

# Structural Studies on the Phosphorus–Nitrogen Bond. V.

## The Crystal Structure of 4-Nitrobenzyl Tris(morpholino)-phosphonium Perchlorate and 4-Nitrobenzyl Tris(piperidino)-phosphonium Perchlorate

CHRISTIAN RØMMING<sup>a</sup> and JON SONGSTAD<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Oslo, Oslo 3, Norway and <sup>b</sup> Department of Chemistry, University of Bergen, 5014 Bergen-Univ., Norway

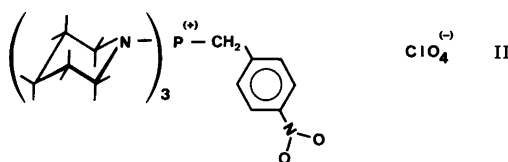
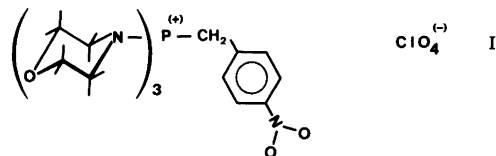
The structures of the title compounds, 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>P<sup>+</sup>[N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O]<sub>3</sub>ClO<sub>4</sub><sup>-</sup>, I, and 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>P<sup>+</sup>[N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>ClO<sub>4</sub><sup>-</sup>, II, have been determined from X-ray data. Full-matrix least squares refinements led to final conventional *R*-values of 0.045(3558) for I and 0.039(3844) for II. (The numbers of observed reflections in parentheses.)

The compounds are monoclinic with the following unit cell dimensions (at -150 °C): I: *a* = 13.964(3) Å; *b* = 17.068(3) Å; *c* = 9.657(1) Å; β = 93.88(2)°; space group *P*2<sub>1</sub>/*n*. II: *a* = 28.059(7) Å; *b* = 10.018(2) Å; *c* = 20.603(5) Å; β = 122.24(2)°; space group *C*2/*c*.

In I, the lone pair of one of the nitrogen atoms is *anti* with respect to the P–C bond; the two other morpholino groups are twisted in opposite directions. In II, the piperidino groups are all twisted in the same direction in a propeller-like arrangement. In both compounds the nitrogen atoms are essentially *sp*<sup>2</sup> hybridized; the P–N bonds are of equal length with a mean of 1.631(4) Å. The P–C bond is 1.81 Å in both compounds.

One of the morpholino rings of compound I is disordered in the crystal. The Cl–O bond length in the perchlorate ions is 1.464(8) Å.

In Parts I and II of this series the crystal and molecular structures of tris(morpholino)phosphine, Mor<sub>3</sub>P, tris(piperidino)phosphine, Pip<sub>3</sub>P, and their corresponding selenides, Mor<sub>3</sub>PSe and Pip<sub>3</sub>PSe, were described.<sup>1,2</sup> The compounds were shown to be highly asymmetrical species with non-equal NPN bond angles, with nitrogen atoms of varying



hybridization and with significantly different P–N bond lengths.

In the present study we have turned to phosphonium salts derived from the same aminophosphines in an attempt to examine the effect of a positive charge on the central phosphorus atom upon the P–N bond length. Furthermore, the question arises whether the asymmetric arrangement of the amino substituents as observed in the trivalent and in the pentavalent species is retained when the phosphorus atom is tetrahedrally coordinated. In the present study we want to report the crystal and molecular structure of the 4-nitrobenzylphosphonium perchlorates, I and II, of tris(morpholino)-

phosphine and of tris(piperidino)phosphine. No structural studies of phosphonium salts derived from tris(dialkylamino)phosphines appear to have been reported so far.

The 4-nitrobenzylphosphonium perchlorates, I and II, were chosen in the present study for several reasons. All attempts to prepare satisfactory crystals of methylphosphonium salts,  $(R_2N)_3P^+MeX^-$  with various anions failed, whereas suitable crystals of I and II were readily obtained from acetonitrile–diethyl ether mixtures. By employing the very weakly basic perchlorate anion<sup>3</sup> it was hoped that interactions between the phosphonium ions, particularly their fairly acidic benzylic methylene protons,<sup>4</sup> and the anions were to be negligible.

## EXPERIMENTAL

**Materials.** The 4-nitrobenzylphosphonium chlorides were made from the parent amino-phosphines<sup>1</sup> and a slight excess of 4-nitrobenzyl chloride in dry acetonitrile at room temperature. The products were precipitated in more than 80 % yield with diethyl ether and carefully washed with benzene to remove traces of the intensely coloured phosphoranes.<sup>4</sup> The perchlorates were precipitated in close to quantitative yield with excess sodium perchlorate in aqueous solution. Crystals suitable for the X-ray experiments were obtained from an acetonitrile–diethyl ether mixture at 0 °C.

I, faintly yellow, m.p. 271–272 °C (dec.). (Found: C 43.42; H 6.33; N 11.02. Calc. for  $C_{19}H_{30}ClN_4O_9P$ : C 43.47; H 5.76; N 10.67.) The specimen used for the X-ray experiment was cut to dimensions  $0.15 \times 0.2 \times 0.3$  mm.

