

Table 2. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

Equivalent isotropic  $U$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	$x$	$y$	$z$	$U_{eq}$
C(1)	151 (3)	8859 (3)	3651 (1)	18 (1)
O(1)	-1381 (2)	9822 (2)	3763 (1)	22 (1)
O(2)	1966 (2)	8564 (2)	3968 (1)	21 (1)
C(2)	2078 (3)	9374 (3)	4517 (1)	18 (1)
C(3)	4029 (3)	10273 (3)	4645 (1)	20 (1)
C(4)	4322 (4)	10945 (3)	5198 (1)	22 (1)
C(5)	2707 (4)	10688 (3)	5608 (1)	23 (1)
C(6)	762 (4)	9774 (3)	5468 (1)	22 (1)
C(7)	434 (3)	9103 (3)	4914 (1)	20 (1)
O(3)	457 (2)	7841 (2)	3180 (1)	25 (1)
C(8)	-1266 (3)	7732 (3)	2773 (1)	18 (1)
C(9)	-3322 (4)	7066 (3)	2920 (1)	22 (1)
C(10)	-4859 (4)	6763 (3)	2492 (1)	24 (1)
C(11)	-4319 (3)	7131 (3)	1925 (1)	24 (1)
C(12)	-2261 (4)	7827 (3)	1788 (1)	25 (1)
C(13)	-699 (3)	8133 (3)	2214 (1)	21 (1)

$hkl$  affected by the correction, and the correction exceeded 15% for only 20 reflections. Details of the data collection are given in Table 1. Scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates are contained in Table 2.\* Fig. 1 illustrates the molecule with the numbering scheme employed. Fig. 2 illustrates the projected packing of the molecules viewed down the  $a$  axis.

**Related literature.** For additional information on related structures and chemistry see King & Bryant (1990), King & Codella (1990), Bicerano & Clark (1988), Perez & Scaringe (1987), Hutnik, Argon &

\* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55582 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1002]

*Acta Cryst.* (1993). C49, 551–554

## Structures of Two Polymorphic Acylpyridinium Salts

BY GAROLD L. BRYANT JR AND JOSEPH A. KING JR\*

*General Electric Company, Corporate Research and Development, Schenectady, NY 12301, USA*

(Received 10 February 1992; accepted 13 July 1992)

**Abstract.** *N*-Methoxycarbonyl-3-methylpyridinium tetraphenylborate (I),  $C_8H_{10}NO_2^+ \cdot C_{24}H_{20}B^-$ ,  $M_r = 471.4$ , monoclinic,  $P2_1/n$ ,  $a = 13.723$  (4),  $b =$

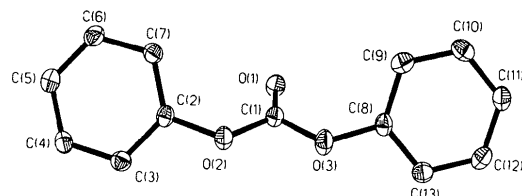


Fig. 1. Thermal ellipsoid (50% probability) plot.

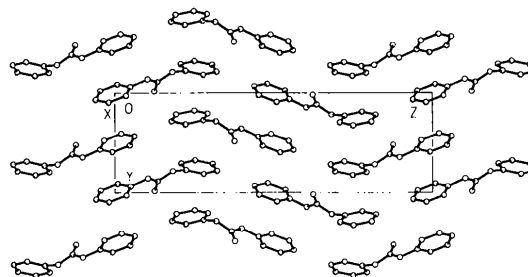


Fig. 2. Projected packing plot viewed down the  $a$  axis.

Suter (1991), and Schmidt, Dybal, Turska & Kalczycki (1991).

