)	2958 (2)	942 (1)	4.7
C(52)	-1378 (1)	2630 (2)	859 (1)	6.6
C(53)	-1888 (1)	3410 (2)	966 (1)	8.9
C(54)	-1739 (1)	4492 (2)	1150 (1)	9.3
C(55)	-1083 (1)	4854 (2)	1227 (1)	7.6
C(56)	-573 (1)	4079 (2)	1121 (1)	5.7
C(61)	630 (1)	2760 (2)	695 (1)	4.2
C(62)	1246 (1)	2686 (2)	957 (1)	5.0
C(63)	1778 (1)	3371 (2)	816 (1)	6.1
C(64)	1708 (1)	4132 (2)	414 (1)	6.5
C(65)	1104 (1)	4202 (2)	144 (1)	6.6
C(66)	569 (1)	3522 (2)	280 (1)	5.7

Table 2. *Selected bond distances* (Å) *and angles* (°)

E.s.d.'s are given in parentheses.

P(1)–N	1.737 (1)	C–C	1.348 (4)–1.393 (3)
P(1)–C(11)	1.840 (5)	C–C(mean)	1.379
P(1)–C(21)	1.825 (2)	C–H	0.92 (1)–0.99 (2)
P(2)–N	1.739 (1)	C–H(mean)	0.96
P(2)–C(31)	1.830 (2)	H(64)⋯H(64 ^a)	2.44 (2)
P(2)–C(41)	1.823 (2)	H(54)⋯H(63 ^b)	2.44 (2)
P(3)–N	1.745 (2)	P(1)⋯H(46 ⁱⁱⁱ)	3.29 (1)
P(3)–C(51)	1.843 (2)	P(2)⋯H(35 ⁱⁱⁱ)	3.31 (2)
P(3)–C(61)	1.827 (2)	P(3)⋯H(16 ^v)	3.90 (2)
P(1)–N–P(2)	120.12 (8)	C(31)–P(2)–C(41)	101.64 (7)
P(2)–N–P(3)	118.39 (8)	C(51)–P(3)–N	103.63 (7)
P(3)–N–P(1)	119.01 (8)	C(61)–P(3)–N	104.08 (7)
C(11)–P(1)–N	103.24 (7)	C(51)–P(3)–C(61)	99.97 (7)
C(21)–P(1)–N	105.92 (7)	C–C–C	117.7 (2)–121.3 (2)
C(11)–P(1)–C(21)	100.82 (7)	C–C–C(mean)	120.0
C(31)–P(2)–N	104.29 (7)		
C(41)–P(2)–N	105.89 (7)		

Symmetry code: (i) $\frac{1}{2}-x, y, -z$; (ii) $\frac{1}{2}+x, -y, z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-x, -y, -z$.

(1985). Until this time only the isomeric form $(\text{C}_6\text{H}_5)_2\text{P}-\text{P}(\text{C}_6\text{H}_5)_2=\text{N}-\text{P}(\text{C}_6\text{H}_5)_2$ could be isolated (Nöth & Meinel, 1967; Schmidbaur, Lauteschläger & Köhler, 1984), and therefore it was assumed that the latter compound was favoured energetically. From the IR spectra of $\text{N}[\text{P}(\text{C}_6\text{H}_5)_2]_3$ in solution Ellermann & Wend (1985) proposed a trigonal-planar structure for the NP_3 skeleton. In order to confirm this unusual local D_{3h} symmetry for the solid state an X-ray analysis was undertaken.

