

Discussion. Positional and equivalent isotropic thermal parameters are given in Table 1.* Bond distances and angles for the two independent cobalt(III) cations are nearly identical as is demonstrated in Table 2 and are in good agreement with the less accurate structures of *trans*-[CoCl₂(en)₂]Cl (Becker, Grosse & Plieth, 1959), *trans*-[CoCl₂(en)₂]Cl.HCl.2H₂O (Nakahara, Saito & Kuroya, 1952), and *trans*-[CoCl₂(en)₂]₂-[CoCl₄] (Schubert, Zimmer-Gasser, Dash & Chaudhury, 1981). The cations are close to C_{2h} symmetry, the deviation arising from a twist of the ethylenediamine ligand. The closest contact distances between the perchlorate anion and the cobalt chelates are N(2)···O(1) 3.047 (5) and N(2A)···O(1) 3.132 (5) Å. Figs. 1 and 2 illustrate the molecular structure of the cations and the unit-cell packing, respectively. Each Co atom occupies a special position (inversion center) in the unit cell. The ethylenediamine ligands must then adopt both δ and λ conformations in each molecule with Cl(C1A) and its symmetry-related pair making up the coordination. However, the two

molecules are crystallographically different since the inversion centers occupy either corner or edge positions. This results in alternating layers of cations which are rotated and tilted with respect to the previous set. The perchlorate anions are situated between the layers.

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cis/trans Disorder in (5-Bromo-4-pentenyl)triphenylphosphonium Iodide

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Abstract. C₂₃H₂₃BrP⁺.I⁻, *M_r* = 537.2, monoclinic, *P*2₁/*c*, *a* = 9.196 (1), *b* = 18.494 (1), *c* = 14.576 (1) Å,

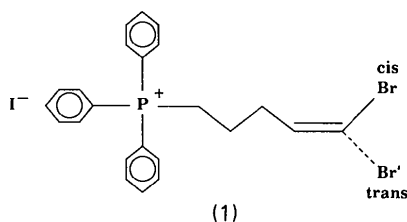
$\beta = 116.53 (1)^\circ$, *V* = 2217.9 Å³, *Z* = 4, *D_x* = 1.609 g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$, $\mu = 143.2 \text{ cm}^{-1}$, *F*(000) = 1056, room temperature, *R* = 0.069 for 3786 observed reflections. The configuration of the triphenylphosphonium ion deviates substantially from that of a symmetrical propeller. The extended alkyl chain is disordered between the *cis* and *trans*

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conformers with occupancies of $\frac{2}{3}$ and $\frac{1}{3}$, respectively. The triphenylphosphonium cations pack head to tail along **c** and head to head along **b**, with the I⁻ anion sitting in a pocket bounded on two sides by alkyl chains of neighboring molecules.

Introduction. The title compound (1) is one of a series of lipophilic phosphonium cations designed for use as myocardial imaging agents. The *trans* iodo analogue of (1) showed high selective myocardial uptake in rats and dogs (Srivastava & Knapp, 1984). This observation prompted the synthesis of the brominated compound (1), which showed similar uptake properties. However, the conformation across the olefinic bond in this agent was unknown. The crystal-structure determination of (1) was thus undertaken.



Experimental. Compound (1) synthesized in a manner similar to that described for the iodo analogue (Srivastava & Knapp, 1984). Clear parallelepiped-shaped crystals by recrystallization from chloroform-petroleum ether. Crystal size 0.27 × 0.13 × 0.07 mm. Enraf-Nonius CAD-4 diffractometer with graphite-monochromated CuK α radiation. Lattice constants by least-squares refinement of 24 reflections in range $\theta = 25-30^\circ$. Data collection by $\omega-2\theta$ scan method in range $2 < \theta < 70^\circ$. 4110 unique reflections measured in quadrant $-11 \leq h \leq 0$, $0 \leq k \leq 22$, $-16 \leq l \leq 16$. 3786 reflections with $|F_o| > \sigma(F_o)$ used in subsequent calculations. Three standard reflections showed no decay. Lp correction and empirical ψ -scan absorption correction (0.65–1.18) applied. I position from Patterson map. Remaining non-H atoms located from Fourier maps, which showed disorder between *cis* and *trans* conformers. All phenyl and two alkyl H atoms located from difference Fourier maps. Full-matrix least-squares refinement. Anisotropic for I, Br atoms and triphenylphosphonium moiety; isotropic for H atoms and disordered alkyl-chain C atoms. On the basis of initial refinements of occupancies of disordered atoms, occupancies fixed at $\frac{2}{3}$ for *cis* conformer, $\frac{1}{3}$ for *trans* conformer. The function minimized was $\sum w(|F_o| - |F_c|)^2 + \sum w'(D_o - D_c)^2$. D_o is the restrained interatomic distance, D_c the distance calculated from the structure. The second sum is over all atom pairs defining restrained bond lengths and angles (Takusagawa, 1982; Sussman, Holbrook, Church & Kim, 1977). Weights were $w = 1/[\sigma^2(F_o) + 0.5A|F_o|^2 +$