II, faintly yellow, m.p. 180–182 °C (dec.). (Found: C 51.40; H 6.67; N 10.80. Calc. for  $C_{22}H_{36}ClN_4O_6P$ : C 50.91; H 6.99; N 10.80.) The specimen used for the X-ray experiment was cut to dimensions  $0.09 \times 0.3 \times 0.4$  mm.

**X-Ray data.** Data for the measurements of cell dimensions and intensity data were collected on a SYNTEX P1 diffractometer using graphite crystal monochromated  $MoK\alpha$  radiation ( $\lambda = 0.71069$  Å). The temperature at the crystal site was –150 °C. Cell parameters were determined by a least squares fit to the diffractometer settings of 15 general reflections with  $2\theta > 30^\circ$ . Intensities were collected with the  $\theta - 2\theta$  scan technique, scan speed  $2 - 4^\circ \text{ min}^{-1}$  depending on the peak intensity, scan width  $\pm 0.8^\circ$  (I) and  $\pm 1.0^\circ$  (II) up to a  $\sin \theta / \lambda$  value of  $0.70 \text{ \AA}^{-1}$  for I and  $0.65 \text{ \AA}^{-1}$  for II. Background counts were taken for 0.35 times the scan time at each of the scan limits. Three standard reflections were measured at regular intervals during the data

collection; variations of 2–3 % were observed and the data were accordingly adjusted. Out of the 4241 unique reflections recorded from I, 3558 with  $I > 2.5\sigma(I)$  were retained for the structure analysis; the corresponding numbers for II were 4385 and 3844. The standard deviations for the intensities were calculated as  $\sigma(I) = [C_T + (0.02 C_N)^2]^{1/2}$ , where  $C_T$  is the total number of counts and  $C_N$  is the scan count minus background count. The intensities were corrected for Lorentz and polarization effects but not for absorption.

A description of the computer programs applied for the structure determinations is given in Ref. 5. Atomic form factors were those of Doyle and Turner<sup>6</sup> for the heavy atoms and of Stewart, Davidson and Simpson<sup>7</sup> for the hydrogen atoms.

## CRYSTAL DATA

I. 4-Nitrobenzyl tris(morpholino)phosphonium perchlorate,  $C_{19}H_{30}ClN_4O_9P$ , m.p. 271–272 °C (dec.). Monoclinic,  $a = 13.964(3)$  Å;  $b = 17.068(3)$  Å;  $c = 9.657(1)$  Å;  $\beta = 93.88(2)^\circ$ ;  $V = 2296.4$  Å<sup>3</sup>; ( $t = -150$  °C);  $M = 524.89$ ;  $Z = 4$ ;  $F(000) = 1104$ ;  $\mu(MoK\alpha) = 3.0 \text{ cm}^{-1}$ ;  $D_x = 1.518 \text{ g cm}^{-3}$ . Absent reflections: ( $h0l$ ) for  $h + l$  odd, ( $0k0$ ) for  $k$  odd. Space group  $P2_1/n$  (No. 14).

II. 4-Nitrobenzyl tris(piperidino)phosphonium perchlorate,  $C_{22}H_{36}ClN_4O_6P$ , m.p. 180–182 °C (dec.). Monoclinic,  $a = 26.059(7)$  Å;  $b = 10.018(2)$  Å;  $c = 21.603(5)$  Å;  $\beta = 122.24(2)^\circ$ ;  $V = 5136.2$  Å<sup>3</sup>; ( $t = 150$  °C);  $M = 518.98$ ;  $Z = 8$ ;  $F(000) = 2208$ ;  $\mu(MoK\alpha) = 2.6 \text{ cm}^{-1}$ ;  $D_x = 1.345 \text{ g cm}^{-3}$ . Absent reflections: ( $hkl$ ) for  $h + k$  odd, ( $h0l$ ) for  $l$  odd. Space group  $C2/c$  (No. 15).

## STRUCTURE DETERMINATIONS

Both structures were determined by direct methods using the program assembly MULTAN and refined in the way described in Ref. 1. It turned out that one of the morpholino rings in I is disordered in the crystal. It was possible, however, to separate the atoms into two discrete “half” rings. The oxygen, nitrogen and one of the carbon atoms were each split between two positions separated by about 0.5 Å, and the positions of these atoms were refined with (fixed) isotropic thermal parameters. The corresponding separations for the other three atoms were all more than 0.8 Å and these were assigned anisotropic thermal parameters. The refinements converged to conventional  $R$ -factors of 0.045 (I) and 0.039 (II); the  $R_w$ -values

Table 1. Fractional atomic coordinates with estimated standard deviations for 4-nitrobenzyl tris(morpholino)phosphonium perchlorate (I) and 4-nitrobenzyl tris(piperidino)phosphonium perchlorate (II).