### References

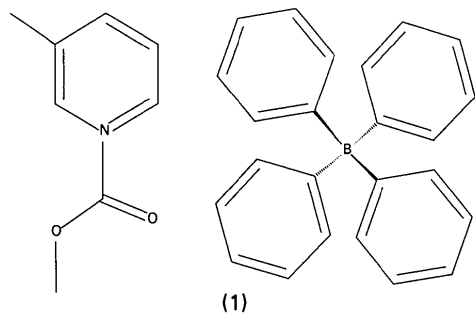
- BICERANO, J. & CLARK, H. A. (1988). *Macromolecules*, **21**, 585–597.  
 HUTNIK, M., ARGON, A. S. & SUTER, U. W. (1991). *Macromolecules*, **24**, 5936–5961.  
 KING, J. A. JR & BRYANT, G. L. JR (1990). *Acta Cryst.* C46, 1330–1332.  
 KING, J. A. JR & CODELLA, P. J. (1990). *Macromolecules*, **23**, 345–348.  
 PEREZ, S. & SCARINGE, P. (1987). *Macromolecules*, **20**, 68–77.  
 SCHMIDT, P., DYBAL, J., TURSKA, E. & KALCZYCKI, A. (1991). *Polymer*, **32**, 1862–1866.  
 SHELDRIK, G. M. (1988). *SHELXTL-Plus. R3m/V Crystallographic System User's Guide*. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.  
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

\* To whom correspondence should be addressed.

9.827 (3),  $c = 19.328$  (7)  $\text{\AA}$ ,  $\beta = 96.57$  (3) $^\circ$ ,  $V = 2589.3$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_x = 1.209$   $\text{g cm}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71069$   $\text{\AA}$ ,  $\mu = 0.69$   $\text{cm}^{-1}$ ,  $F(000) = 1000$ ,  $T = 173$  K,  $R = 0.0543$  for 3472 unique reflections with  $I > 4\sigma(I)$ . *N*-Methoxycarbonyl-3-methylpyridinium

tetraphenylborate (II),  $C_8H_{10}NO_2^+ \cdot C_{24}H_{20}B^-$ ,  $M_r = 471.4$ , monoclinic,  $P2_1/n$ ,  $a = 10.090$  (4),  $b = 14.762$  (6),  $c = 18.057$  (7) Å,  $\beta = 105.12$  (3)°,  $V = 2596.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.206$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.69$  cm<sup>-1</sup>,  $F(000) = 1000$ ,  $T = 213$  K,  $R = 0.0678$  for 2033 unique reflections with  $I > 4.5\sigma(I)$ . (I) and (II) are *N*-acylpyridinium salts. The N—C<sub>carbonyl</sub> bond lengths are 1.470 (3) in (I) and 1.474 (8) Å in (II). The O<sub>carbonyl</sub>—C<sub>carbonyl</sub> bond lengths of the carbonyl moieties are 1.188 (3) in (I) and 1.171 (7) Å in (II). The C<sub>methyl</sub>—O—C<sub>carbonyl</sub> angles are 114.0 (2)° in (I) and 115.0 (4)° in (II). The O<sub>methyl</sub>—C<sub>carbonyl</sub>—N angles are 108.9 (2) in (I) and 107.9 (4)° in (II). The N—C<sub>carbonyl</sub>—O<sub>carbonyl</sub> angles are 121.1 (2)° in (I) and 122.0 (6)° in (II). The molecules are essentially coplanar with the carboxyl moiety rotated slightly out of the plane of the pyridine in each case: 14.5 (2) in (I) and 15.0 (4)° in (II), respectively. The polymorphism may be the result of two minimal energy sites for the bulky tetraphenylborate anions relative to the acylpyridinium cation. The two tetraphenylborate anions differ primarily in their relative orientation of the appended phenyl groups.

**Experimental.** Yellow prisms of (1) were prepared by reacting methyl chloroformate, 3-methylpyridine and sodium tetraphenylborate in acetonitrile. The compounds were recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane at



253 K. The two polymorphs were separated in the manner of Pasteur. Crystals were sealed in glass capillaries for low-temperature data collection on a Siemens R3m/V upgrade of a Nicolet P3F automated diffractometer, using Wyckoff scans of variable scan speed. Both structures were solved by direct methods and refined on  $F$  using the *SHELXTL-Plus* (MicroVAX II) program package (Sheldrick, 1988). H atoms were placed in idealized positions and constrained to have C—H = 0.96 Å and isotropic thermal parameters,  $U = 0.08$  Å<sup>2</sup>. All non-H atoms were treated as anisotropic. No absorption correction was necessary for either structure. A correction for secondary extinction of the type described by Zachariasen (1967) refined in the later stages with a maximum correction of 21.4% (I) for the 052 reflec-

