worthy that all calculated intermolecular packing contacts which were approximately equal to or less than the sum of the van der Waals radii for the atoms involved consisted of what may be described as weak C—H···O interactions. O(6)···H(18C) (ADC = 45404) distance = 2·54 (4) Å; O(5)···H(14A) (ADC = 45504) distance = 2·61 (4) Å; O(3)···H(17A) (ADC = 65603) distance = 2·61 (4) Å.* According to the criteria set forth by Taylor & Kennard (1982), it is clear that none of these interactions can be considered to be a C—H···O hydrogen bond; however, it is likely that these interactions may play a role in determining the molecular packing of this compound. Berkovitch-Yellin & Leiserowitz (1984) in their atom–atom potential-energy calculation approach to the question of Coulomb and van der Waals energy contributions to C(sp^3)—H···O, C(sp^2)—H···O, and C(sp)—H···O interactions in a variety of crystal structures concluded that Coulombic contributions are dominant and are thus important even for long H···O distances.

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* The ADC (atom designator code) specifies the positions of the target atom in a crystal. The five-digit number is a composite of three one-digit numbers and one two-digit number: TA (1st digit) + TB(2nd digit) + TC (3rd digit) + SN (4th and 5th digits), where TA, TB, and TC are the crystal lattice translation digits along cell edges *a*, *b*, and *c* with a value of 5 indicating the origin unit cell and SN refers to the number of the symmetry operator used to generate the coordinates of the target atom.

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Structure of Antischistosome Compounds. V. 1,6-Hexanediylbis(triphenylphosphonium) Dibromide

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Abstract. $C_{42}H_{42}P_2^{2+}.2Br^-$, $M_r = 768·6$, triclinic, $P\bar{1}$, $a = 13·328$ (2), $b = 23·110$ (3), $c = 9·417$ (1) Å, $\alpha = 90·75$ (1), $\beta = 109·62$ (1), $\gamma = 91·23$ (1)°, $V = 2730·86$ Å^3, $Z = 3$, $D_x = 1·402$ g cm^{-3}, graphite-monochromatized Cu $K\alpha$ radiation, $\lambda = 1·5418$ Å, $\mu = 52·0$ cm^{-1}, $F(000) = 1182$, $T = 292$ K. Final $R =$

0108-2701/89/071034-06$03.00

0·051 for 5225 reflections with $I > 3\sigma(I)$. Structure solved by Patterson methods and ΔF syntheses. One molecule is located at the center of symmetry of the unit cell. The hexane moieties of all three molecules are in the *trans* extended conformation. However, one of the P–C–C–C torsion angles in the complete molecule in the asymmetric unit is 118·4 (6)°, the corresponding P–C–C–C torsion angle about the other P atom being 178·7 (5)°. This creates a conformational asymmetry in an otherwise symmetric molecule. This conformation permits the formation of a nearly square, planar, noncovalent interaction involving this P atom with one of the Br^- ions and a symmetry-related Br^-–P interaction. The remaining P atoms and Br^- ions are noncovalently linked to this square, approximately along the *a* axis. This noncovalent network is nearly parallel to the {011} plane, but does not extend beyond the {020} and {0$\bar{2}$0} planes. The half-molecule in the asymmetric unit is approximately 45° to the whole molecule, with two of its phenyl rings directed toward and perpendicular to one of the phenyl rings of the asymmetric triphenylphosphonium group of the whole molecule. There are no Br^- ions in the region between the phenyl rings, nor are there any intermolecular contacts involving C atoms. The orientations of the nine phenyl rings around the three P atoms in the asymmetric unit are different.

