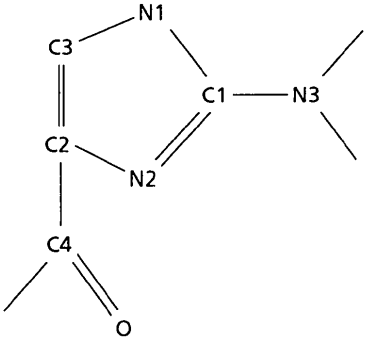
(1·470 Å) values. The C2—C3 bond at 1·354 (3) Å is also intermediate between a double (1·330 Å) and a single C—C bond (1·541 Å). These results indicate, as in other aminoimidazole derivatives (Vega *et al.*, 1988; Pérez-Garrido *et al.*, 1988), some electronic delocalization in the imidazole ring and a major contribution from the following resonance structure:



Crystal packing is governed by van der Waals contacts, although there is one short contact, N3—H···O1($x-1, y, z$) = 3·025 (3) Å (N—H···O angle 142°), which may be a weak intermolecular hydrogen bond.

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The Structure of [(4-Nitrophenyl)methyl]triphenylphosphonium Bromide Methanol Solvate

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Abstract. $C_{25}H_{21}NO_2P^+.Br^-.2{\cdot}2CH_3OH$, M_r = 548·8, monoclinic, $C2/c$, a = 20·794 (2), b = 18·899 (2), c = 14·547 (1) Å, β = 107·55 (1)°, V = 5450·7 (9) Å^3, Z = 8, D_x = 1·337 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 15·8 cm^{-1}, F(000) = 2268·8, R = 0·048 for 2815 observed [$I \geq 2{\cdot}5\sigma(I)$] unique reflexions measured at 295 K. The methanol molecules are found as an inhomogeneous electron density inside a continuous channel in the **c** direction. Through this channel, formed by hydrophobic phenyl groups, the loosely bound hydrophilic methanol molecules can easily escape from the crystal, resulting in the observed rapid disintegration of the crystals when removed from the mother liquor. The contribution of the disordered methanol molecules to the calculated structure factor is determined using a special method based on direct Fourier transformation of the observed electron density. The phenyl rings of the title compound are in a propeller configuration around the P atom. The C—C bond lengths in the phenyl groups are on average 0·016 (4) Å shorter for the bonds far from the P atom compared to the bonds near this atom.

Introduction. Crystals of the title compound could be obtained from several solvents. The crystals from

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Table 1. *Final coordinates and equivalent isotropic thermal parameters with their e.s.d.'s in parentheses*

$$U_{\rm eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
Br(1)	0·36687 (3)	0·36807 (3)	0·05235 (4)	0·0616 (2)
P(1)	0·27732 (6)	0·20062 (6)	0·23171 (9)	0·0419 (4)
O(1)	0·5384 (2)	0·0021 (2)	0·1212 (3)	0·106 (2)
O(2)	0·4585 (2)	−0·0732 (2)	0·0809 (3)	0·103 (2)
N(1)	0·4793 (3)	−0·0128 (3)	0·0995 (3)	0·070 (2)
C(1)	0·2891 (2)	0·2019 (2)	0·1132 (3)	0·046 (2)
C(11)	0·3395 (2)	0·1469 (2)	0·1041 (3)	0·040 (2)
C(12)	0·4081 (2)	0·1628 (2)	0·1259 (3)	0·052 (2)
C(13)	0·4534 (2)	0·1105 (3)	0·1215 (3)	0·058 (2)
C(14)	0·4307 (2)	0·0429 (3)	0·0994 (3)	0·049 (2)
C(15)	0·3633 (3)	0·0265 (3)	0·0729 (3)	0·055 (2)
C(16)	0·3182 (2)	0·0790 (3)	0·0770 (3)	0·053 (2)
C(21)	0·2565 (2)	0·1126 (2)	0·2583 (2)	0·045 (2)
C(22)	0·3065 (2)	0·0631 (3)	0·2959 (3)	0·056 (2)
C(23)	0·2900 (3)	−0·0052 (3)	0·3134 (4)	0·073 (3)
C(24)	0·2238 (4)	−0·0237 (3)	0·2929 (5)	0·093 (3)
C(25)	0·1734 (3)	0·0242 (3)	0·2545 (5)	0·094 (3)
C(26)	0·1893 (3)	0·0931 (3)	0·2356 (4)	0·069 (3)
C(31)	0·2092 (2)	0·2593 (2)	0·2310 (4)	0·043 (2)
C(32)	0·1589 (2)	0·2762 (3)	0·1456 (4)	0·059 (2)
C(33)	0·1073 (3)	0·3202 (3)	0·1506 (4)	0·068 (2)
C(34)	0·1037 (3)	0·3460 (3)	0·2349 (5)	0·067 (3)
C(35)	0·1527 (3)	0·3293 (3)	0·3202 (4)	0·075 (3)
C(36)	0·2052 (3)	0·2856 (3)	0·3172 (4)	0·066 (2)
C(41)	0·3520 (2)	0·2306 (3)	0·3211 (3)	0·044 (2)
C(42)	0·3899 (2)	0·2840 (3)	0·2958 (3)	0·055 (2)
C(43)	0·4467 (3)	0·3099 (3)	0·3643 (4)	0·065 (2)
C(44)	0·4654 (3)	0·2843 (3)	0·4563 (4)	0·071 (3)
C(45)	0·4273 (3)	0·2326 (3)	0·4827 (4)	0·073 (2)
C(46)	0·3707 (2)	0·2059 (3)	0·4139 (4)	0·059 (2)