Table 1. *Experimental details*

Crystal	(I)	(II)
	Color/habit	Yellow prism
Size (mm)	0.26 × 0.24 × 0.20	0.36 × 0.32 × 0.30
Lattice-parameter determination		
No. of reflections	26	22
2θ range(°)	5.4–21.5	5.4–24.3
Reflection range		
<i>h</i>	0 to 17	0 to 13
<i>k</i>	0 to 12	0 to 19
<i>l</i>	–25 to 24	–23 to 23
Maximum sin θ/λ (Å <sup>-1</sup> )	0.650	0.650
Check reflections		
Variation (%)	311, 410	200, 033, 040
	5, 5	5, 5, 5
Reflections		
Collected	6542	6556
Unique observed	3472	2033
$R_{int}$	0.0196	0.0375
Observed criterion	$I > 4\sigma(I)$	$I > 4.5\sigma(I)$
No. of parameters	326	326
$R$	0.0543	0.0678
$wR$	0.0517	0.0546
$S$	1.47	1.38
Secondary-extinction parameter,		
$\chi$ , in $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	0.00080 (12)	0.00069 (12)
Weighting factor, $g$ ,		
in $w^{-1} = \sigma^2(F) + gF^2$	0.0003	0.0002
Difference Fourier peaks		
Minimum (e Å <sup>-3</sup> )	–0.24	–0.32
Maximum (e Å <sup>-3</sup> )	0.33	0.33
Maximum ( $\Delta\rho$ )	0.004	0.006

Table 2. *Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors (Å<sup>2</sup> × 10<sup>3</sup>) for (I)*

Equivalent isotropic  $U$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
N(1)	3160 (1)	2941 (2)	252 (1)	21 (1)
C(1)	2698 (2)	3949 (3)	–131 (1)	22 (1)
C(2)	2246 (2)	4996 (3)	187 (1)	23 (1)
C(3)	2273 (2)	4956 (3)	911 (1)	24 (1)
C(4)	2739 (2)	3900 (3)	1293 (1)	24 (1)
C(5)	3181 (2)	2892 (3)	955 (1)	23 (1)
C(6)	1738 (2)	6117 (3)	–241 (1)	39 (1)
C(7)	3646 (2)	1817 (3)	–75 (1)	24 (1)
O(1)	3885 (1)	810 (2)	241 (1)	31 (1)
O(2)	3761 (1)	2158 (2)	–715 (1)	31 (1)
C(8)	4155 (2)	1065 (3)	–1118 (2)	44 (1)
B(1)	146 (2)	2790 (3)	–2006 (1)	19 (1)
C(9)	314 (2)	1999 (3)	–2734 (1)	20 (1)
C(10)	86 (2)	610 (3)	–2831 (1)	26 (1)
C(11)	158 (2)	–62 (3)	–3456 (2)	33 (1)
C(12)	463 (2)	633 (3)	–4017 (1)	34 (1)
C(13)	683 (2)	2003 (3)	–3947 (1)	31 (1)
C(14)	610 (2)	2659 (3)	–3315 (1)	25 (1)
C(15)	–1054 (2)	2758 (2)	–2001 (1)	18 (1)
C(16)	–1688 (2)	3570 (3)	–2452 (1)	21 (1)
C(17)	–2708 (2)	3488 (3)	–2496 (1)	24 (1)
C(18)	–3142 (2)	2562 (3)	–2081 (1)	26 (1)
C(19)	–2545 (2)	1736 (3)	–1629 (1)	25 (1)
C(20)	–1525 (2)	1832 (3)	–1595 (1)	22 (1)
C(21)	610 (2)	4330 (3)	–1994 (1)	19 (1)
C(22)	1626 (2)	4478 (3)	–2057 (1)	23 (1)
C(23)	2087 (2)	5732 (3)	–2064 (1)	28 (1)
C(24)	1554 (2)	6923 (3)	–1996 (1)	28 (1)
C(25)	571 (2)	6827 (3)	–1912 (1)	26 (1)
C(26)	118 (2)	5554 (3)	–1911 (1)	22 (1)
C(27)	659 (2)	2014 (3)	–1302 (1)	22 (1)
C(28)	468 (2)	2503 (3)	–647 (1)	30 (1)
C(29)	811 (2)	1863 (3)	–27 (1)	41 (1)
C(30)	1379 (2)	703 (4)	–38 (2)	45 (1)
C(31)	1611 (2)	213 (3)	–666 (2)	44 (1)
C(32)	1255 (2)	860 (3)	–1289 (2)	33 (1)