Introduction. This communication is the fifth 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. The four compounds of this series whose structures have been reported have similar conformations and similar low biological activity (Czerwinski, 1986; Ponnuswamy & Czerwinski, 1986; Czerwinski & Ponnuswamy, 1988*a*,*b*). The diylbis compounds are particularly effective in blocking the acetylcholine receptor of the schistosomes from the paralytic effect of carbachol (McAllister *et al.*, 1980). 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), 0·05 × 0·13 × 0·05 mm; Enraf–Nonius CAD-4 diffractometer, cell parameters from 2θ values for 25 reflections from least-squares refinement, $14 < 2\theta < 36°$; ω–2θ scan, width $(0{\cdot}90 + 0{\cdot}15\tan\theta)°$, $[(\sin\theta)/\lambda]_{max} = 0{\cdot}6092$ Å^{-1}, $-15 \le h \le 15$, $-28 \le k \le 28$, $0 \le l \le 11$; intensities of three standard reflections monitored every 3600 s showed a non-linear increase in intensity of 9·6%, anisotropic correction applied; 10364 unique reflections measured, 5225 reflections with $I > 3\sigma(I)$; Lp corrections; structure solved by Patterson method which revealed two P and three Br atoms, remaining P and all C and H atoms revealed by Fourier and difference Fourier syntheses; full-matrix least squares minimizing $\sum w(F_o - F_c)^2$ with unit weights; min. and max. absorption correction of 0·796 and 1·331, respectively, using program *DIFABS* (Walker & Stuart, 1983); final $R = 0{\cdot}051$, $wR = 0{\cdot}057$; all H atoms from ΔF map and refined isotropically; 893 variables with secondary-extinction correction, $g = 1{\cdot}46\ (19) \times 10^{-6}$ (Stout & Jensen, 1968), included but not refined; $S = 2{\cdot}32$, max. $\Delta/\sigma = 0{\cdot}05$ for non-H atoms, 0·08 for H atoms; no significant features in final ΔF synthesis with $\Delta\rho$ max. and min. = 0·54 (4) and −0·73 (4) e Å^{-3}, respectively, around the Br^- ions; 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 molecules in the asymmetric unit with the thermal vibration ellipsoids of the non-H atoms. The packing of the molecules is shown in Fig. 2. All intermolecular distances involving C and H correspond to normal van der Waals interactions. Bond lengths, angles and selected torsion angles of the non-H atoms, and noncovalent-interaction distances and angles between P^+ and Br^- ions are given in Table 2. The phenyl-ring numbers and atom numbers are assigned as previously described (Czerwinski, 1986), with one modification required because of the presence of one and one-half molecules in the asymmetric unit. The first digit following the atom type refers to the propyltriphenylphosphonium fragment of the complete molecule. Least-squares-planes calculations show that all the phenyl rings are planar.

The P atoms have nearly perfect tetrahedral arrangements (Table 2). The average P–C bond lengths are 1·793 (6), 1·795 (7) and 1·794 (5) Å for fragments 1, 2

* 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 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51636 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and 3, respectively. The average C—P—C bond angles for each of the three P atoms is 109·5° with standard deviations of 1·3, 1·1 and 2·0° for fragments 1, 2 and 3, respectively. The bond-angle ranges observed are well within the 2·1–7·3° range observed in other alkyl-substituted triphenylphosphonium compounds (Skapski & Stephens, 1974; Bart, Bassi & Calcaterra, 1980, 1981; Archer, Modro & Nassimbeni, 1981; Kovacs & Parkanyi, 1982; Henichart, Houssin,