I				II			
ATOM	X	Y	Z	ATOM	X	Y	Z
CL	.65626( 4)	.07542( 3)	.79961( 6)	CL	.23211( 2)	.44453( 5)	.35459( 2)
P	.30354( 4)	.39836( 3)	.62585( 6)	P	.17593( 2)	.46887( 4)	.67678( 2)
O1	.0481( 1)	.1803( 1)	.3727( 1)	O1	-.1359( 0)	.9495( 2)	.0641( 1)
O2	.3848( 1)	.1327( 1)	1.0644( 1)	O2	-.0213( 1)	.832( 2)	.1565( 1)
O4	.4370( 1)	.4890( 1)	.1723( 1)	O3	.2628( 0)	.5528( 1)	.3639( 1)
O5	.4813( 2)	.4585( 1)	.3699( 2)	O4	.2686( 0)	.4391( 2)	.4168( 1)
O6	.6380( 2)	.1481( 1)	.7383( 2)	O5	.2338( 0)	.4658( 2)	.2911( 1)
O7	.6853( 2)	.0135( 1)	.7268( 2)	O6	.2660( 1)	.3197( 2)	.3495( 1)
O8	.6221( 2)	.0817( 1)	.9337( 2)	N1	.2392( 0)	.4348( 1)	.1855( 0)
O9	.7543( 1)	.0564( 1)	.8163( 4)	N2	.1385( 0)	.3715( 1)	.0638( 0)
N1	.2144( 1)	.1251( 1)	.5263( 2)	N3	.1427( 0)	.5367( 1)	-.0087( 0)
N2	.3031( 1)	.1394( 1)	.7705( 1)	N4	-.0092( 0)	.8677( 2)	.1122( 1)
N4	.4523( 1)	.4044( 1)	.2981( 2)	C1	.1855( 0)	.6295( 1)	.1348( 1)
C1	.4183( 1)	.1034( 1)	.5530( 2)	C2	.1338( 0)	.6899( 1)	.1279( 1)
C2	.4269( 1)	.1837( 1)	.4889( 2)	C3	.1815( 0)	.7843( 2)	.0739( 1)
C3	.4640( 1)	.2473( 1)	.5646( 2)	C4	.0546( 0)	.8413( 2)	.0682( 1)
G4	.4699( 1)	.3199( 1)	.5032( 2)	C5	.0403( 0)	.8039( 2)	.1178( 1)
C5	.4398( 1)	.3286( 1)	.3645( 2)	C6	.0716( 0)	.7120( 2)	.1726( 1)
C6	.4023( 1)	.2662( 1)	.2866( 2)	C7	.1184( 0)	.6556( 2)	.1774( 1)
C7	.3967( 1)	.1937( 1)	.3495( 2)	C11	.2820( 0)	.4660( 2)	.1835( 1)
C11	.1911( 1)	.2108( 1)	.5196( 2)	C12	.3378( 0)	.4678( 2)	.2837( 1)
C12	.0843( 1)	.2195( 1)	.4966( 2)	C13	.3568( 0)	.4138( 2)	.1543( 1)
C13	.0786( 1)	.0991( 1)	.3799( 2)	C14	.3111( 1)	.4362( 2)	.0742( 1)
C14	.1775( 1)	.0859( 1)	.3964( 2)	C15	.2553( 0)	.3796( 2)	.0561( 1)
C21	.2139( 1)	.1478( 1)	.8435( 2)	C21	.0788( 0)	.3987( 2)	.0588( 1)
C22	.2225( 2)	.1049( 2)	.9809( 2)	C22	.0663( 0)	.3327( 2)	.1137( 1)
C23	.3892( 1)	.1164( 1)	.9965( 2)	C23	.0840( 1)	.1867( 2)	.1295( 1)
C24	.3885( 1)	.1689( 1)	.8610( 2)	C24	.1454( 1)	.1695( 2)	.1530( 1)
C32A	.1846( 3)	-.1186( 2)	.6314( 7)	C25	.1954( 0)	.2290( 2)	.0988( 1)
C33A	.3577( 3)	-.1358( 3)	.6514( 6)	C31	.1688( 0)	.6503( 2)	-.0314( 1)
C34A	.3675( 3)	-.0535( 2)	.7822( 5)	C32	.1095( 1)	.7227( 2)	-.0982( 1)
C32B	.1918( 4)	-.0991( 3)	.7508( 7)	C33	.0767( 1)	.6200( 3)	-.1589( 1)
C33B	.3564( 4)	-.1207( 3)	.7312( 7)	C34	.0806( 0)	.5031( 3)	-.1333( 1)
C34B	.3601( 4)	-.0657( 3)	.6128( 6)	C35	.1126( 0)	.4385( 2)	-.0690( 1)
O3A	.2813( 3)	-.1658( 2)	.6894( 3)	H1C1	.2862	.6954	.1271
O3B	.2641( 3)	-.1577( 2)	.7345( 3)	H2C1	.2182	.5974	.1842
N3A	.2864( 3)	-.0029( 3)	.6502( 3)	H3C	.1128	.8099	.0422
N3B	.2853( 3)	-.0056( 3)	.6148( 4)	H4C	.0335	.9078	.0306
C31A	.1940( 3)	-.0344( 3)	.6881( 5)	H6C	.0893	.6893	.2036
C31B	.1890( 3)	-.0407( 3)	.6323( 5)	H7C	.1411	.5926	.2154
H1C1	.4193	.0653	.4838	H111	.2842	.3078	.1908
H2C1	.4621	.0900	.6131	H112	.2699	.4430	.2162
H3C	.4876	.2482	.6587	H121	.3643	.4580	.2525
H4C	.4921	.3627	.5532	H122	.3345	.5633	.1979
H6C	.3813	.2748	.1937	H131	.3647	.3282	.1637
H7C	.3724	.1514	.2997	H132	.3901	.4518	.1661
H111	.2191	.2349	.4389	H141	.3218	.3952	.0438
H112	.2129	.2332	.6040	H142	.3049	.5292	.0649
H121	.0709	.2769	.4887	H151	.2593	.2826	.0620
H122	.0980	.1957	.5852	H152	.2250	.3978	.0848
H131	.0492	.0796	.2959	H211	.0541	.3473	.0093
H132	.0388	.0743	.4601	H212	.0684	.4860	.0487
H141	.2898	.1079	.3138	H221	.0266	.3425	.0932
H142	.1894	.0386	.4038	H222	.0874	.3833	.1600
H211	.1601	.1294	.7834	H231	.0596	.1332	.0861
H212	.2050	.2024	.8667	H232	.0760	.1526	.1645
H221	.2275	.0411	.9584	H241	.1554	.0768	.1569
H222	.1691	.1207	1.0321	H242	.1699	.2146	.2005
H231	.3967	.0595	.9742	H251	.1334	.1819	.0498
H232	.4415	.1344	1.0556	H252	.1948	.2198	.1103
H241	.4467	.1586	.8157	H311	.1878	.6388	-.0457
H242	.3863	.2214	.8815	H312	.1796	.7176	.0886
A311	.1418	-.0007	.6375	H321	.1226	.7969	-.1101
A312	.1891	-.0334	.7857	H322	.0856	.7567	-.0818
A321	.1891	-.1187	.5242	H331	.0995	.5957	-.1785
A322	.1224	-.1414	.6588	H332	.0417	.6666	-.1970
A331	.3984	-.1363	.5462	H341	.0412	.4376	-.1710
A332	.4036	-.1781	.6898	H342	.0329	.5255	-.1230
A341	.4783	-.0327	.6653	H351	.1374	.4092	-.0856
A342	.3728	-.0528	.8046	H352	.1041	.3616	-.0500
B311	.1684	-.0684	.5448				
B312	.1434	.0024	.6503				
B321	.1265	-.1247	.7551				
B322	.2063	-.0711	.8428				
B331	.4758	-.1624	.7225				
B332	.3688	-.0915	.8190				
B341	.3923	-.0949	.5222				
B342	.4258	-.0392	.6175				