tion, and 33.3% (II) for the  $\bar{3},9,16$  reflection. There were no apparent groups of  $hkl$  affected by the correction, and the correction exceeded 10% for only six reflections for (I) and four reflections for (II). Details of the data collection for both structures are

Table 3. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) for (II)

Equivalent isotropic  $U$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$
N(1)	551 (5)	2492 (3)	5637 (2)	23 (2)
C(1)	1554 (6)	1954 (3)	6068 (3)	25 (2)
C(2)	1258 (6)	1385 (4)	6602 (3)	27 (2)
C(3)	-81 (6)	1366 (4)	6678 (3)	31 (2)
C(4)	-1079 (6)	1933 (4)	6245 (3)	30 (2)
C(5)	-750 (6)	2504 (4)	5723 (3)	29 (2)
C(6)	2345 (6)	777 (4)	7087 (3)	46 (3)
C(7)	792 (6)	3092 (4)	5033 (3)	28 (2)
O(1)	5 (4)	3652 (3)	4743 (2)	40 (2)
O(2)	1959 (4)	2847 (2)	4893 (2)	26 (1)
C(8)	2350 (6)	3373 (4)	4295 (3)	37 (2)
B(1)	-3921 (6)	3707 (4)	7041 (3)	19 (2)
C(9)	-4857 (5)	4538 (3)	6597 (3)	18 (2)
C(10)	-4419 (6)	5439 (4)	6649 (3)	24 (2)
C(11)	-5269 (6)	6162 (4)	6339 (3)	27 (2)
C(12)	-6628 (6)	6007 (4)	5948 (3)	29 (2)
C(13)	-7131 (6)	5126 (4)	5886 (3)	28 (2)
C(14)	-6261 (5)	4414 (4)	6198 (3)	27 (2)
C(15)	-4237 (5)	3727 (3)	7895 (3)	21 (2)
C(16)	-3476 (6)	4247 (4)	8510 (3)	28 (2)
C(17)	-3855 (6)	4387 (4)	9189 (3)	32 (2)
C(18)	-5054 (6)	4001 (4)	9275 (3)	36 (2)
C(19)	-5836 (6)	3459 (4)	8700 (3)	32 (2)
C(20)	-5428 (6)	3334 (4)	8025 (3)	29 (2)
C(21)	-4294 (5)	2727 (3)	6610 (3)	21 (2)
C(22)	-4625 (6)	2656 (4)	5807 (3)	30 (2)
C(23)	-4829 (6)	1821 (4)	5435 (3)	40 (2)
C(24)	-4701 (6)	1022 (4)	5852 (4)	40 (3)
C(25)	-4359 (6)	1071 (4)	6645 (4)	33 (2)
C(26)	-4165 (5)	1907 (4)	7005 (3)	25 (2)
C(27)	-2276 (5)	3854 (3)	7105 (3)	20 (2)
C(28)	-1244 (6)	3467 (3)	7688 (3)	27 (2)
C(29)	147 (6)	3532 (4)	7714 (3)	35 (2)
C(30)	547 (6)	3998 (4)	7137 (3)	32 (2)
C(31)	-447 (6)	4380 (4)	6549 (3)	34 (2)
C(32)	-1838 (6)	4300 (4)	6521 (3)	27 (2)

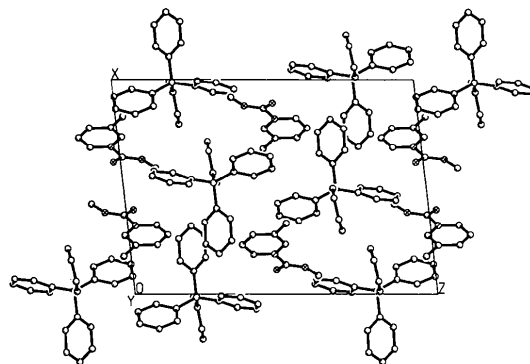


Fig. 3. Projected packing plot of (I) viewed down the  $b$  axis.

