Table 3. *Comparison of the* C(3)—C(3′) *bond distance and heat of formation between bis(benzofuranonyl) and bisphthalidyl*

Compound	Bond distance X-ray	PM3 (Å)	ΔH_f (kcal mol^{-1})
(I*a*) *gauche*	1.596 (5)	1.564	− 14.50
(I*a*) *anti*		1.574	− 14.71
(I*b*) *gauche*	1.624 (4)	1.564	
(II*a*) *anti*	—	1.586	− 22.10
(II*b*) *anti*	1.571	—	

6.05 and 6.93 with an integration ratio of 1:1 at 203 K. At 263 K the exchange rate was 530 s^{-1} and the free activation energy ΔG (263 K) was estimated to be 12 kcal mol^{-1}. If molecule (I) exists in the conformation observed in the crystal, C(5)—H, which is located above the 3′-phenyl group, is probably more shielded than C(5′)—H. The observed dynamic process is probably due to the interconversion between (+)-*gauche* and (−)-*gauche* forms through restricted rotation around the C(3)—C(3′) bond. No other signal assignable to 4- and 4′-H was observed, indicating that the population of the *anti* form was negligibly small.

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Structure and Thermal Motion of Tetrakis(trichlorophosphazeno)phosphonium Dichloroiodate(I), $[P(NPCl_3)_4]^+[ICl_2]^-.2[(CCl_4)_x(CHCl_3)_{1-x}]$, $x = 0.67$ (2)

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Dedicated to Professor Dr Josef Schurz on the occasion of his 70th birthday

Abstract

$[P(NPCl_3)_4]^+[ICl_2]^-.2[(CCl_4)_x(CHCl_3)_{1-x}]$, $x = 0.67$ (2), $M_r = 1119.1$, tetragonal, $I4_1/acd$, $a = 16.114$ (4), $c = 27.777$ (7) Å, $V = 7213$ (1) Å^3, $Z = 8$, $D_x = 2.06$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.76$ mm^{-1}, $F(000) = 4251.5$, $T = 293$ K, $R = 0.0434$, $wR = 0.0452$ for 596 unique observed reflections and 80 parameters. The cation, anion and solvent molecules show site symmetries of S_4, D_2 and C_2, respectively. In the cation, the observed P—N distances of 1.452 (17) and 1.481 (17) Å are extremely short. Taking the observed P···P distance of 2.928 (4) Å as a basis, a correlation of the P—N—P bond angles with the P···P distances found in the Cambridge Structural Database (CSD) suggests a P—N—P angle of *ca* 136° rather than the observed angle of 173.3 (11)°. The N and Cl atoms especially have unusually large displacement parameters. The thermal motion analysis shows that the 'rigid-bond' test is fulfilled. The PN_4 tetrahedron, the almost regular $P(\cdots P)_4$ tetrahedron and the $NPCl_3$ tetrahedron appear to be rigid bodies; the $[P(NPCl_3)_4]^+$ cation as a whole does not. Furthermore, the non-rigid body motion cannot be explained by allowance for intramolecular torsion. All these facts can only be

explained by an exceptionally high flexibility of the P—N—P bond angle or by a precession motion of the N atom about the P···P connecting line with a P—N—P angle of *ca* 136° or by some similar disorder. The anion is linear and symmetric [I—Cl 2.535 (3) Å].

Introduction

Recently structural data of the $[Cl—P(NPCl_3)_3]^+$ cation were obtained for the first time (Belaj, 1992). Due to the high flexibility at the N atoms, this cation shows crystallographic C_3 (3) symmetry in $[Cl—P(NPCl_3)_3]^+Cl^-$, but C_s (*m*) symmetry in $[Cl—P(NPCl_3)_3]^+PCl_6^-.0.5C_2H_2Cl_4$. In the ^{31}P NMR spectrum of the title compound (Schmidpeter & Weingand, 1969), a quintet corresponding to an AB_4 spin system is observed, establishing the constitution of the cation. The present study is the first to describe a crystal structure determination of the highly symmetric $[P(NPCl_3)_4]^+$ cation. As this structure determination results in extremely short P—N distances and unusually large displacement parameters, two models of non-rigid body motion and a similar model of disorder will be discussed.

Experimental

The title compound was obtained by the reaction of $P(NH_2)_4I$ with PCl_5 (Schmidpeter & Weingand, 1969). Yellow crystals could be grown by diffusion of CCl_4 into a $CHCl_3$ solution, they are very moisture sensitive. All the following measurements were carried out on a modified Stoe four-circle diffractometer using graphite-monochromatized Mo *Kα* radiation:

Several attempts to determine the structure at low temperature failed: In the best case, a random search for reflections at 105 K yielded 49 reflections; 31 of them could be indexed with a body-centred orthorhombic cell, the rest corresponded to a twinned lattice. Refinement of the positions of 50 symmetrically equivalent reflections (2θ range 9–21°) confirmed orthorhombic symmetry; the least-squares fit resulted in the cell constants $a = 15.534$ (18), $b = 16.298$ (6), $c = 27.06$ (4) Å. Data were collected at 105 K for all reflections of a quadrant with 2θ from 3 to 48°. The structure could be solved by direct methods (space group *Ibca*), but refined only to $R = 0.136$ (844 unique reflections, 133 parameters).