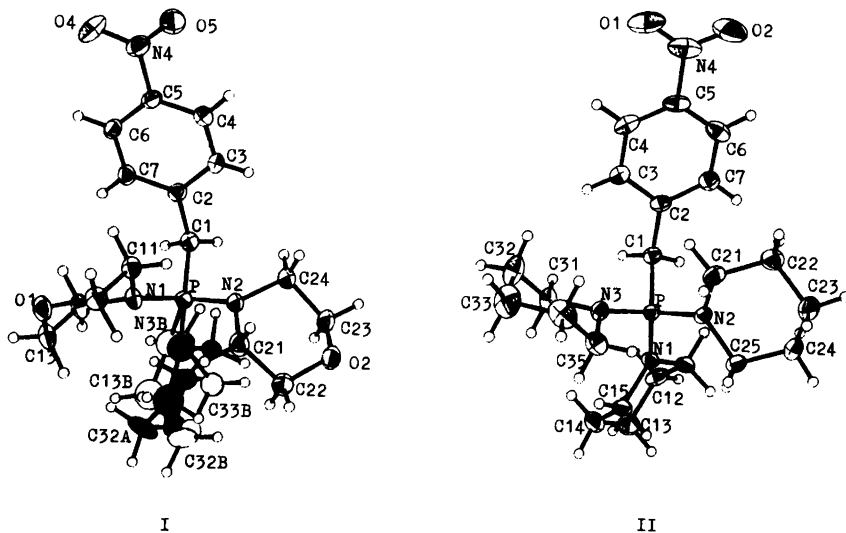


Fig. 1. ORTEP drawings of the phosphonium ions.

were 0.048 (I) and 0.042 (II) and the standard deviation of an observation of unit weight,  $[\omega\Delta F^2/(m-n)]^{\frac{1}{2}}$ , was 1.75 and 1.46, respectively. The overdetermination ratios were 11.0 (I) and 9.0 (II).

Final atomic parameters are listed in Table 1. Tables of observed and calculated structure factors with standard deviations and of thermal parameters are available from the authors.

ORTEP drawings of the molecules are shown in Fig. 1, where the numbering of the atoms is also indicated. In Table 2 are listed bond lengths, bond angles, torsion angles and other structural data. Estimated standard deviations are calculated from the correlation matrices.

