reduced conjugation with the acetyl group as indicated by the relatively long N(1)–C(3) bond. Further, there is a rotation of the acetyl group about the N(1)–C(3) bond [the C(1)–C(2)–C(3) and N(1)–O(3)–C(4) planes lie at an angle of about 8°].

As shown in Fig. 2 the almost planar molecules lie perpendicular to crystallographic mirror planes passing through C(1), O(1) and the midpoint of the C(2)–C(2′) bond and are closely packed in a herring-bone pattern to form layers parallel to these planes. The closeness of the intra-layer packing is shown by the presence of relatively short intermolecular contacts [H(3)–O(3′), O(1)–C(2′), H(1)–O(3′), O(2)–N(1′) and O(2)–C(3′) of 2·68 (8), 2·794 (8), 2·80 (6), 2·977 (6) and 2·994 (8) Å respectively] and is reflected in the relatively high density of the material. The separation between the layers of molecules is determined primarily by intermolecular H–H′ contacts ranging from 2·49 (9) to 2·61 (10) Å.

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Structure of Antischistosome Compounds. III. (3-Cyanopropyl)triphenylphosphonium Bromide

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Abstract. $C_{22}H_{21}NP^+.Br^-$, $M_r = 410·3$, monoclinic, $P2_1/c$, $a = 11·284\,(1)$, $b = 10·236\,(1)$, $c = 17·392\,(2)$ Å, $\beta = 105·33\,(45)$°, $V = 1937·37$ Å^3, $Z = 4$, $D_x = 1·407$ g cm^{-3}, graphite-monochromatized Cu $K\alpha$ radiation, $\lambda = 1·5418$ Å, $\mu = 37·1$ cm^{-1}, $F(000) = 840$, $T = 292$ K. Final $R = 0·044$ for 3335 observed reflections. Structure solved by direct methods. The cyanopropyl moiety is in an extended conformation. However, the C–C–C–C torsion angle in this group is *gauche*$^+$, which points the cyano group in a direction similar to the direction of the N–Br1 vector observed in the (2-aminoethyl)triphenylphosphonium bromide hydrobromide structure and the C–Br vector in the (3-bromopropyl)triphenylphosphonium bromide structure. This suggests a basis for the biological activities of these three compounds.

Introduction. This communication is the third structure to be reported in a series of 17 triphenylphosphonium compounds which exhibit varying effects on the cholinergic nervous system of *Schistosoma mansoni* (McAllister, Dotson, Grim & Hillman, 1980). The differences in the biological effects of these 17 compounds cannot be explained solely on the basis of the differences in the chemical properties of the substituted moiety. Differences in the torsion angles in the substituted moieties may be the reason for the observed biological activities of these 17 triphenylphosphonium compounds. In order to ascertain if there is a structural basis for the observed biological activities of these triphenylphosphonium compounds, the crystal-structure determinations of the compounds in this series were initiated.

Experimental. Sample provided by Professor G. Hillman, synthesized as described in McAllister *et al.* (1980); colorless crystals (from ethanol), 0·20 × 0·30 × 0·70 mm; Enraf–Nonius CAD-4 diffractometer, cell parameter from 2θ values for 25 reflections from least-squares refinement with $11 \le 2\theta \le 64$°; ω–2θ scan, width $(1·00 + 0·15\tan\theta)$°, $[(\sin\theta)/\lambda]_{max} = 0·6092$ Å^{-1}, $-14 \le h \le 0$, $-13 \le k \le 0$, $-22 \le l \le 22$; intensities of three standard reflections monitored every 7200 s showed a linear decline in intensity of 3·0%, correction applied; 3672 unique reflections measured, 3335 reflections with $I > 3\sigma(I)$; Lp correc-

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Table 1. *Positional and equivalent isotropic thermal parameters*

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as:

$$B_{eq} = \tfrac{4}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23}).$$

Numbers in parentheses are e.s.d.'s in the least-significant digits.