$0.5B(\sin\theta/\lambda)^2]^{1/2}$. Weights w' were adjusted to provide tight restraints, the maximum shift $|D_o - D_c|$ being 0.01 Å (Konnert, 1976; Rollett, 1970). Convergence to $R = 0.069$, $wR = 0.082$, $S = 1.51$ for 3786 reflections. $\Delta/\sigma < 0.1$ and 1.4 for unrestrained and restrained atoms, respectively. $\Delta\rho_{\max} = 2.1 \text{ e } \text{Å}^{-3}$ in the region of the disordered alkyl chain. Restrained distances were 1.54 Å for C(1)–C(2), C(2)–C(3), C(2')–C(3'); 1.52 Å for C(3)–C(4), C(3')–C(4'); 1.34 Å for C(4)–C(5), C(4')–C(5') and 1.89 Å for C(5)–Br, C(5')–Br' (Sutton, 1965). Restrained angles about sp^2 and sp^3 C atoms in the alkyl chain were 120 and 109.5°, respectively. Atomic scattering factors and anomalous-dispersion corrections (for I and Br) from *International Tables for X-ray Crystallography* (1974). Computations using the DNA system (Takusagawa, 1981) and a modification of program CRLS (Takusagawa, 1982).

Discussion. Atomic coordinates are listed in Table 1.* Unrestrained bond lengths, angles and selected torsion angles are listed in Table 2.

The molecular structure is illustrated in Fig. 1. The crystal is composed of a mixture of $\frac{2}{3}$ *cis* and $\frac{1}{3}$ *trans* conformers with random site-occupancy. The alkyl chain is extended in both cases, the Br and Br' positions lying within 0.5 Å of each other. Subsequent NMR and radiolabeling studies have confirmed that both conformers are taken up preferentially by myocardial cells *in vivo* (Srivastava, Knapp & Goldstein, 1985).

The P–C(1)–C(2) bond angle is 120.9 (5)°. This is probably due in part to a distortion in the P...C(2) distance introduced by the restraint placed on the C(1)–C(2) bond. However, large distortions from tetrahedral angles are not uncommon about sp^3 -hybridized alkyl-chain C atoms. Values of 117.0 (3), 117.2 (4) and 118.6 (2)° have been observed about C(sp^3) atoms in other triphenylphosphonium structures, due to both intra- and intermolecular steric factors (Kovács & Párkányi, 1982; Hjortås, 1973; Toupet, Weinberger, Abbayes & Gross, 1984).

The P–C(1) bond length of 1.773 (7) Å falls within the rather wide range of observed Ph₃P–C(sp^3) bond lengths [e.g. 1.755 (3) Å (Toupet *et al.*, 1984), 1.814 (3) Å (Kovács & Párkányi, 1982)]. The P–C(sp^2) bond lengths are within the expected range and the bond angles about the P atom show only small deviations from a tetrahedral geometry. The phenyl groups are planar within experimental error. The triphenylphosphonium moiety shows significant deviations from C₃ symmetry, ring *a* being rotated about the P–C(sp^2) bond to a greater extent than rings

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b and *c*. On the basis of a survey of a large number of triphenylphosphine structures, Bye, Schweizer & Dunitz (1982) have proposed a pathway for the stereo-isomerization of an equilibrium C_3 -symmetric structure to its enantiomer. The triphenylphosphonium geometry observed here [$\varphi_a = -65.9$ (5), $\varphi_b = +18.1$ (4), $\varphi_c = -22.7$ (6) $^\circ$] would lie along this pathway roughly between the C_3 -symmetric structure and a putative transition-state structure with torsion angles $\varphi_a = -90$, $\varphi_b = +10$, $\varphi_c = -10^\circ$ (Bye *et al.*, 1982).