Analyses of the rigid body vibrations of the ions were carried out. The perchlorate ions showed fairly large librational motion, amounting to r.m.s. amplitudes of up to  $15.1^\circ$  in I and  $13.0^\circ$  in II. For the phosphonium ions the best description of the thermal motion seems to be a translational vibration of the ions and an oscillation of each of the four substituents mainly about directions close to the axes of least inertia. The r.m.s. amplitudes of oscillation of the morpholino moieties were found to be  $4.1$  and  $6.9^\circ$  for the ordered rings 1 and 2, respectively, and  $7.7^\circ$  for the *p*-nitrobenzyl moiety in I. In compound II the corresponding figures are  $5.9$ ,  $5.5$  and  $6.5^\circ$  for the piperidine rings 1, 2

and 3, respectively, and  $8.4^\circ$  for the 4-nitrobenzyl part. The corrected bond lengths given in Table 2 refer to this analysis.

*The disordered morpholino substituent.* As mentioned above, one of the morpholino substituents (ring 3) in I is disordered between two distinct sites A and B, cf. Fig. 1. One position is related to the other by a rotation of about  $160^\circ$  around an axis near the N—O direction. A perhaps physically more probable way of transfer from one site to the other is the combination of inversion of the ring, a small rotation about N—O and a small tilt which brings the lone pair direction of the nitrogen atom nearly to coincide with its original direction (cf. Fig. 3).

The potential energy through a rotation was simulated using the energy calculation program written by Shmueli and Goldberg.<sup>8</sup> The ring in position A was rotated through  $360^\circ$  about an axis defined by the points midway between N3A and N3B and between O3A and O3B. For every  $6^\circ$  of rotation the sum of interatomic potentials between the ring atoms and the atoms of surrounding molecules, including atoms of the rest of the molecule, was calculated. The resulting potential curve showed two distinct minima separated by  $158^\circ$  of rotation (Fig. 2), corresponding closely to the two positions found for the ring. The two minima were calculated to nearly the same energy value, suggesting the population factor for the sites to be

Table 2. Structural data.