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *with their e.s.d.'s in parentheses*

P(1)—C(1)	1·813 (4)	C(22)—C(23)	1·379 (8)
P(1)—C(21)	1·790 (4)	C(23)—C(24)	1·363 (11)
P(1)—C(31)	1·797 (4)	C(24)—C(25)	1·370 (10)
P(1)—C(41)	1·790 (5)	C(25)—C(26)	1·391 (8)
O(1)—N(1)	1·206 (7)	C(31)—C(32)	1·398 (7)
O(2)—N(1)	1·222 (7)	C(31)—C(36)	1·375 (8)
N(1)—C(14)	1·459 (8)	C(32)—C(33)	1·375 (8)
C(1)—C(11)	1·510 (6)	C(33)—C(34)	1·343 (9)
C(11)—C(12)	1·397 (6)	C(34)—C(35)	1·384 (9)
C(11)—C(16)	1·376 (7)	C(35)—C(36)	1·379 (9)
C(12)—C(13)	1·380 (7)	C(41)—C(42)	1·396 (7)
C(13)—C(14)	1·366 (8)	C(41)—C(46)	1·369 (7)
C(14)—C(15)	1·372 (8)	C(42)—C(43)	1·385 (7)
C(15)—C(16)	1·379 (8)	C(43)—C(44)	1·365 (8)
C(21)—C(22)	1·383 (6)	C(44)—C(45)	1·383 (9)
C(21)—C(26)	1·385 (8)	C(45)—C(46)	1·390 (8)

C(1)—P(1)—C(21)	109·2 (2)	C(22)—C(21)—C(26)	119·9 (4)
C(1)—P(1)—C(31)	108·6 (2)	C(21)—C(22)—C(23)	120·5 (4)
C(1)—P(1)—C(41)	110·5 (2)	C(22)—C(23)—C(24)	119·4 (5)
C(21)—P(1)—C(31)	109·5 (2)	C(23)—C(24)—C(25)	121·2 (6)
C(21)—P(1)—C(41)	110·5 (2)	C(24)—C(25)—C(26)	120·1 (6)
C(31)—P(1)—C(41)	108·6 (2)	C(21)—C(26)—C(25)	119·0 (5)
O(1)—N(1)—O(2)	122·6 (6)	P(1)—C(31)—C(32)	121·6 (4)
O(1)—N(1)—C(14)	118·9 (5)	P(1)—C(31)—C(36)	118·8 (4)
O(2)—N(1)—C(14)	118·4 (5)	C(32)—C(31)—C(36)	119·5 (5)
P(1)—C(1)—C(11)	111·7 (3)	C(31)—C(32)—C(33)	118·5 (5)
C(1)—C(11)—C(12)	121·3 (3)	C(32)—C(33)—C(34)	121·8 (6)
C(1)—C(11)—C(16)	119·7 (4)	C(33)—C(34)—C(35)	120·4 (6)
C(12)—C(11)—C(16)	118·9 (4)	C(34)—C(35)—C(36)	119·0 (5)
C(11)—C(12)—C(13)	120·0 (4)	C(31)—C(36)—C(35)	120·7 (5)
C(12)—C(13)—C(14)	119·2 (4)	P(1)—C(41)—C(42)	118·2 (3)
N(1)—C(14)—C(13)	119·0 (4)	P(1)—C(41)—C(46)	122·3 (4)
N(1)—C(14)—C(15)	119·1 (5)	C(42)—C(41)—C(46)	119·4 (4)
C(13)—C(14)—C(15)	121·9 (5)	C(41)—C(42)—C(43)	119·5 (4)
C(14)—C(15)—C(16)	118·4 (5)	C(42)—C(43)—C(44)	120·6 (5)
C(11)—C(16)—C(15)	121·3 (4)	C(43)—C(44)—C(45)	120·3 (6)
P(1)—C(21)—C(22)	120·8 (3)	C(44)—C(45)—C(46)	119·2 (5)
P(1)—C(21)—C(26)	119·2 (4)	C(41)—C(46)—C(45)	120·9 (5)