Experimental. The compound was prepared as described by Ellermann & Wend (1985), recrystallization from methylene chloride/*n*-pentane gave colourless crystals of dimensions $0.42 \times 0.34 \times 0.22$ mm; Philips PW 1100 diffractometer, Mo *K*α radiation, graphite monochromator, $\omega-2\theta$ scans with scan width $(1.000 + 0.345 \tan\theta)^\circ$, profile analysis with a modified Lehmann & Larsen (1974) procedure; lattice parameters improved by least-squares refinement (GIVER: Krogmann, 1966) of 48 reflections ($10.5 \leq \theta \leq 13.4^\circ$); no absorption correction was applied, $(\sin\theta)_{\text{max}}/\lambda = 0.562 \text{ Å}^{-1}$, index range $h \pm 22, k 0/12, l 0/29$; six standard reflections used as intensity control (intensity variation 0.4%); 18 373 reflections were measured ($2.3 \leq \theta \leq 23.5^\circ$), after averaging equivalents 4432 reflections remained [including 20 unobserveds with $I < 3\sigma(I)$], $R_{\text{int}} = 0.020$; the positions of P atoms were located by direct methods, subsequent difference Fourier map revealed all C atoms, after refinement all H positions were taken from difference Fourier map; possible space groups: $I2/a, Ia, I2/a$ gave the best agreement in structure refinement; blocked least-squares refinement based on *F* and weights $w = 1/\sigma^2(F_o)$; final cycles refined scale factor, coordinates, anisotropic temperature factors for non-H atoms and isotropic for H atoms; $R = 0.057, wR = 0.027, S = 3.40, \text{max. } \Delta/\sigma = 0.50, \Delta\rho = -0.12 \text{ to } 0.11 \text{ e Å}^{-3}$; scattering factors taken from *International Tables for X-ray Crystallography* (1974). The CRYSTAN system (Buzlaff, Gomm & Zimmermann, 1986) was used for all computations and diagrams were drawn with ORTEPII (Johnson, 1977).

Discussion. Positional coordinates of the non-H atoms and equivalent isotropic temperature factors are reported in Table 1.* Table 2 lists bond lengths and angles. Fig. 1 shows the molecule and numbering scheme.

The central N atom is surrounded by three P atoms in the shape of an almost equilateral triangle. The

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43986 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distance between the N atom and the plane through the three P atoms is 0.16 Å. The PNP angles do not differ significantly from 120° [P(1)–N–P(2): 120.12 (8), P(2)–N–P(3): 118.39 (8), P(3)–N–P(1): 119.01 (8)°]. These results are in accord with a planar NP₃ group. For a P–N single bond a distance of 1.80 Å is calculated from the sum of covalent radii (Pauling, 1973). The differences between this estimated value and the measurements [P(1)–N: 1.737 (1), P(2)–N: 1.739 (1), P(3)–N: 1.745 (2) Å] indicate single bonds with some *pπ*–*dπ* interactions between N and P.

A comparable NP₃ moiety is contained in N(PF₂)₃ (Arnold, Rankin, Todd & Seip, 1979). The molecular structure was determined by electron diffraction in the gas phase to give an N–P distance of 1.712 (4) Å for a trigonal-planar NP₃ arrangement. These authors note that the N–P distance in molecules of the NP₂ type is shorter than in comparable molecules with an NP₃ unit. This fact can be confirmed by comparing our results

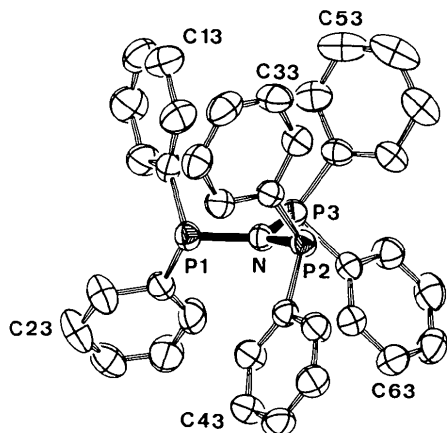


Fig. 1. Perspective view of the molecule with 50% probability thermal ellipsoids. The C atoms possess a two-digit symbol, whereby the first digit stands for the ring number and the second for the atom number. All C atoms which are attached to the P atoms have the atom number one. The H atoms are omitted for clarity.