Bond lengths (Å)				Bond angles (°)											
I		corr.	II		corr.	I		II							
C1	O6	1.423(2)	1.453	C1	O3	1.437(2)	1.456	O6	C1	O7	110.4(2)	O3	C1	O4	109.5(1)
C1	O7	1.432(2)	1.473	C1	O4	1.426(2)	1.467	O6	C1	O8	107.9(2)	O3	C1	O5	109.9(1)
C1	O8	1.435(3)	1.475	C1	O5	1.412(2)	1.455	O6	C1	O9	112.9(2)	O3	C1	O6	111.3(1)
C1	O9	1.405(3)	1.465	C1	O6	1.425(2)	1.465	O7	C1	O8	108.3(2)	O4	C1	O5	108.2(1)
P	C1	1.807(3)		P	C1	1.813(2)		O7	C1	O9	109.5(2)	O4	C1	O6	108.0(2)
C1	C2	1.511(3)	1.514	C1	C2	1.507(3)	1.509	O8	C1	O9	107.4(2)	O5	C1	O6	109.9(2)
C2	C3	1.389(4)	1.401	C2	C3	1.396(3)	1.406	N1	P	N2	105.7(1)	N1	P	N2	110.9(1)
C3	C4	1.380(4)	1.382	C3	C4	1.379(3)	1.381	N1	P	N3A	109.1(2)	N1	P	N3	112.1(1)
C4	C5	1.384(4)	1.392	C4	C5	1.381(4)	1.394	N1	P	C1	112.7(1)	N1	P	C1	105.3(1)
C5	C6	1.378(4)	1.389	C5	C6	1.383(4)	1.393	N2	P	N3A	111.7(2)	N2	P	N3	108.1(1)
C6	C7	1.383(4)	1.385	C6	C7	1.381(3)	1.383	N2	P	C1	109.0(1)	N2	P	C1	111.1(1)
C7	C2	1.393(3)	1.401	C7	C2	1.393(3)	1.406	N3A	P	C1	108.6(2)	N3	P	C1	109.4(1)
C5	N4	1.469(3)	1.471	C5	N4	1.474(3)	1.476	N1	P	N3B	102.3(2)	P	C1	C2	117.8(1)
N4	O4	1.221(3)	1.229	N4	O1	1.217(3)	1.226	N2	P	N3B	123.5(2)	P	C1	C3	121.0(2)
N4	O5	1.209(3)	1.220	N4	O2	1.228(3)	1.240	N3B	P	C1	103.5(2)	C1	C2	C7	120.2(2)
P	N1	1.632(2)		P	N1	1.626(2)		P	C1	C2	111.6(2)	C2	C3	C4	121.1(2)
N1	C11	1.485(3)	1.488	N1	C11	1.487(2)	1.491	C1	C2	C3	122.0(2)	C3	C4	C5	118.5(2)
C11	C12	1.503(4)	1.505	N1	C12	1.515(3)	1.523	C1	C2	C7	118.6(2)	C4	C5	C6	122.0(2)
C12	O1	1.432(3)	1.438	C12	C13	1.524(3)	1.531	C2	C3	C4	120.5(2)	C5	C6	C7	118.8(2)
C1	C13	1.422(3)	1.426	C13	C14	1.523(3)	1.527	C3	C4	C5	118.8(2)	C6	C7	C2	120.8(2)
C13	C14	1.508(4)	1.511	C14	C15	1.508(3)	1.515	C4	C5	C6	122.2(2)	C7	C2	C3	118.8(2)
C14	N1	1.483(3)	1.489	C15	N1	1.471(3)	1.478	C5	C6	C7	118.4(2)	C4	C5	N4	118.1(2)
P	N2	1.629(2)		P	N2	1.632(2)		C6	C7	C2	120.2(2)	C6	C5	N4	119.9(2)
N2	C21	1.479(3)	1.490	N2	C21	1.472(3)	1.480	C7	C2	C3	119.4(2)	C5	N4	O1	119.1(2)
C21	C22	1.514(4)	1.521	C21	C22	1.518(3)	1.525	C4	C5	N4	118.2(2)	C5	N4	O2	116.9(2)
C22	O2	1.430(4)	1.436	C22	C23	1.524(4)	1.529	C6	C5	N4	119.6(2)	O1	N4	O2	124.0(2)
O2	C23	1.424(4)	1.435	C23	C24	1.524(4)	1.532	C5	N4	O4	118.3(2)	P	N1	C11	123.6(1)
C23	C24	1.513(4)	1.521	C24	C25	1.522(3)	1.528	C5	N4	O5	118.3(2)	P	N1	C15	122.8(1)
C24	N2	1.477(3)	1.483	C24	N2	1.483(3)	1.489	O4	N4	O5	123.4(2)	N1	C11	C12	108.4(2)
P	N3A	1.629(5)		P	N3	1.636(2)		P	N1	C11	122.4(2)	C11	C12	C13	110.3(2)
N3A	C31A	1.468(8)		N3	C31	1.479(3)	1.491	P	N1	C14	122.8(2)	C12	C13	C14	110.3(2)
C31A	C32A	1.539(8)		C31	C32	1.520(3)	1.531	C11	C12	O1	111.4(2)	C13	C14	C15	111.6(2)
C32A	O3A	1.424(7)		C32	C33	1.513(4)	1.522	C12	O1	C13	110.5(2)	C14	C15	N1	120.4(2)
O3A	C33A	1.420(7)		C33	C34	1.513(4)	1.525	O1	C13	C14	111.4(2)	N1	C11	C12	108.4(2)
C33A	C34A	1.501(8)		C34	C35	1.521(3)	1.531	C13	C14	N1	107.9(2)	N2	C21	C22	112.4(1)
C34A	N3A	1.483(7)		C35	N3	1.486(3)	1.494	C14	N1	C11	110.0(2)	P	N2	C25	123.0(1)
P	N3B	1.660(5)		P	N2	1.632(2)		P	N2	C21	120.8(2)	N2	C21	C22	110.8(2)
N3B	C31B	1.482(8)		P	N2	1.632(2)		P	N2	C24	125.8(2)	C21	C22	C23	111.1(2)
C31B	C32B	1.516(8)		P	N2	1.632(2)		N2	C21	C22	110.6(2)	C22	C23	C24	110.9(2)
C32B	O3B	1.437(8)		C21	C22	110.3(2)		C21	C22	O2	110.3(2)	C23	C24	C25	110.6(2)
O3B	C33B	1.438(8)		C22	O2	C23	109.4(2)	C22	O2	C23	109.4(2)	C24	C25	N2	109.9(2)
C33B	C34B	1.483(9)		O2	C23	C24	110.1(2)	O2	C23	C24	110.1(2)	N2	C21	C12	112.6(2)
C34B	N3B	1.465(8)		C23	C24	N2	110.2(2)	P	N3	C31	121.8(1)	P	N3	C31	121.8(1)
				C24	N2	C21	111.5(2)	P	N3	C34A	120.1(4)	P	N3	C35	120.5(1)
				P	N3A	C31A	122.3(4)	P	N3A	C34A	120.1(4)	N3	C31	C32	110.0(2)
				P	N3A	C34A	120.1(4)	P	N3A	C32A	107.9(5)	C31	C32	C33	111.7(2)
				N3A	C31A	C32A	107.9(5)	C31A	C32A	O3A	110.2(5)	C32	C33	C34	110.6(2)
				C31A	C32A	O3A	110.2(5)	C32A	O3A	C33A	110.1(4)	C33	C34	C35	110.7(2)
				C32A	O3A	C33A	110.1(4)	O3A	C33A	C34A	112.0(4)	C34	C35	N3	109.8(2)
				C33A	C34A	N3A	109.5(4)	C33A	C34A	N3A	109.5(4)	C35	N3	C31	112.4(2)
				C34A	N3A	C31A	111.5(4)	C34A	N3A	C31A	111.5(4)				
				P	N3B	C31B	121.8(4)	P	N3B	C34B	125.8(4)				
				P	N3B	C34B	125.8(4)	N3B	C31B	C32B	112.4(5)				
				N3B	C31B	C32B	112.4(5)	C31B	C32B	O3B	110.6(5)				
				C31B	C32B	O3B	110.6(5)	C32B	O3B	C33B	109.5(5)				
				C32B	O3B	C33B	109.5(5)	O3B	C33B	C34B	111.9(5)				
				O3B	C33B	C34B	111.9(5)	C33B	C34B	N3B	111.8(5)				
				C33B	C34B	N3B	111.8(5)	C34B	N3B	C31B	111.5(5)				