methanol disintegrate vehemently when removed from the mother liquor as a result of loss of solvent. The structure determination was undertaken to find out the role of the solvent in this disintegration process; it is part of our research on the influence of solvents on crystallization and crystal structures.

Experimental. Yellow transparent crystal, 0·5 × 0·25 × 0·25 mm, mounted in a closed capillary together with a drop of the mother liquor, Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo $K\alpha$ radiation. Cell dimensions from angular settings of 14 reflexions, $9 < \theta < 14°$, 5198 reflexions were scanned: $\omega/2\theta$ scan technique with $\omega = (0{\cdot}40 + 0{\cdot}35\tan\theta)°$, $\theta_{\max} = 25°$, h −23,24, k 0,−22, l −17,0; 2815 unique observed for which $I > 2{\cdot}5\sigma(I)$, $\sigma(I) = \sigma(I)_{\rm cs} + (pI)^2$ with $p = 0{\cdot}02$ (McCandlish, Stout & Andrews, 1975). Three reference reflexions (400; 060; 00$\bar{2}$) showed insignificant changes in intensities during the 95 h of X-ray exposure time. Systematic absences indicated space group $C2/c$. Lp correction applied. Br atoms located from Patterson map (*SHELXS*86; Sheldrick, 1986). All other non-H atoms found after tangent formula expansion (*SHELXS*86). Isotropic and anisotropic least-squares refinement on F (*SHELX*76; Sheldrick, 1976). All H atoms refined in the riding mode on their carrier atoms (C—H = 0·98 Å) with one common isotropic thermal parameter. Convergence reached at $R = 0{\cdot}103$. A subsequent difference Fourier map showed channels with nearly continuous residual density. This electron density was interpreted as originating from the solvent. The BYPASS procedure (van der Sluis & Spek, 1990) was used to take into account the electron density in the channel in the refinement. Final convergence was reached at $R = 0{\cdot}048$ [$wR = 0{\cdot}037$, $w = 1{\cdot}458/\sigma^2(F)$, $S = 3{\cdot}01$, $(\Delta/\sigma)_{\max} = 0{\cdot}04$, number of refined parameters = 272]. Minimal and maximal electron density −0·41 and 0·51 e Å^{-3}. The program package *EUCLID* (Spek, 1982) was used for geometry calculations and illustrations. Scattering factors from Cromer & Mann (1968), anomalous dispersion from Cromer & Liberman (1970).

Discussion. Relevant geometrical data are collected in Tables 1 and 2.* Fig. 1 gives a perspective view of the molecule with atomic numbering. Fig. 2 shows the molecular packing down **c** together with a Fourier map calculated from the solvent contributions to the calculated structure factors at $z = \frac{1}{3}$. After solving the ordered part of the structure an irregular tubular

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* Anisotropic thermal parameters, H-atom positions, bond angles and distances involving H atoms, torsion angles and a list of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52715 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

electron density was found around $x = \frac{1}{2}$, $y = \frac{1}{2}$, $0 < z < 1$ in a difference Fourier map. Attempts to interpret this electron density in terms of methanol molecules failed because of severe disorder. Simply attributing the scattering factor of partially occupied C atoms to peaks in a difference Fourier map resulted in an R value of 0·058, high standard deviations in the positional parameters of the atoms of the ordered part of the structure and a high residual electron density (0·9 e Å^{-3}) far from the Br atom. We therefore decided to use a special procedure to bypass the influence of the solvent on the rest of the structure and simultaneously obtain information on the distribution of the solvent in the unit cell and about the amount of included solvent (see *Experimental*).