Crystal packing is illustrated in Fig. 2. The triphenylphosphonium cations pack head to tail along *c* and head to head along *b*. The I^- anion sits in a pocket bounded on two sides by alkyl chains of neighboring molecules. It forms marginally close contacts of 3.842 (9) Å with C(3')(x, y, z), 3.780 (6) Å with C(4)(2-x, 1-y, -z) and 3.831 (5) Å with C(5)(2-x, 1-y, -z).

Table 1. Fractional coordinates and isotropic thermal parameters

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> / <i>B</i> _{eq} (Å ²)
I	0.75355 (7)	0.57845 (3)	0.15598 (5)	6.0 (1)
P	0.7315 (2)	0.30747 (8)	0.1379 (1)	3.2 (1)
C(1a)	0.7488 (8)	0.2247 (3)	0.0787 (4)	3.4 (4)
C(2a)	0.6113 (12)	0.2031 (4)	-0.0097 (6)	4.9 (5)
C(3a)	0.6251 (12)	0.1439 (5)	-0.0634 (7)	6.3 (6)
C(4a)	0.7675 (12)	0.1072 (5)	-0.0307 (7)	5.7 (5)
C(5a)	0.8994 (10)	0.1274 (5)	0.0562 (7)	5.3 (5)
C(6a)	0.8919 (9)	0.1866 (4)	0.1113 (6)	4.4 (5)
C(1b)	0.9098 (7)	0.3216 (3)	0.2570 (4)	3.3 (4)
C(2b)	0.9802 (9)	0.3891 (4)	0.2819 (6)	4.2 (4)
C(3b)	1.1152 (10)	0.3996 (5)	0.3759 (6)	5.3 (5)
C(4b)	1.1762 (10)	0.3437 (5)	0.4433 (6)	5.6 (5)
C(5b)	1.1068 (10)	0.2765 (5)	0.4204 (6)	5.4 (5)
C(6b)	0.9718 (12)	0.2653 (4)	0.3278 (5)	4.6 (4)
C(1c)	0.5566 (7)	0.3030 (3)	0.1604 (5)	3.5 (4)
C(2c)	0.4557 (8)	0.3626 (4)	0.1446 (6)	4.2 (4)
C(3c)	0.3244 (9)	0.3588 (5)	0.1664 (7)	5.1 (5)
C(4c)	0.2928 (9)	0.2959 (5)	0.2037 (7)	5.2 (5)
C(5c)	0.3889 (10)	0.2353 (5)	0.2184 (7)	5.1 (5)
C(6c)	0.5221 (9)	0.2392 (4)	0.1978 (6)	4.4 (4)
C(1)	0.7086 (6)	0.3787 (3)	0.0511 (5)	4.1 (4)
C(2)	0.8175 (6)	0.3832 (4)	-0.0043 (6)	7.1 (4)
C(3)*	0.7290 (7)	0.4297 (7)	-0.1012 (6)	8.2 (4)
C(3)†	0.8089 (11)	0.4609 (4)	-0.0435 (7)	8.3 (8)
C(4)*	0.8425 (7)	0.4429 (6)	-0.1492 (2)	6.1 (3)
C(4)†	0.6798 (9)	0.4641 (5)	-0.1546 (7)	12.2 (14)
C(5)*	0.7872 (5)	0.4428 (7)	-0.2511 (4)	5.8 (3)
C(5)†	0.7206 (10)	0.4483 (10)	-0.2300 (5)	4.0 (3)
Br*	0.5665 (5)	0.4644 (2)	-0.3376 (2)	6.8 (2)
Br†	0.5657 (8)	0.4591 (4)	-0.3688 (3)	4.9 (4)
H(1)	0.708 (8)	0.423 (3)	0.083 (5)	4 (1)
H(1')	0.603 (8)	0.379 (3)	0.003 (5)	3 (1)
H(2a)	0.502 (10)	0.229 (5)	-0.037 (6)	6 (2)
H(3a)	0.525 (12)	0.127 (5)	-0.108 (8)	8 (2)
H(4a)	0.788 (11)	0.069 (5)	-0.078 (8)	7 (2)
H(5a)	0.994 (9)	0.103 (4)	0.083 (6)	5 (2)
H(6a)	0.977 (12)	0.201 (6)	0.161 (8)	8 (3)
H(2b)	0.934 (9)	0.431 (4)	0.225 (6)	5 (2)
H(3b)	1.167 (11)	0.450 (5)	0.392 (8)	7 (2)
H(4b)	1.277 (11)	0.352 (5)	0.503 (8)	7 (2)
H(5b)	1.156 (11)	0.231 (5)	0.470 (7)	7 (2)
H(6b)	0.916 (9)	0.215 (4)	0.314 (6)	5 (2)
H(2c)	0.485 (10)	0.406 (5)	0.128 (7)	6 (2)
H(3c)	0.242 (11)	0.407 (6)	0.150 (7)	7 (3)
H(4c)	0.199 (9)	0.290 (4)	0.224 (6)	5 (2)
H(5c)	0.390 (12)	0.189 (6)	0.249 (8)	9 (3)
H(6c)	0.576 (9)	0.197 (4)	0.203 (6)	4 (2)

* Occupancy = $\frac{2}{3}$.