Table 1. *Positional and equivalent isotropic thermal parameters*

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

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

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

	x	y	z	B_{eq}(Å^2)
Br1	0·40195 (8)	0·23358 (5)	0·0164 (1)	5·99 (2)
Br2	−0·04306 (7)	0·10671 (4)	1·2943 (1)	4·69 (2)
Br3	0·79729 (9)	0·41979 (5)	0·0733 (1)	7·34 (3)
P1	0·2711 (1)	0·02205 (8)	0·5610 (2)	2·98 (4)
C111	0·1504 (5)	0·0270 (3)	0·6038 (7)	3·3 (2)
C112	0·1656 (6)	0·0484 (3)	0·7667 (8)	4·1 (2)
C113	0·1108 (6)	0·1042 (3)	0·7727 (8)	4·4 (2)
C121	0·2450 (5)	−0·0206 (3)	0·3914 (7)	3·2 (1)
C122	0·3135 (6)	−0·0640 (3)	0·3854 (8)	4·0 (2)
C123	0·2938 (7)	−0·0966 (4)	0·2541 (9)	5·2 (2)
C124	0·2073 (7)	−0·0856 (4)	0·1299 (8)	5·2 (2)
C125	0·1395 (7)	−0·0427 (4)	0·1357 (9)	5·1 (2)
C126	0·1570 (6)	−0·0098 (3)	0·2666 (8)	4·2 (2)
C131	0·3232 (5)	0·0921 (3)	0·5341 (7)	3·1 (1)
C132	0·3353 (6)	0·1058 (3)	0·4004 (8)	4·5 (2)
C133	0·3746 (7)	0·1603 (4)	0·3814 (9)	5·4 (2)
C134	0·3997 (7)	0·2014 (4)	0·498 (1)	5·3 (2)
C135	0·3896 (6)	0·1873 (3)	0·6297 (9)	4·7 (2)
C136	0·3497 (6)	0·1333 (3)	0·6514 (8)	4·2 (2)
C141	0·3693 (5)	−0·0134 (3)	0·7097 (7)	3·1 (1)
C142	0·3388 (6)	−0·0601 (3)	0·7785 (8)	3·9 (2)
C143	0·4163 (6)	−0·0913 (3)	0·8817 (9)	4·6 (2)
C144	0·5228 (7)	−0·0762 (4)	0·9136 (9)	5·2 (2)
C145	0·5529 (6)	−0·0294 (4)	0·8519 (8)	4·6 (2)
C146	0·4768 (6)	0·0020 (3)	0·7479 (8)	4·0 (2)
P2	0·0364 (1)	0·26579 (8)	1·1290 (2)	3·30 (4)
C211	0·0998 (5)	0·1995 (3)	1·1098 (7)	3·5 (2)
C212	0·0755 (6)	0·1802 (3)	0·9448 (8)	4·2 (2)
C213	0·1327 (6)	0·1251 (3)	0·9354 (8)	4·4 (2)
C221	0·0645 (5)	0·2823 (3)	1·3263 (7)	3·3 (2)
C222	0·1230 (6)	0·2464 (3)	1·4359 (8)	4·1 (2)
C223	0·1435 (6)	0·2610 (4)	1·5872 (8)	4·6 (2)
C224	0·1048 (6)	0·3123 (4)	1·6206 (8)	5·0 (2)
C225	0·0458 (6)	0·3476 (3)	1·5135 (8)	4·6 (2)
C226	0·0256 (6)	0·3336 (3)	1·3623 (8)	4·1 (2)
C231	0·0881 (5)	0·3237 (3)	1·0471 (7)	3·3 (2)
C232	0·1950 (6)	0·3228 (3)	1·0569 (8)	4·4 (2)
C233	0·2395 (6)	0·3686 (4)	1·0023 (9)	4·8 (2)
C234	0·1812 (7)	0·4157 (4)	0·9439 (9)	5·2 (2)
C235	0·0765 (7)	0·4168 (3)	0·9342 (9)	5·2 (2)
C236	0·0291 (6)	0·3712 (3)	0·9856 (9)	4·7 (2)
C241	−0·1049 (5)	0·2579 (3)	1·0428 (8)	3·4 (2)
C242	−0·1503 (6)	0·2594 (4)	0·8853 (8)	4·3 (2)
C243	−0·2598 (6)	0·2500 (4)	0·8205 (8)	4·6 (2)
C244	−0·3201 (6)	0·2409 (4)	0·906 (1)	4·9 (2)
C245	−0·2773 (6)	0·2397 (4)	1·0613 (9)	5·1 (2)
C246	−0·1691 (6)	0·2474 (4)	1·1250 (8)	4·4 (2)
P3	0·6210 (2)	0·38003 (9)	0·4210 (2)	3·90 (4)
C311	0·5682 (6)	0·3959 (4)	0·2242 (8)	4·6 (2)
C312	0·5330 (8)	0·4581 (4)	0·1872 (9)	5·8 (2)
C313	0·5106 (7)	0·4693 (4)	0·0181 (9)	5·3 (2)
C321	0·6824 (6)	0·3107 (3)	0·4385 (8)	3·9 (2)
C322	0·6155 (6)	0·2622 (3)	0·3840 (9)	4·6 (2)
C323	0·6573 (7)	0·2083 (4)	0·3946 (9)	5·4 (2)
C324	0·7657 (7)	0·2013 (4)	0·4555 (9)	5·4 (2)
C325	0·8308 (6)	0·2496 (4)	0·5041 (8)	4·9 (2)
C326	0·7903 (6)	0·3044 (3)	0·4977 (8)	4·3 (2)
C331	0·7206 (6)	0·4341 (3)	0·5148 (8)	4·3 (2)
C332	0·7852 (7)	0·4554 (4)	0·4402 (9)	5·5 (2)
C333	0·8645 (7)	0·4961 (4)	0·508 (1)	6·8 (3)
C334	0·8817 (8)	0·5146 (4)	0·657 (1)	7·4 (3)
C335	0·8172 (9)	0·4924 (5)	0·728 (1)	8·1 (3)
C336	0·7352 (8)	0·4519 (4)	0·6619 (9)	6·0 (2)
C341	0·5197 (6)	0·3742 (3)	0·5054 (8)	4·1 (2)
C342	0·4148 (7)	0·3866 (4)	0·430 (1)	6·1 (2)
C343	0·3393 (7)	0·3794 (5)	0·501 (1)	7·6 (3)
C344	0·3702 (7)	0·3619 (5)	0·647 (1)	7·1 (3)
C345	0·4728 (7)	0·3489 (4)	0·7223 (9)	5·7 (2)
C346	0·5484 (6)	0·3559 (4)	0·6558 (9)	5·1 (2)