	x	y	z	B_{eq}(Å^2)
Br	0·38605 (4)	0·13151 (5)	0·83567 (3)	3·917 (9)
P	0·22390 (8)	−0·1983 (1)	0·96228 (5)	2·63 (2)
C11	0·3215 (3)	−0·0685 (4)	1·0121 (2)	2·95 (7)
C12	0·2782 (4)	−0·0091 (4)	1·0811 (2)	3·56 (8)
C13	0·3480 (4)	0·1164 (5)	1·1121 (3)	4·1 (1)
C14	0·3034 (4)	0·2257 (5)	1·0597 (3)	4·8 (1)
N15	0·2619 (6)	0·3072 (5)	1·0182 (3)	8·2 (2)
C21	0·3039 (3)	−0·3003 (4)	0·9090 (2)	2·88 (7)
C22	0·3438 (4)	−0·2451 (4)	0·8470 (2)	3·48 (8)
C23	0·4070 (4)	−0·3215 (5)	0·8056 (2)	4·12 (9)
C24	0·4303 (4)	−0·4509 (5)	0·8252 (3)	4·26 (9)
C25	0·3895 (4)	−0·5059 (5)	0·8859 (3)	4·5 (1)
C26	0·3274 (4)	−0·4307 (4)	0·9275 (2)	3·76 (9)
C31	0·1788 (3)	−0·2933 (4)	1·0367 (2)	2·98 (7)
C32	0·2718 (4)	−0·3447 (5)	1·0981 (2)	4·07 (9)
C33	0·2418 (4)	−0·4175 (5)	1·1567 (2)	4·5 (1)
C34	0·1225 (4)	−0·4381 (5)	1·1555 (2)	4·7 (1)
C35	0·0297 (4)	−0·3878 (5)	1·0957 (3)	4·7 (1)
C36	0·0575 (4)	−0·3154 (4)	1·0350 (2)	3·79 (9)
C41	0·0927 (3)	−0·1323 (4)	0·8915 (2)	2·85 (7)
C42	0·0745 (4)	0·0013 (4)	0·8814 (2)	3·54 (8)
C43	−0·0264 (4)	0·0477 (5)	0·8240 (3)	4·3 (1)
C44	−0·1083 (4)	−0·0367 (6)	0·7773 (3)	4·8 (1)
C45	−0·0909 (4)	−0·1701 (6)	0·7858 (3)	4·8 (1)
C46	0·0091 (4)	−0·2180 (5)	0·8428 (3)	3·95 (9)

tions; structure solved by *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) which revealed the Br, N, P and five C atoms, remaining C and H atoms revealed by Fourier and difference Fourier syntheses; full-matrix least squares minimizing $w(F_o-F_c)^2$ with unit weights; min. and max. absorption correction of 0·776 and 1·495, respectively, using program *DIFABS* (Walker & Stuart, 1983); final $R = 0·044$, $wR = 0·048$; all H atoms from ΔF map and refined isotropically; 311 variables with secondary-extinction correction, $g = 8·27\ (19) \times 10^{-7}$ (Stout & Jensen, 1968), $S = 1·45$, max. $\Delta/\sigma = 0·02$ for non-H atoms, 0·06 for H atoms; no significant features in final ΔF synthesis with $\Delta\rho$ max. and min. = 0·59 (7) and −0·71 (7) e Å^{-3}, respectively, around the Br$^-$ ion; atomic scattering factors, f' and f'', from *International Tables for X-ray Crystallography* (1974); all calculations with a DEC PDP 11/44 computer using Enraf–Nonius *SDP-Plus* package (Frenz, 1985).

Discussion. Table 1* lists the fractional atomic coordinates of the non-H atoms and isotropic thermal parameters. Fig. 1 shows the structure of the molecule with the thermal vibration ellipsoids of the non-H atoms. The packing of the molecules is shown in Fig. 2. Ring 3 and ring 4 appear to form stacking arrangements with their respective equivalent rings at $-x,-1-y,2-z$ and $-x,\frac{1}{2}+y,1\frac{1}{2}-z$. However, the closest contact between these rings is only 3·766 Å. The cyano group is no closer than 3·465 Å and makes an angle of 50·5° with ring 2 at equivalent position $1-x,-y,2-z$. All other intermolecular distances correspond to normal van der Waals interactions. Bond lengths and