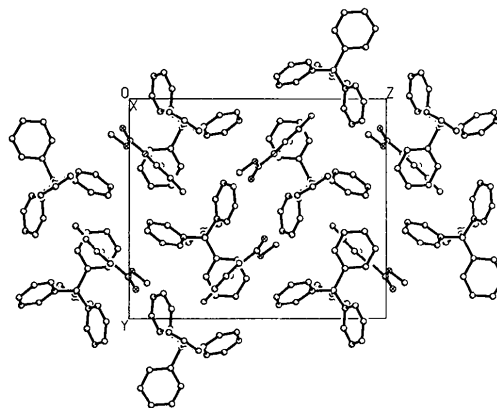


Fig. 4. Projected packing plot of (II) viewed down the  $a$  axis.

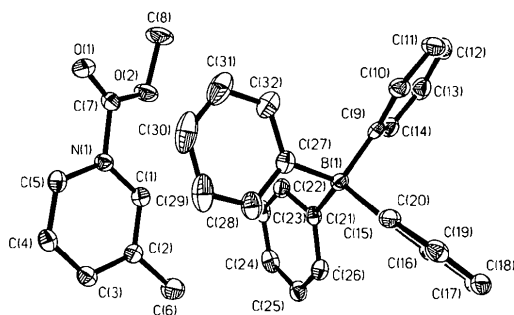


Fig. 1. Thermal ellipsoid (50% probability) plot of (I).

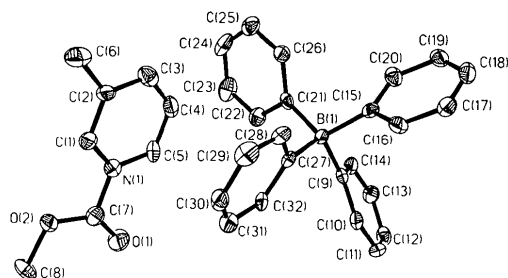


Fig. 2. Thermal ellipsoid (50% probability) plot of (II).

given in Table 1. Scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates are contained in Tables 2 and 3.\* Figs. 1 and 3 illustrate the molecules with the numbering scheme employed, while Figs. 2 and 4 illustrate the projected packing of the molecules viewed down the  $b$  and  $a$  axes, respectively.

**Related literature.** For additional information on related  $N$ -acylammonium salt reactions and structures see King & Bryant (1991), Bryant & King (1993), King (1988), and King, Donahue & Smith (1988).

\* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55583 (53 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1001]

#### References

- BRYANT, G. L. JR & KING, J. A. JR (1993). *Acta Cryst.* **C49**, 550–551.  
 KING, J. A. JR (1988). *J. Am. Chem. Soc.* **110**, 5764–5767.

KING, J. A. JR & BRYANT, G. L. JR (1991). *Acta Cryst.* C47, 2249–2252.

KING, J. A. JR, DONAHUE, P. E. & SMITH, J. E. (1988). *J. Org. Chem.* 53, 6145–6147.

SHELDRICK, G. M. (1988). *SHELXTL-Plus. R3m/V Crystallographic System User's Guide*. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* 23, 558–564.