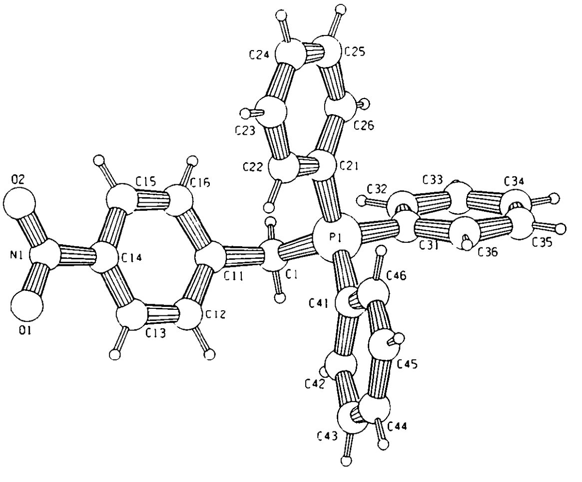

Fig. 1. Molecular conformation and atomic labelling of the cation.

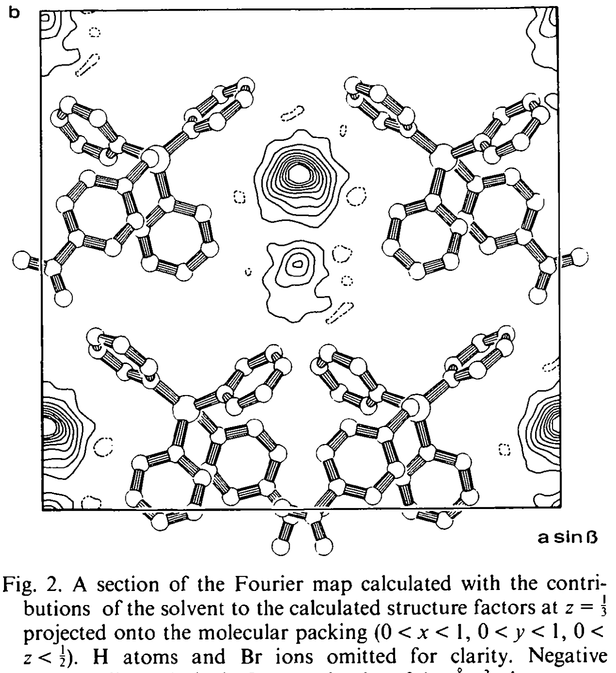

Fig. 2. A section of the Fourier map calculated with the contributions of the solvent to the calculated structure factors at $z = \frac{1}{3}$ projected onto the molecular packing ($0 < x < 1$, $0 < y < 1$, $0 < z < \frac{1}{2}$). H atoms and Br ions omitted for clarity. Negative contour lines dashed. Lowest level $-0{\cdot}1$ e Å^{-3}, increments 0·2 e Å^{-3}.

The methanol was found to be inhomogeneously distributed in continuous channels formed by the hydrophobic phenyl groups of the ordered part of the structure around $x = \frac{1}{2}$, $y = \frac{1}{2}$ and symmetry-related positions. It is now obvious that the hydrophilic methanol molecules can easily escape from the crystals thus resulting in the observed complete disruption of the crystals. Integration of the electron density resulting from the contributions of the solvent to the calculated structure factors resulted in 2·2 methanol molecules per asymmetric unit. The maximal residual density found in the final difference Fourier map (0·51 e Å^{-3}) near the Br atom is interpreted as an absorption artefact. The standard deviations in positional parameters for the ordered part of the structure are halved after application of the BYPASS procedure. In the phenyl rings, the C—C bond lengths closer to the P atom are on average slightly shorter than those further away from the P atom. The average values are 1·384 (3), 1·382 (3), 1·368 (2) Å, in each case averaged over six bonds. A similar effect was found by Hjortas (1973) in (3,7-dimethyl-2,6-octadienyl)triphenylphosphonium bromide, and Goldstein, Seff & Trueblood (1968) in the tetraphenylphosphonium ion; the latter suggested as a possible explanation either non-rigid thermal motion or resonance effect. The phenyl groups are arranged around the P atom as 'propeller paddles'. The average P—C(phenyl) bond is 1·792 (2) Å and the P—C(methylene) bond is 1·813 (4) Å. The angles around the P atom differ at most by 1·1 (2)° from the tetrahedral angle.

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