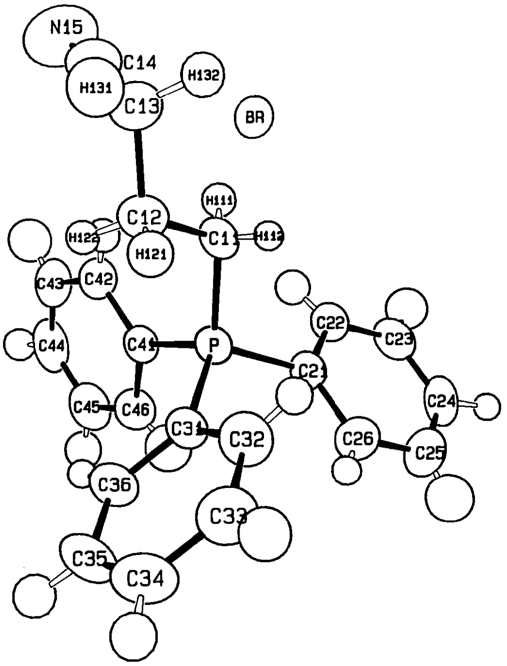

Fig. 1. A perspective view of the molecule showing the atom-labeling scheme. Only the cyanopropyl H atoms are labeled. Thermal ellipsoids are drawn at the 50% probability level.

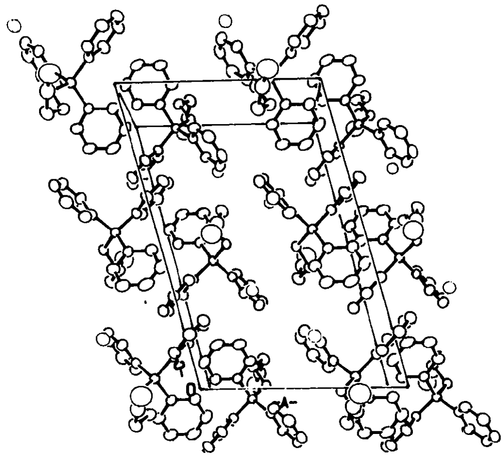

Fig. 2. The packing of the molecules in the unit cell viewed along the *b* axis.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and thermal parameters, bond lengths and angles involving H atoms, torsion angles and least-squares-planes' calculations (Tables 3–8) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44680 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *angles* (°) *and selected torsion angles* (°)

Numbers in parentheses are e.s.d.'s in the least-significant digits.

P	C11	1·796 (3)	C25	C26	1·368 (5)
P	C21	1·792 (3)	C31	C32	1·388 (5)
P	C31	1·797 (3)	C31	C36	1·379 (5)
P	C41	1·788 (3)	C32	C33	1·375 (5)
C11	C12	1·536 (5)	C33	C34	1·357 (6)
C12	C13	1·529 (5)	C34	C35	1·367 (6)
C13	C14	1·446 (6)	C35	C36	1·391 (5)
C14	N15	1·122 (6)	C41	C42	1·387 (5)
C21	C22	1·393 (5)	C41	C46	1·398 (5)
C21	C26	1·382 (5)	C42	C43	1·385 (5)
C22	C23	1·382 (5)	C43	C44	1·365 (6)
C23	C24	1·377 (6)	C44	C45	1·382 (6)
C24	C25	1·378 (6)	C45	C46	1·380 (5)