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

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

Molecular fragment 1

P1—C111	1·790 (5)	C131—C132	1·363 (7)
P1—C121	1·793 (4)	C131—C136	1·395 (6)
P1—C131	1·802 (5)	C132—C133	1·390 (7)
P1—C141	1·786 (5)	C133—C134	1·388 (8)
C111—C112	1·551 (6)	C134—C135	1·338 (8)
C112—C113	1·506 (7)	C135—C136	1·390 (7)
C113—C213	1·530 (7)	C141—C142	1·388 (6)
C121—C122	1·384 (6)	C141—C146	1·393 (7)
C121—C126	1·384 (7)	C142—C143	1·381 (7)
C122—C123	1·384 (7)	C143—C144	1·384 (8)
C123—C124	1·371 (8)	C144—C145	1·350 (8)
C124—C125	1·367 (8)	C145—C146	1·379 (7)
C125—C126	1·389 (7)		

C111—P1—C121	109·0 (2)	P1—C131—C132	121·1 (4)
C111—P1—C131	112·2 (2)	P1—C131—C136	119·3 (4)
C111—P1—C141	109·9 (2)	C132—C131—C136	119·6 (5)
C121—P1—C131	108·6 (2)	C131—C132—C133	120·2 (5)
C121—P1—C141	108·1 (2)	C132—C133—C134	120·1 (5)
C131—P1—C141	109·1 (2)	C133—C134—C135	119·4 (5)
P1—C111—C112	114·7 (3)	C134—C135—C136	121·8 (5)
C111—C112—C113	113·3 (4)	C131—C136—C135	119·1 (5)
C112—C113—C213	111·4 (4)	P1—C141—C142	119·4 (4)
P1—C121—C122	119·8 (4)	P1—C141—C146	120·6 (4)
P1—C121—C126	120·1 (4)	C142—C141—C146	119·8 (4)
C122—C121—C126	120·2 (4)	C141—C142—C143	119·2 (5)
C121—C122—C123	119·8 (5)	C142—C143—C144	119·9 (5)
C122—C123—C124	120·0 (5)	C143—C144—C145	121·3 (5)
C123—C124—C125	120·3 (5)	C144—C145—C146	119·5 (5)
C124—C125—C126	120·8 (5)	C141—C146—C145	120·3 (5)
C121—C126—C125	119·0 (5)		

C121—P1—C111—C112	164·7 (5)	P1—C111—C112—C113	118·4 (6)
C131—P1—C111—C112	−75·1 (6)	C111—C112—C113—C213	−177·1 (6)
C141—P1—C111—C112	46·4 (6)	C112—C113—C213—C212	−178·1 (7)

Molecular fragment 2

P2—C211	1·802 (5)	C231—C232	1·397 (7)
P2—C221	1·801 (5)	C231—C236	1·381 (7)
P2—C231	1·790 (5)	C232—C233	1·390 (7)
P2—C241	1·787 (5)	C233—C234	1·362 (8)
C211—C212	1·535 (6)	C234—C235	1·369 (8)
C212—C213	1·514 (7)	C235—C236	1·390 (8)
C221—C222	1·368 (7)	C241—C242	1·403 (7)
C221—C226	1·387 (7)	C241—C246	1·354 (7)
C222—C223	1·393 (7)	C242—C243	1·392 (7)
C223—C224	1·377 (8)	C243—C244	1·328 (7)
C224—C225	1·347 (8)	C244—C245	1·383 (8)
C225—C226	1·389 (7)	C245—C246	1·369 (7)