Various derived and averaged data									
	I				II				
Nx	N1	N2	N3A	N3B	N1	N2	N3		
$\overline{N-C}$ (Å)	1.489	1.487	1.476	1.474	1.485	1.485	1.493		
$\overline{C-C}$ (Å)	1.508	1.521	1.520	1.500	1.524	1.529	1.527		
$\overline{C-O}$ (Å)	1.432	1.436	1.422	1.438					
Deviation of Nx									
from plane PCC (Å)	0.20	0.12	0.22	0.08	0.11	0.13	0.21		
Sum of Nx bond angles (°)	355.2	358.1	353.9	359.1	358.4	358.0	354.6		
Torsion angle									
C1-P-Nx-Lone pair (Nx) (°)	177.4	73.3	-65.5	-69.6	-47.1	-32.7	-55.3		
Sum of NPN angles	326.5(A)			331.6(B)			331.1		
Sum of CPN angles	330.3(A)			325.2(B)			325.7		

close to 0.5. This was indeed used during the structure refinement as a fixed value because of its correlation with the thermal parameters. The half-widths of the two energy wells at a height of  $kT$

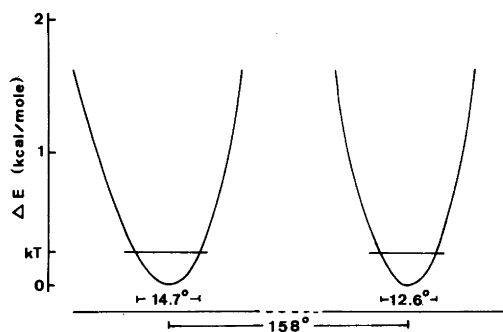


Fig. 2. Potential curve calculated for a rotation of the disordered morpholino ring.

(0.22 kcal/mol) above the minima were found to be 7.4° and 6.3°, respectively, which agrees well with the r.m.s. amplitudes for the oscillation about corresponding axes of the other two morpholino moieties of the ion.

## DISCUSSION

*The perchlorate ions.* In both structures the perchlorate ions appear to be at sufficient distances from the cations to allow one to conclude that they are to be considered as discrete and uncoordinated ions. The OCIO bond angles (in the range 107.4–112.9°) in the perchlorate ions and, similarly, the chlorine–oxygen bond lengths of  $1.464 \pm 0.008$  Å, are of the expected magnitude for non-coordinated perchlorate ions<sup>3</sup> and seem to substantiate this conclusion.

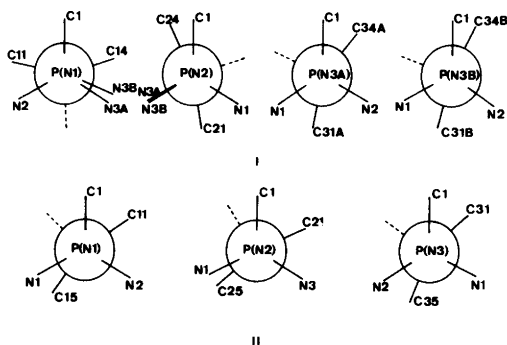


Fig. 3. Newman projections along the P–N bonds. The broken lines indicate torsion angles as defined in Ref. 1.

**Conformational considerations.** Newman diagrams of the conformation about the P–N bonds are presented in Fig. 3. The significant difference in the structure of the cations in I and II is the arrangement of the amino substituents. In I, the lone pair of one of the nitrogen atoms (N1) is *anti* with respect to the P–C bond; the two remaining morpholino groups are twisted in opposite directions. The directions of the nitrogen lone pairs in the latter two groups are roughly orthogonal to the P–C bond and to each other (angles in the range 50–80°). The arrangement of the amino substituents in I is thus quite analogous to what has previously been observed in the parent aminophosphine<sup>1</sup> and its selenide.<sup>2</sup>

In II, however, all the piperidino groups are twisted and in the same direction with C1–P–N–lone pair (N) torsion angles of –47, –33 and –55°, respectively, forming a propeller-shaped arrangement of the amino substituents. The arrangement of two twisted piperidino groups and one in the *anti* position as observed in the trivalent<sup>1</sup> and in the pentacovalent<sup>2</sup> species is thus not retained in II. The nitrogen lone pair directions<sup>1</sup> form angles in the range 83–102° with each other.