C11	P	C21	110·6 (1)	C21	C26	C25	120·9 (4)
C11	P	C31	107·9 (2)	P	C31	C32	117·4 (3)
C11	P	C41	110·1 (2)	P	C31	C36	122·8 (3)
C21	P	C31	109·6 (2)	C32	C31	C36	120·0 (3)
C21	P	C41	107·6 (1)	C31	C32	C33	119·5 (4)
C31	P	C41	111·1 (1)	C32	C33	C34	120·7 (4)
P	C11	C12	112·8 (2)	C33	C34	C35	120·7 (4)
C11	C12	C13	111·6 (3)	C34	C35	C36	119·8 (4)
C12	C13	C14	111·5 (3)	C31	C36	C35	119·5 (4)
C13	C14	N15	175·8 (5)	P	C41	C42	121·8 (3)
P	C21	C22	118·3 (3)	P	C41	C46	118·9 (3)
P	C21	C26	122·3 (3)	C42	C41	C46	119·2 (3)
C22	C21	C26	119·3 (3)	C41	C42	C43	119·7 (4)
C21	C22	C23	119·4 (4)	C42	C43	C44	120·6 (4)
C22	C23	C24	120·5 (4)	C43	C44	C45	120·5 (4)
C23	C24	C25	120·2 (4)	C44	C45	C46	119·6 (4)
C24	C25	C26	119·8 (4)	C41	C46	C45	120·4 (4)

C21	P	C11	C12	−159·3 (3)	P	C11	C12	C13	−169·4 (3)
C31	P	C11	C12	−39·4 (3)	C11	C12	C13	C14	77·2 (5)
C41	P	C11	C12	81·9 (3)	C12	C13	C14	N15	35·4 (77)

angles of the non-H atoms and selected torsion angles are given in Table 2. The phenyl-ring numbers and atom numbers are assigned as previously described (Czerwinski, 1986).

The P atom of the cation has a nearly perfect tetrahedral arrangement. The average P—C distance is 1·793 (4) Å. The C—P—C angles vary from 107·6 to 111·1° with an average of 109·5 (14)°. The 3·5° range is comparable to the 2·1–7·3° ranges observed in other triphenylphosphonium compounds (Skapski & Stephens, 1974; Bart, Bassi & Calcaterra, 1980, 1981; Archer, Modro & Nassimbeni, 1981; Kovacs & Parkanyi, 1982; Henichart, Houssin, Vaccher, Foulon & Baert, 1983; Goldstein, Takusagawa, Srivastava & Knapp, 1986; Czerwinski, 1986; Ponnuswamy & Czerwinski, 1986). The Br^- ion is 3·914 (3) Å from the closest C atom and 4·661 (1) Å from the P atom. As observed in other similar-type structures, the Br^- ion is face-oriented with respect to the phosphonium center (Archer *et al.*, 1981; Czerwinski, 1986; Ponnuswamy & Czerwinski, 1986).

The average C—C bond length of the three phenyl rings is 1·380 (11) Å. Least-squares-planes' calculations show that the three phenyl rings are planar with a maximum displacement of 0·007 (4) Å. The dihedral angles of rings 3 and 4 relative to the C21–C31–C41 plane, 38·3 (2) and 94·7 (1)°, respectively, are nearly the same as found in the 2-aminoethyl structure (Table 8; Czerwinski, 1986). The cyanopropyl compound and the 2-aminoethyl compound crystallize in different space groups which could mean that the ring orientations are not determined by the crystal packing forces. The substituted moiety may exert a greater influence on the ring orientations than previously thought.

The bond angles of the cyanopropyl groups are within normal limits. The length of the C14—N15 bond is 0·04 Å shorter than the corresponding value reported for propionitrile (Lerner & Dailey, 1957). The C12—C13 and the C13—C14 bonds are 0·02Å shorter. The C11—C12 bond distance is also shorter but within experimental limits. These shorter-than-expected bond lengths are most likely due to the high thermal motion in this group (Table 1).

The cyanopropyl group is in an extended conformation. The P—C11—C12—C13 torsion angle of the cyanopropyl group is *trans*. However, the C11—C12—C13—C14 torsion angle is *gauche*$^+$, which directs the cyano moiety along a vector nearly parallel to the P–C41 vector. Interestingly, this vector is qualitatively in a direction similar to the N13–Br1 and the C13–Br14 vectors observed in the 2-aminoethyl structure (Czerwinski, 1986) and the 3-bromopropyl structure (Czerwinski & Ponnuswamy, 1988), respectively. Furthermore, the distances of the atoms in the substituted moiety from the C21–C31–C41 reference plane [2·393 (4), 2·954 (4), 4·464 (5), 4·778 (5), 4·953 (6) Å] are remarkably similar in these three structures (Table 8; Czerwinski, 1986; Czerwinski & Ponnuswamy, 1988). These three structures have similar biological activities (McAllister *et al.*, 1980). It may be that this particular conformation of the substituted moieties results in the observed biological activity. However, the structures of the compounds in this series which are active and inactive must be determined before a definite conclusion can be made.