*Acta Cryst.* (1993). C49, 554–556

## Structure of 19-Methylstrychninium (*S*)-{*S*-[(*R*)-1,2-Di(ethoxycarbonyl)ethyl] *O*-Methyl Phosphorodithioate}

BY C. E. BERKMAN, E. J. FERNANDEZ, C. M. THOMPSON AND S. F. PAVKOVIC\*

*Department of Chemistry, Loyola University Chicago, Chicago, Illinois 60626, USA*

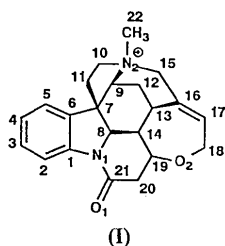
(Received 17 March 1992; accepted 15 July 1992)

**Abstract.**  $C_{22}H_{25}N_2O_2^+ \cdot C_9H_{16}O_6PS_2^-$ ,  $M_r = 664.77$ , monoclinic,  $P2_1$ ,  $a = 8.3925$  (14),  $b = 8.0054$  (14),  $c = 24.3050$  (42) Å,  $\beta = 98.518$  (6)°,  $V = 1614.9$  (6) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.42$  (3),  $D_x = 1.37$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å (Zr filter, no monochromator),  $\mu = 2.2$  cm<sup>-1</sup>,  $F(000) = 704$ ,  $T = 294$  (2) K,  $R = 0.049$  and  $wR = 0.046$  for 2417 unique observed reflections. The crystal structure consists of sheets of *N*-methylstrychninium cations in a bilayer, which alternate with sheets of phosphorodithioate anions, also in a bilayer. The anion is a dealkylated precursor to a specific stereoisomer of isomalathion, and its two chiral centers are identified as *S* at the P atom and *R* at the C atom.

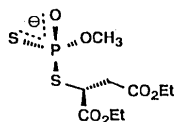
**Experimental.** Berkman prepared the title compound using a procedure modified from that of Hilgetag (1969), and obtained suitable crystals (as large flat parallelepipeds) from 1:5 methanol–ether. The crystal is composed of *N*-methylstrychninium cations (I) and phosphorodithioate diester anions (II).

The data crystal was a cut fragment of dimensions  $0.40 \times 0.24 \times 0.20$  mm. Cell constants were determined from  $\pm 2\theta$  values of 25 reflections in the range  $22 < 2\theta < 28^\circ$ , and intensities were measured by  $\theta$ - $2\theta$  scans of width  $(1.25 + 0.5 \tan \theta)^\circ$ , bracketed by stationary counting at edges for 10 s. Intensity data were collected to  $2\theta_{\text{max}} = 50^\circ$  (maximum  $\sin \theta / \lambda = 0.59$  Å<sup>-1</sup>) and encompassed  $h$ ,  $\pm k$ ,  $\pm l$  indices spanning limits of  $0 \rightarrow 9$ ,  $\pm 9$  and  $\pm 28$ , respectively. Of the 5806 reflections surveyed, 3063 were unique ( $R_{\text{int}} = 0.0459$ ) and 2417 were considered observed by the criterion  $I > 2.5\sigma(I)$ . Intensities of four standard reflections (112,  $22\bar{1}$ ,  $1\bar{2}3$  and  $1\bar{2}\bar{1}$ ), monitored after every 150 measurements, showed random variations of  $\pm 2\%$ . Intensities of  $0k0$  reflections as a function of  $\varphi$  angle (with  $\chi$  at  $90^\circ$ ) showed less than 5% variation. Consequently, corrections for decay and absorption were not deemed necessary. No correction was made for extinction effects.

The structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and was facilitated by input of model coordinates for strychnine. Refinement was based on least-squares minimization of  $\sum w(\Delta F)^2$  using *SHELX76* (Sheldrick, 1976). Atomic scattering factors and real and imaginary components for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All non-H atoms behaved well during anisotropic refinement except for the terminal atom C31 of an anion ester group which was too close to C30. Nevertheless, subsequent difference Fourier electron density maps revealed all H atoms. Refinement continued on 396 parameters with H atoms fixed at idealized positions ( $d = 0.95$  Å,  $U_H = 0.06$  Å<sup>2</sup>), and with the C31–C30 distance set to match that of the similar C26–C27



(I)



(II)

Density was determined by flotation in a  $\text{CCl}_4$ – $\text{CHCl}_3$  mixture. All other measurements were made with a modified Picker FACS-I diffractometer using Zr-filtered Mo radiation without a monochromator.

\* To whom correspondence should be addressed.