In both I and II all nitrogen atoms are essentially  $sp^2$  hybridized. Apparently, owing to the predominant *s*-character of the nitrogen lone pairs and thus their lower directionality combined with the larger NPN angles, phosphonium cations derived from tris(dialkylamino)phosphines,  $(R_2N)_3P$ , may have either of the structures observed in I and II.

**Bond angles around the phosphorus atoms.** Because of the poor accuracy in the determination of the atomic position of the atoms of the disordered

morpholino substituent, these are left out of the following discussion.

The coordination of the phosphorus atoms is essentially tetrahedral. All the CPN and NPN angles have values in the 105.3–112.7° range. The deviation from the tetrahedral angle does not seem to indicate that the benzylic substituent is unique in the way found for the phosphorus lone pair in the parent tris(dialkylamino)phosphines<sup>1</sup> and for the double bonds in their selenides<sup>2</sup> and tellurides.<sup>9</sup> We have to conclude that the deviations are mainly dependent on the bulkiness of the substituents combined with the tendency of the nitrogen lone pair directions to be orthogonal.

**Bond angles around the nitrogen atoms.** In both I and II all nitrogen atoms are essentially  $sp^2$  hybridized as viewed from the sum of the bond angles around these atoms, *cf.* Table 2. It may be noted that in I, even the nitrogen atom (N1) with its lone pair *anti* relative to the P–C bond is essentially  $sp^2$  hybridized. In the tellurium(II) complex, bromophenyl (trismorpholinophosphine)-selenide tellurium(II),  $Mor_3P-Se-Te(Ph)(Br)$ ,<sup>10</sup> the one  $sp^3$  hybridized nitrogen atom of the selenide<sup>2</sup> is transferred into an essentially  $sp^2$  hybridized one. Presumably, with only some positive formal charge on the central phosphorus atom, none of the nitrogen atoms retain their  $sp^3$  hybridization as observed in noncharged trivalent<sup>1</sup> and pentacovalent<sup>2,9</sup> species. Apparently, the  $p_N-d_p$  transfer<sup>11</sup> is more efficient in ionic tetrahedrally coordinated phosphonium cations and even in pentacovalent species containing only some fractional positive charge<sup>10</sup> than in non-charged pentacovalent phosphorus compounds.

The N–P direction is about midway between an axial and an equatorial direction with regard to the morpholino and the piperidino rings. For most of the rings the direction is on the equatorial side, but for N2 in I it is slightly closer to the axial direction.

**The phosphorus–nitrogen bond lengths.** In the trivalent<sup>1</sup> and the pentacovalent<sup>2</sup> species the P–N bond lengths were found within the ranges 1.65–1.73 Å. All bond lengths may in principle be considered as P–N single bond lengths, but the variation apparently depends upon charge and oxidation state of the central phosphorus atom and the torsion angle of the P–N bond with its consequences for the hybridization of the nitrogen atom.

In the present phosphonium cations all P–N bonds to the ordered rings are of equal length,

mean value 1.631 Å, with a sample standard deviation of 0.004 Å. Apparently the P–N bond length is independent of whether the nitrogen lone pair is *gauche* or *anti* relative to the P–C bond, and the P–C bond does thus not exert the same influence on the geometry as does a lone pair or a double bond. The results in Refs. 1 and 2 and from the present investigation indicate that the shortening of the P–N bond is dependent on  $p_N \rightarrow d_P$  transfer; the P–N bond lengths in I and II are significantly shorter than in  $\text{Mor}_3\text{PSe}^2$  and also in the tellurium(II) complex<sup>10</sup> in which  $\text{Mor}_3\text{PSe}$  acts as a selenium donor.

*The phosphorus-carbon bond length.* A number of structures of various salts of alkyltriphenylphosphonium cations,  $\text{RP}^+\text{Ph}_3$ , have been determined in recent years. The P–C(n-alkyl) bond length is known to fall in the 1.78–1.82 Å range<sup>11</sup> and is not significantly dependent upon the alkyl group. Apparently dialkylamino substituents in phosphonium cations have about the same influence as phenyl groups on the P–C (alkyl) bond lengths.

*The 4-nitrobenzyl moieties.* The coordination of the nitrogen atom in the nitro groups is planar in both compounds. The plane of the nitro group in I forms an angle of 7° with the benzene ring, in II they are coplanar. As in numerous other nitro-substituted benzene derivatives,<sup>12</sup> the internal phenyl CCC bond angle at the nitro group is significantly larger than 120°.

An interesting problem arises with regard to the PCC bond angles, 111.6(2)° in I and 117.8(1)° in II, both being significantly greater than the tetrahedral angle. The bond angle increment may solely be due to short intramolecular distances between atoms of the benzene ring and the morpholino and piperidino protons, and in both compounds there are also short intramolecular separations of the benzylic protons and the methylene protons in the  $\alpha$  positions to the nitrogen atoms. However, in several 4-nitrobenzylsubstituted phosphorus compounds with highly varying steric conditions, bond angles of corresponding magnitude are found; this may indicate that the methylene carbon atom has some  $sp^2$  character, which may be partly the cause of the high acidity of the methylene hydrogen atoms in this class of compounds.<sup>4</sup>

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