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Structure of 4-Methylumbelliferyl-*β*-D-glucopyranoside

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Abstract. $C_{16}H_{17}O_8.1{\cdot}5H_2O$, $M_r = 364{\cdot}33$, monoclinic, $C2$, $a = 14{\cdot}314\,(3)$, $b = 6{\cdot}851\,(1)$, $c = 18{\cdot}178\,(5)$ Å, $\beta = 100{\cdot}90\,(2)°$, $V = 1750{\cdot}46$ Å^3, $Z = 4$, $D_x = 1{\cdot}382$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}933$ mm^{-1}, $F(000) = 768$, $T = 294$ K, $R = 0{\cdot}078$ for all 2160 reflections. The structure is characterized by the close stacking along the *b* axis of the planar 4-methylumbelliferyl ring system which is nearly perpendicular to **b** and the extensive hydrogen bonding scheme in which all hydroxyl groups are within 2·95 Å of at least two other O atoms.

Introduction. The structure of 4-methylumbelliferyl-*β*-D-glucopyranoside was determined as part of a conformational study of substrates of *β*-glucosidases. This compound is used as a fluorogenic substrate for the determination of *β*-glucosidase activity. Clinical applications include the diagnosis of Gaucher disease (Yaqoob & Carroll, 1980). Information regarding the geometry of the sugar–chromophore link and the overall conformation of the molecule is useful for mapping of the active site and for the determination of the enzymatic mechanism.

Experimental. The compound was purchased from Sigma (St Louis, Missouri). Needle-shaped crystals were obtained by slow evaporation of an aqueous acetone solution. The crystal used had approximate dimensions of 0·61 × 0·15 × 0·17 mm. Systematic absences ($h + k = 2n$) observed on Weissenberg photographs. The chirality of the molecule excluded all space groups other than *C*2. Nicolet *P*3 diffractometer, Mo $K\alpha$ radiation, Nb filter. Unit-cell dimensions and orientation matrix were determined from 25 reflections with 2θ values in the range 20·0 to 28·5°. 2617 total data with $4 < \theta < 55°$, $-1 < h < 19$, $0 < k < 9$, $-24 < l < 24$, $h + k = 2n$. Intensities of five standard reflections (227, 62$\bar{8}$, 621, 24$\bar{1}$, 33$\bar{4}$) were monitored after every 139th measurement but did not decline significantly. Validity of the orientation matrix was not monitored. Lorentz and polarization corrections were applied but no absorption correction. Of the 2190 unique data, 1605 had $F > 4\sigma(F)$ and were considered observed. $\sigma(F)$ was calculated according to Stout & Jensen (1968): $\sigma^2(F) = (k/4\text{Lp}I)[\sigma^2(I) + (0{\cdot}01I)^2]$.

E statistics were appropriate for a centrosymmetric space group, indicative of a high degree of pseudosymmetry. Structure determination attempts using *MULTAN* (Germain, Main & Woolfson, 1971) and *SHELX*84 (Sheldrick, 1984) resulted in false solutions. Both programs yielded two-dimensional 'chicken wire' solutions perpendicular to the *b* axis in which one or more possible solutions for the umbelliferyl portion of the molecule could be identified. However, the peaks in these solutions were offset from the correct positions. The structure was determined using the program *QTAN* (Langs & DeTitta, 1975) after the removal of 18 of the top 200 triples which cosine seminvariant analysis (Hauptman, 1972) indicated to be less likely to be correct and after the starting set was expanded to ten phases to force certain groups of reflections (including *ggg*) to participate in the phasing early on. The correct solution had the lowest NQEST figure-of-merit (DeTitta, Edmonds, Langs & Hauptman, 1975) but not

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