C211—P2—C221	109·3 (2)	P2—C231—C232	118·4 (4)
C211—P2—C231	109·7 (2)	P2—C231—C236	122·6 (4)
C211—P2—C241	110·5 (2)	C232—C231—C236	118·8 (5)
C221—P2—C231	108·8 (2)	C231—C232—C233	120·0 (5)
C221—P2—C241	107·7 (2)	C232—C233—C234	120·8 (6)
C231—P2—C241	110·0 (2)	C233—C234—C235	119·4 (5)
P2—C211—C212	112·9 (3)	C234—C235—C236	121·2 (4)
C211—C212—C213	110·6 (4)	C231—C236—C235	119·8 (5)
C113—C213—C212	112·5 (4)	P2—C241—C242	119·4 (4)
P2—C221—C222	121·6 (4)	P2—C241—C246	121·7 (4)
P2—C221—C226	117·0 (4)	C242—C241—C246	118·8 (5)
C222—C221—C226	121·5 (5)	C241—C242—C243	118·3 (5)
C221—C222—C223	119·8 (5)	C242—C243—C244	120·9 (5)
C222—C223—C224	118·0 (5)	C243—C244—C245	122·0 (5)
C223—C224—C225	122·8 (5)	C244—C245—C246	117·2 (5)
C224—C225—C226	119·7 (5)	C241—C246—C245	122·8 (5)
C221—C226—C225	118·4 (5)		

C221—P2—C211—C212	177·0 (5)	P2—C211—C212—C213	178·7 (5)
C231—P2—C211—C212	−63·8 (6)	C211—C212—C213—C113	−179·9 (7)
C241—P2—C211—C212	58·7 (6)		

Table 2 (*cont.*)

Molecular fragment 3

P3–C311	1·794 (5)	C331–C332	1·369 (7)
P3–C321	1·800 (5)	C331–C336	1·388 (7)
P3–C331	1·794 (5)	C332–C333	1·377 (8)
P3–C341	1·786 (5)	C333–C334	1·40 (1)
C311–C312	1·530 (8)	C334–C335	1·35 (1)
C312–C313	1·545 (8)	C335–C336	1·393 (9)
C313–C313^{i}	1·476 (8)	C341–C342	1·377 (7)
C321–C322	1·396 (7)	C341–C346	1·411 (7)
C321–C326	1·368 (7)	C342–C343	1·390 (9)
C322–C323	1·367 (8)	C343–C344	1·37 (1)
C323–C324	1·377 (8)	C344–C345	1·354 (9)
C324–C325	1·374 (8)	C345–C346	1·361 (8)
C325–C326	1·382 (7)		

C311–P3–C321	107·9 (3)	P3–C331–C332	118·2 (4)
C311–P3–C331	109·0 (3)	P3–C331–C336	120·8 (5)
C311–P3–C341	112·5 (3)	C332–C331–C336	120·8 (5)
C321–P3–C331	109·0 (2)	C331–C332–C333	120·8 (6)
C321–P3–C341	106·9 (2)	C332–C333–C334	119·6 (6)
C331–P3–C341	111·6 (3)	C333–C334–C335	118·0 (6)
P3–C311–C312	115·7 (4)	C334–C335–C336	124·0 (7)
C311–C312–C313	110·3 (5)	C331–C336–C335	116·7 (6)
C312–C313–C313^{i}	111·9 (5)	P3–C341–C342	123·0 (5)
P3–C321–C322	117·3 (4)	P3–C341–C346	118·5 (4)
P3–C321–C326	122·7 (4)	C342–C341–C346	118·5 (5)
C322–C321–C326	119·9 (5)	C341–C342–C343	120·0 (6)
C321–C322–C323	120·1 (5)	C342–C343–C344	119·7 (7)
C322–C323–C324	120·6 (6)	C343–C344–C345	121·0 (6)
C323–C324–C325	118·7 (6)	C344–C345–C346	120·5 (6)
C324–C325–C326	121·8 (6)	C341–C346–C345	120·2 (6)
C321–C326–C325	119·0 (5)		