† Occupancy = $\frac{1}{3}$.

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Table 2. Selected bond distances (Å), angles ($^\circ$) and torsion angles ($^\circ$)

P-C(1)	1.773 (7)	C(2b)-C(3b)	1.392 (9)
P-C(1a)	1.798 (7)	C(3b)-C(4b)	1.363 (12)
P-C(1b)	1.797 (5)	C(4b)-C(5b)	1.368 (13)
P-C(1c)	1.782 (8)	C(5b)-C(6b)	1.381 (9)
C(1a)-C(2a)	1.402 (8)	C(6b)-C(1b)	1.395 (9)
C(2a)-C(3a)	1.385 (14)	C(1c)-C(2c)	1.392 (10)
C(3a)-C(4a)	1.358 (15)	C(2c)-C(3c)	1.381 (14)
C(4a)-C(5a)	1.358 (11)	C(3c)-C(4c)	1.369 (13)
C(5a)-C(6a)	1.378 (13)	C(4c)-C(5c)	1.384 (13)
C(6a)-C(1a)	1.377 (10)	C(5c)-C(6c)	1.388 (15)
C(1b)-C(2b)	1.377 (9)	C(6c)-C(1c)	1.394 (11)
C(1)-P-C(1a)	107.4 (3)	C(6b)-C(1b)-C(2b)	119.5 (5)
C(1)-P-C(1b)	110.3 (3)	C(1b)-C(2b)-C(3b)	119.5 (6)
C(1)-P-C(1c)	109.7 (3)	C(2b)-C(3b)-C(4b)	120.2 (8)
C(1a)-P-C(1b)	110.5 (3)	C(3b)-C(4b)-C(5b)	121.0 (7)
C(1b)-P-C(1c)	109.7 (3)	C(4b)-C(5b)-C(6b)	119.5 (7)
C(1c)-P-C(1a)	109.2 (3)	C(5b)-C(6b)-C(1b)	120.2 (7)
P-C(1)-C(2)	120.9 (5)	C(6c)-C(1c)-C(2c)	119.0 (8)
C(6a)-C(1a)-C(2a)	120.1 (7)	C(1c)-C(2c)-C(3c)	120.5 (7)
C(1a)-C(2a)-C(3a)	118.2 (7)	C(2c)-C(3c)-C(4c)	119.8 (8)
C(2a)-C(3a)-C(4a)	121.0 (7)	C(3c)-C(4c)-C(5c)	121.0 (9)
C(3a)-C(4a)-C(5a)	120.6 (9)	C(4c)-C(5c)-C(6c)	119.3 (8)
C(4a)-C(5a)-C(6a)	120.4 (8)	C(5c)-C(6c)-C(1c)	120.3 (7)
C(5a)-C(6a)-C(1a)	119.7 (6)		
φ_a C(1)-P-C(1a)-C(2a)		-65.9 (5)	
φ_b C(1)-P-C(1b)-C(2b)		18.1 (4)	
φ_c C(1)-P-C(1c)-C(2c)		-22.7 (6)	

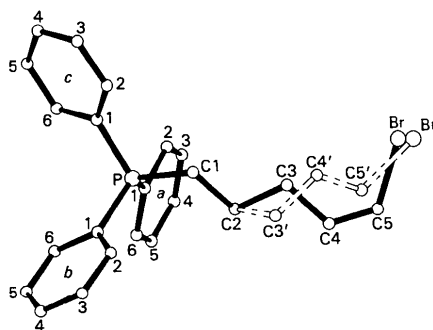


Fig. 1. Molecular structure of (1). The *trans* conformer is illustrated with unshaded dashed bonds.

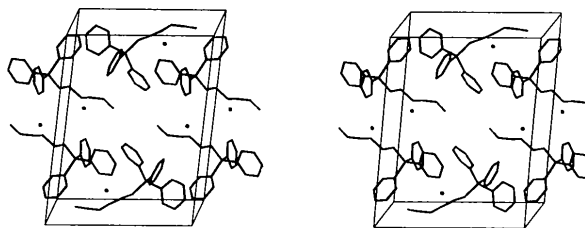


Fig. 2. Molecular packing viewed approximately down the *a* axis. Only the *cis* conformer is shown. The shaded circles represent the I^- anions.