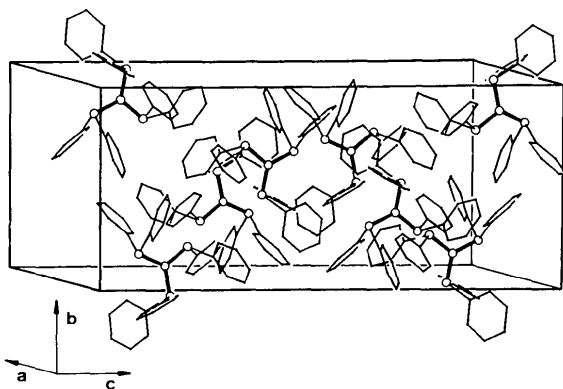


Fig. 2. Molecular packing in the crystal of tris(diphenylphosphino)amine.

with data for the following compounds: (C₆H₅)₂P–NH–P(C₆H₅)₂ (Nöth & Fluck, 1984) N–P: 1.692 (2), (C₆H₅)₂P–N(ⁱPr)–P(C₆H₅)₂ (Keat, Manojlović-Muir, Muir & Rycroft, 1981) N–P: 1.706 (4), 1.711 (4) Å.

According to the VSEPR method of Gillespie (1967) a pyramidal configuration is deduced for trivalent P. The angles found (see Table 2) are as expected and agree within the limits of error with other phosphines such as P(C₆H₅)₃ (Daly, 1964) C–P–C: 103.0° (mean value), or (C₆H₅)₂P–N(ⁱPr)–P(C₆H₅)₂ (Keat *et al.*, 1981) C–P–C: 101.8° (mean value). The planes formed by each P atom and its two C substituents are almost perpendicular to the P₃ plane [C(11)–P(1)–C(21): 82.5, C(31)–P(2)–C(41): 84.0, C(51)–P(3)–C(61): 84.9°].

In each diphenylphosphino group one ring lies above and the other below the P₃ plane (see Fig. 1). The P–C distances are normal and range from 1.823 (2) to 1.843 (2) Å. The phenyl rings are inclined to the P₃ plane at the following angles (ring 1–ring 6): 85.9, 54.4, 78.2, 61.6°, 82.0, 61.2°. This arrangement reduces the highest possible point group *D*_{3h} to *C*₁. Phenyl-ring geometry is unexceptional (Table 2).

The nearest intermolecular contacts are between H(64)⋯H(64ⁱ) and H(54)⋯H(63ⁱⁱ) at a distance of 2.44 (2) Å. The P atoms have only H atoms as nearest neighbours (see Table 2). Thus van der Waals forces are responsible for the crystal packing, which can be described as a [100]-stacking of distorted hexagonal nets (Fig. 2).

We thank Dr W. Wend for preparation of the compound. This work was supported by the Deutsche Forschungsgemeinschaft, the Verband der Chemischen Industrie and the Fonds der Chemischen Industrie.

References

- ARNOLD, D. E. J., RANKIN, D. W. H., TODD, M. R. & SEIP, R. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1290–1293.
- BURZLAFF, H., GOMM, M. & ZIMMERMANN, H. (1986). *CRYSTAN. A Crystallographic Program System for Minicomputers*. Univ. of Erlangen, Federal Republic of Germany.
- DALY, J. J. (1964). *J. Chem. Soc.* pp. 3799–3810.
- ELLERMANN, J. & WEND, W. (1985). *J. Organomet. Chem.* **281**, C29–C32.
- GILLESPIE, R. J. (1967). *Angew. Chem.* **79**, 885–896; *Angew. Chem. Int. Ed. Engl.* **6**, 819–830.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1977). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KEAT, R., MANOJLOVIĆ-MUIR, L., MUIR, K. W. & RYCROFT, D. S. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2192–2198.
- KROGMANN, K. (1966). *GIVER. Algol-Programm zur Verfeinerung von Gitterkonstanten und einiger Dinge mehr*. Univ. of Stuttgart, Federal Republic of Germany.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.

NÖTH, H. & FLUCK, E. (1984). *Z. Naturforsch. Teil B*, **39**, 744–753.
 NÖTH, H. & MEINEL, L. (1967). *Z. Anorg. Allg. Chem.* **349**, 225–240.

PAULING, L. (1973). *Die Natur der chemischen Bindung*, 3rd ed. p. 217. Weinheim/Bergstrasse: Verlag Chemie.
 SCHMIDBAUR, H., LAUTESCHLÄGER, S. & KÖHLER, F. H. (1984). *J. Organomet. Chem.* **271**, 173–180.