C321–P3–C311–C312	−168·0 (6)	P3–C311–C312–C313	168·8 (6)
C331–P3–C311–C312	−49·9 (8)	C311–C312–C313–C313^{i}	−172·9 (8)
C341–P3–C311–C312	74·4 (7)	C312–C313–C313^{i}–C312^{i}	180·0 (6)

Noncovalent interactions

Br1–P2^{ii}	5·386 (2)	Br2–P2	4·261 (2)
Br1–P3	5·124 (2)	Br3–P2^{v}	4·745 (2)
Br2–P1^{iii}	4·592 (2)	Br3–P3	4·715 (3)
Br2–P1^{iv}	4·738 (2)		

P2^{ii}–Br1–P3	94·67 (4)	Br2^{ii}–P1–Br2^{iv}	83·24 (3)
P1^{iii}–Br2–P1^{iv}	96·76 (3)	Br1^{iii}–P2–Br2	106·89 (4)
P1^{iii}–Br2–P2	107·30 (4)	Br1^{iii}–P2–Br3^{v}	135·65 (5)
P1^{iv}–Br2–P2	154·20 (4)	Br2–P2–Br3^{v}	117·43 (5)
P2^{v}–Br3–P3	104·36 (4)	Br1–P3–Br3	84·24 (4)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x, y, z-1$; (iii) $x, y, z+1$; (iv) $-x, -y, 2-z$; (v) $x+1, y, z-1$.

Vaccher, Foulon & Baert, 1983; Goldstein, Takusagawa, Srivastava & Knapp, 1986; Czerwinski, 1986; Ponnuswamy & Czerwinski, 1986; Czerwinski & Ponnuswamy, 1988*a*,*b*).

The hexane moiety of fragments 1 and 2 and the propane moiety of fragment 3 are in the *trans* extended conformation (Table 2). However, the P–C11–C12–C13 torsion angle of fragment 1 is 118·4°. This results in ring 3 of fragment 1 being closely centered between rings 2 and 4 of fragment 3 and at right angles to them (Figs. 1 and 2). The *gauche* conformation of the P1–C11–C12–C13 torsion angle may be due to crystal packing considerations since the symmetry-related hexane moiety of fragment 3 is completely *trans*. On the other hand, fragment 3 may be forced into its conformation by the molecule composed of fragments 1 and 2. In any event, this arrangement permits the formation of an interesting and complicated noncovalent P^+–Br^- interaction system.

The $P1^+$ and $P3^+$ ions interact with two Br ions, whereas $P2^+$ interacts with three Br^- ions (Table 2 and Fig. 3). This results in a network in the crystal which is approximately parallel to the {011} plane, but does not extend beyond the {020} and {0$\bar{2}$0} planes. The regions between the noncovalent networks are devoid of Br^- ions and are occupied only by phenyl rings and the hexane moieties which connect the P^+ ions. The $Br2^-$–$P1^+$ distances are similar to the previously reported Br^-–P^+ distances in this series of compounds (Table 2). These interactions form a nearly square parallelogram (Fig. 3). Least-squares-plane calculations indicate that this parallelogram is planar to ±0·002 Å, with the $P2^+$ ions ±0·667 (2) Å out of the plane. The plane of the parallelogram is inclined at an angle of 53·58 (1)° to the *ac* plane and 37·87 (1)° to the *ab* plane. The $Br2^-$–$P2^+$ distance is short compared to those distances previously reported, whereas the $Br1^-$–$P2^+$ and Br1–$P3^+$ distances are rather long.

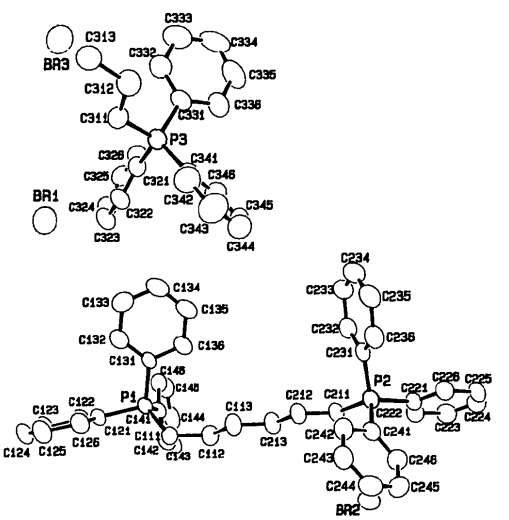

Fig. 1. Perspective view of the molecule showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. H atoms omitted for clarity.