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Structure of 3-Nitro-4-oxopyrido[1,2-*a*]pyrimidin-1-ium-2-olate and its Ammonium Salt

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Abstract. $C_8H_5N_3O_4$ (N-acid), $M_r = 207.15$, monoclinic, $P2_1/c$, $a = 4.7663$ (6), $b = 13.825$ (1), $c = 12.205$ (2) Å, $\beta = 96.45$ (1)°, $V = 799.1$ (5) Å³, $Z = 4$, $D_m = 1.71$ (1), $D_x = 1.722$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.132$ mm⁻¹, $F(000) = 424$, $T = 295$ K, $R = 0.039$ for 1727 unique observed reflections. $NH_4^+.C_8H_4N_3O_4^-$ (NH_4^+ -salt), $M_r = 224.18$, monoclinic, $P2_1/c$, $a = 7.489$ (1), $b = 7.524$ (2), $c = 16.401$ (4) Å, $\beta = 94.37$ (1)°, $V = 921.5$ (8) Å³, $Z = 4$, $D_m = 1.62$ (1), $D_x = 1.616$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.124$ mm⁻¹, $F(000) = 464$, $T = 295$ K, $R = 0.056$ for 1517 unique observed reflections. The nitro group is out of plane with the ring system both in the N-acid and the NH_4^+ -salt. Introduction of a nitro group between the two C–O groups does not change the H-tautomeric form of the molecule, but induces a shortening of the C–O bonds and an elongation of the C–C bonds in α position to the nitro group. Formation of the NH_4^+ -salt causes delocalization of negative charge from N to O through four bonds. The N-acid packs with centrosymmetric hydrogen-bonded dimers. The NH_4^+ -salt structure contains layers of cations.

Introduction. The structure determinations of 3-nitro-4-oxopyrido[1,2-*a*]pyrimidin-1-ium-2-olate and its ammonium salt are parts of a study of structural changes associated with the steps in the series: compound, nitro compound, anion of nitro compound.

Experimental. N-acid, prepared as described by Tschitschibabin (1924). Yellow-brown needles (a-direction needle axis) were obtained from the slow cooling of a solution in boiling water. D_m by flotation in a mixture of $CHCl_3$ and $CHBr_3$. NH_4^+ -salt, yellow needles (b-direction needle axis) separated from an NH_3 – H_2O solution of the N-acid. D_m by flotation in a mixture of CCl_4 and CH_2BrCl .

Crystals: $0.4 \times 0.2 \times 0.1$ mm (both N-acid and NH_4^+ -salt), Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized $Mo K\alpha$, lattice parameters from Guinier–Hägg photographs with $Cu K\alpha_1$ ($\lambda = 1.54051$ Å), N-acid, 30 reflections with $4.85 < \theta < 40.41^\circ$, NH_4^+ -salt, 25 reflections with $5.40 < \theta < 19.69^\circ$, Si used as an internal standard. N-acid, 2415 unique reflections ($h -6 \rightarrow 6$, $k 0 \rightarrow 19$, $l 0 \rightarrow 17$) with $2.0 < \theta < 30.0^\circ$, 1727 with $I > 2.5\sigma(I)$ used in refinement process. NH_4^+ -salt, 2681 unique reflections ($h 0 \rightarrow 10$, $k 0 \rightarrow 10$, $l -22 \rightarrow 22$) with $2.0 < \theta < 30.0^\circ$, 1517 with $I > 2.5\sigma(I)$ used in refinement process together with ‘less-than’ reflections [$I < 2.5\sigma(I)$] with calculated values greater than the observed (2306 contributing reflections). Mixed $\omega/2\theta$ scan technique, scan angle (N-acid: $1.00^\circ + 0.35^\circ \tan \theta$, NH_4^+ -salt: $1.40^\circ + 0.35^\circ \tan \theta$), standard reflections (N-acid: 153 and $3\bar{1}\bar{3}$, NH_4^+ -salt: $2\bar{3}2$, $20\bar{8}$ and $10\bar{6}$) used for orientation control every 100 reflections, intensity check every 10 800 s of exposure time by using (N-acid: 006, NH_4^+ -salt: $2\bar{3}\bar{3}$), standard intensity variations