Acta Cryst. (1987). **C43**, 1798–1800

Structure of 5-(Diphenylphosphino)uracil

BY HELMUTH ZIMMERMANN* AND MARTIN GOMM

*Institut für Angewandte Physik, Lehrstuhl für Kristallographie der Universität Erlangen-Nürnberg,
 Bismarckstrasse 10, D-8520 Erlangen, Federal Republic of Germany*

AND JOCHEN ELLERMANN AND EBERHARD KÖCK

*Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-8520 Erlangen,
 Federal Republic of Germany*

(Received 6 March 1987; accepted 21 April 1987)

Abstract. $C_{16}H_{13}N_2O_2P$, $M_r = 296.27$, monoclinic, $P2_1/c$, $a = 12.005$ (4), $b = 9.804$ (2), $c = 12.628$ (3) Å, $\beta = 106.02$ (2)°, $V = 1429$ (2) Å³, $Z = 4$, $D_x = 1.38$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 1.91$ cm⁻¹, $F(000) = 616$, room temperature, final $R^2 = 0.042$ for 3294 unique reflections including unobserved. The title compound is a modified uracil in which the H atom at position C(5) is replaced by a diphenylphosphine group. The uracil ring has expected bond lengths and angles but deviates from planarity more than usual. The P atom shows normal pyramidal coordination geometry. Hydrogen bonds connect the molecules to form (100) layers in the crystal. These layers are held together by van der Waals forces.

Introduction. The title compound was synthesized in order to study the coordination properties of a diphenylphosphine-substituted uracil molecule. In chemotherapy, C(5)-substituted pyrimidine nucleosides are used as cytostatic drugs, hence it was of interest to test this substance for possible anticancer effects. Experiments showed only a very small antitumour activity (Ellermann & Demuth, 1983), and for this reason the X-ray structure of 5-(diphenylphosphino)uracil is of great interest to our continuing investigations.

Experimental. The compound was prepared using the procedure reported by Ellermann & Demuth (1983). Recrystallization from a mixture of dimethyl sulfoxide and water gave transparent plates of dimensions $0.56 \times 0.56 \times 0.28$ mm. Philips PW 1100 diffrac-

tometer (graphite monochromator, Mo $K\alpha$ radiation); ω - 2θ scan mode, scan width $(0.900 + 0.345 \tan\theta)^\circ$, profile analysis with a modified Lehmann & Larsen (1974) procedure; lattice parameters refined by least-squares procedure *GIVER* (Krogmann, 1966) on the basis of 47 reflections with $17.3 \leq 2\theta \leq 22.6^\circ$; no absorption correction was applied; $(\sin\theta_{\max})/\lambda = 0.65$ Å⁻¹, index range $-15 \leq h \leq 15$, k 0–12, l 0–16; eight standard reflections (intensity variation 0.4%); 13208 reflections ($2 \leq \theta \leq 27.5^\circ$) were measured, after averaging symmetrical equivalents, 3300 reflections [12 unobserved included, $I < 3\sigma(I)$] remained; $R_{\text{int}} = 0.012$. Structure solved by direct methods, subsequent Fourier map revealed all non-H atoms and all H atoms could be located from a difference Fourier map; final refinement by blocked least-squares methods (based on $|F|$) of scale factor, coordinates and anisotropic temperature parameters (H atoms isotropic). Reflections with strong extinction effects were omitted. Refinement was concluded with 3294 reflections after omission of $\bar{3}11$, 111 , 012 , $\bar{1}13$, 013 and 113 . $R = 0.042$, $wR = 0.036$, $S = 6.93$, $w = 1/\sigma^2(|F_o|)$, max. $\Delta/\sigma = 0.16$; $\Delta\rho$ in the final difference Fourier synthesis $+0.34$ and -0.23 e Å⁻³; scattering factors from *International Tables for X-ray Crystallography* (1974). Computations employed the *CRYSTAN* system (Burzlaff, Böhme & Gomm, 1977) and *ORTEPII* (Johnson, 1977) for plotting purposes.

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43978 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Author for correspondence.