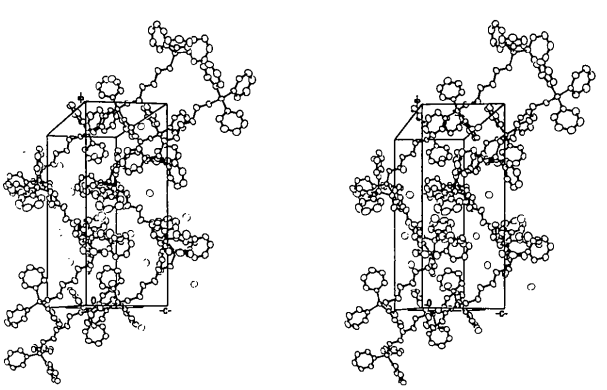

Fig. 2. Stereoview along the a^* axis showing the packing of the molecules in the unit cell.

It is axiomatic that the ions in a crystal must be neutralized. To neutralize the charge on the $Br2^-$ ion then, the short $Br2^-$—$P2^+$ interaction must neutralize half of the charge. The two longer $Br2^-$—$P1^+$ interactions would then neutralize the remaining $\frac{1}{2}$ charge. Since each $Br3^-$ ion is involved in two interactions of nearly equal distance which is similar in magnitude to the $Br2^-$—$P1^+$ distance, then each interaction neutralizes a quarter of the charge. The $Br1^-$ ions form weak interactions with $P2^+$ and $P3^+$ ions with distances of more than 5 Å. If each of the $Br1^-$—P^+ interactions neutralizes a quarter of the charge, then there remains $\frac{1}{2}$ charges on $Br1^-$, $Br3^-$, $P1^+$ and $P3^+$ to be neutralized. The closest anion to $P1^+$, at 6·277 (2) Å, is $Br1^-$ at symmetry position $x,y,z+1$. The nearest anion to $P3^+$, at 5·846 (3) Å, is $Br3^-$, also at $x,y,z+1$. Although these are long distances, the ions must be close enough to effectively neutralize their respective charges as the difference electron-density maps do not indicate the presence of any type of ion in this vicinity. This would result in complete charge neutralization in the crystal. However, this postulate requires that $Br1^-$—$P1^+$ and $Br3^-$—$P3^+$ distances of more than 5·8 Å allows each to neutralize half of a charge. This is unlikely, yet it appears to be the only possibility.

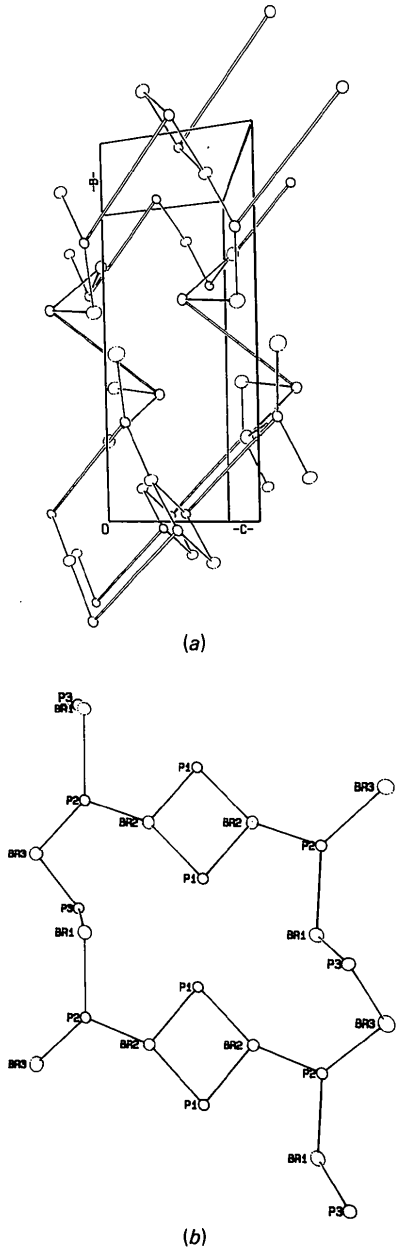

Fig. 3. (*a*) Perspective view along the *a* axis with single lines representing noncovalent interactions between the P^+ and Br^- ions. Double lines represent the hexane moiety connecting the P^+ ions in the molecule. C atoms omitted for clarity. (*b*) Perspective view of the noncovalent network perpendicular to the $P1^+$—$Br2^-$—$P1^+$—$Br2^-$ plane. The *a* axis is in the vertical direction and the *b* axis is in the horizontal direction.

The diylbis compounds have been shown to be particularly effective in blocking the interaction of carbachol with the acetylcholine receptors of schistosomes (McAllister *et al.*, 1980). The four compounds in this series whose crystal structures have been determined are not very effective in blocking the paralytic effect of carbachol. These four compounds have very similar conformations with their respective C11—C12—C13—C14 torsion angles all *gauche*$^+$ (Czerwinski, 1986; Ponnuswamy & Czerwinski, 1986; Czerwinski & Ponnuswamy, 1988*a*,*b*) whereas the comparable torsion angles of the title compound are all *trans* (Table 2). The distances of the C*n*11, C*n*12 and C*n*13 atoms from the C*n*21—C*n*31—C*n*41 reference plane in fragments 2 and 3 [2·407 (7), 3·017 (8), 4·529 (8); 2·399 (7), 3·095 (8), 4·591 (8) Å, respectively] are very similar to the same distances observed in the 2-aminoethyl (Czerwinski, 1986), 3-cyanopropyl (Czerwinski & Ponnuswamy, 1988*a*) and 3-bromopropyl (Czerwinski & Ponnuswamy, 1988*b*) structures. The fourth C atom in the chain from the C*n*21—C*n*31—C*n*41 reference plane in fragments 2 and 3, C113 and C313 (1−*x*, 1−*y*, −*z*), respectively, is 5·182 (8) and 5·260 (8) Å away. These are 0·35–0·50 Å farther than the observed distances in the 3-cyanopropyl and 3-bromopropyl structures. However, the C213 atom is 0·22–0·40 Å closer [4·558 (8) Å] to the C121—C131—C141 reference plane. The C111, C112 and C113 distances in fragment 1 are 2·412 (7), 3·085 (8) and 3·973 (8) Å. The shorter distance of C113 is because of the *gauche* P1—C111—C112—C113 torsion angle. This torsion angle places the P1 and the two H atoms of C111 in the eclipsed position with respect to the C112 substituents, which is of a higher energy than the *gauche*- or *trans*-position energies (Eisenberg & Crothers, 1979). This conformation of the molecule suggests that one end of the molecule preferentially binds to the acetylcholine receptor. However, because fragment 3, as well as the 2-aminoethyl, 3-cyanopropyl and 3-bromo-

propyl structures, has its P—C11—C12—C13 torsion angle in the lower-energy *trans* conformation, it is probable that the *gauche* P1—C111—C112—C113 torsion angle is a crystal packing phenomena and that it is the extended conformation which is required for biological activity. This is in agreement with the suggestion by Czerwinski & Ponnuswamy (1988*a*) that the conformation of the substituted moieties is the primary cause of the biological activity. However, it may be that the presence of a positive charge at the end of this extended hydrophobic chain and/or the length of the alkyl chain is the predominant factor in determining the biological effectiveness of the compound. Structure determinations of other active and inactive compounds in this series are currently underway to resolve this question.

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Structural and Molecular Orbital Study of Ergoline Derivatives. Ethyl 2(*S*)- and 2(*R*)-Cyano-2-(6-methylergolin-8β-yl)methylbutyrate

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Abstract. (I): $C_{23}H_{29}N_3O_2$, m.p. 510–512 K, $M_r = 379{\cdot}5$, monoclinic, $P2_1$, $a = 6{\cdot}189$ (2), $b = 13{\cdot}211$ (2), $c = 12{\cdot}855$ (2) Å, $\beta = 102{\cdot}76$ (2)°, $V = 1025{\cdot}1$ (4) Å^3, $Z = 2$, $D_x = 1{\cdot}22$ Mg m^{-3}, graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), $\mu = 0{\cdot}07$ mm^{-1}, $F(000) = 408$, $T = 293$ K, final $R = 0{\cdot}047$ for 1626 independent reflections. (II): $C_{23}H_{29}N_3O_2$, m.p. 496–498 K, $M_r = 379{\cdot}5$, monoclinic, $P2_1$, $a = 6{\cdot}224$ (1),

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