The following measurements were carried out at room temperature on another single crystal (0.15 × 0.15 × 0.10 mm) sealed in a Mark capillary: Cell parameters were determined from a least-squares fitting of 93 well positioned reflections (2θ range 9–26°). 2623 reflections were measured using ω-scans (scan range 1.5°) for 2θ from 3 to 45° (h $0\rightarrow17$, k $0\rightarrow17$, l $0\rightarrow29$) and no significant intensities were observed above $2\theta = 45°$. 1069 reflections had $I > 3\sigma(I)$, 596 were unique. Two standard reflections (125, 2,2,12) measured every 100 reflections showed maximum variations in intensity of 1.77% and 2.67%, respectively; the internal consistency factor was computed to $R_{int} = 0.0442$. Data were corrected for Lp effects, but not for absorption. The structure was solved by direct methods ($I4_1/acd$) using *SHELXS*86 (Sheldrick, 1985). Whereas the site occupation factor (s.o.f.) of Cl lying on a twofold rotation axis refines to a value not significantly different from 0.5 [0.52 (2)], the s.o.f.'s of Cl5 and Cl6 lying on general positions refine to 0.916 (9) and 0.920 (12), respectively. Crystal growth by the diffusion method evidently caused a partial substitution of the CCl_4 molecules by the solvent $CHCl_3$.

Full-matrix least squares refinements (on F, weighting scheme $w = 1/[\sigma^2(F_o) + 5.8 \times 10^{-5} F_o^2]$) with anisotropic displacement parameters for all atoms and a common s.o.f. for the Cl atoms of the solvent molecule [refining to 0.917 (6)] until no parameter shifts occurred ($\Delta/\sigma \leq 0.001$) gave $R = 0.0434$, $wR = 0.0452$, $S = 2.42$ (596 reflections, 80 parameters). From the s.o.f. for the Cl atoms of the solvent molecule the value of x in the empirical formula is computed to be 0.67 (2) [from the equation $x + 0.75(1 - x) = 0.917$ (6)]. The maximum and minimum peaks of the final difference-Fourier map were 0.40 and −0.35 e Å^{-3}, respectively. The three strongest peaks were found near Cl (1.36–1.59 Å), the fourth near N1 (0.92 Å, 0.23 e Å^{-3}). Cooling this crystal below 230 K resulted in a broadening, splitting and strong weakening of the reflections, which deteriorates on cooling further, but being fully reversible.

Scattering factors and anomalous dispersion corrections from *International Tables for X-ray Crystallography* (Ibers & Hamilton, 1974). A VAX/VMS 6000 computer was used with the programs *ORTEP* (Johnson, 1965), *PLATON* (Spek, 1982), *PLUTO* (Motherwell, 1976), *SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1985), and *THMI*-2 (Schomaker & Trueblood, 1968; Dunitz & White, 1973; Trueblood, 1978).

Discussion

For the structure determination at room temperature, final atomic positional and displacement parameters are listed in Table 1,* bond lengths and angles are given in Table 2 and the atom labelling is

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* Lists of structure factors of the room-temperature structure determination, and final atomic parameters and bond lengths and angles of the structure determination at 105 K have been deposited with the IUCr (Reference: SE0139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* (× 10^4) *and displacement parameters* (× 10^3 Å^2) *with standard deviations in parentheses*

$$T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots\ldots 2hka^*b^*U_{12} + \ldots\ldots)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P1	5000	2500	1250	87 (2)	87 (2)	64 (3)	0	0	0
N1	4648 (9)	1830 (10)	948 (6)	192 (14)	219 (16)	248 (18)	− 35 (14)	− 73 (13)	− 140 (14)
P2	4209 (2)	1201 (2)	673 (1)	92 (2)	119 (3)	71 (2)	17 (2)	− 13 (2)	− 33 (2)
Cl1	4288 (3)	1313 (3)	− 22 (1)	218 (5)	186 (4)	81 (3)	43 (4)	20 (3)	2 (3)
Cl2	3032 (2)	1175 (3)	800 (2)	95 (3)	229 (5)	161 (4)	11 (3)	7 (3)	− 22 (4)
Cl3	4607 (3)	90 (3)	804 (2)	214 (5)	151 (4)	134 (4)	81 (4)	− 22 (4)	− 3 (3)
I1	0	2500	1250	84 (1)	84 (1)	49 (1)	− 23 (1)	0	0
Cl4	1112 (2)	1388 (2)	1250	113 (2)	113 (2)	88 (3)	5 (3)	− 5 (2)	− 5 (2)
C1	2500	3707 (15)	0	110 (15)	154 (20)	140 (19)	0	6 (17)	0
Cl5	1865 (4)	3152 (4)	365 (3)	255 (8)	235 (7)	242 (8)	− 90 (6)	51 (6)	45 (6)
Cl6	3117 (4)	4286 (5)	350 (2)	214 (7)	321 (9)	180 (7)	− 104 (7)	− 34 (5)	− 23 (6)

Table 2. *Bond distances* (Å), *angles* (°) *and selected torsion angles* (°) *as a result of the structure determination at room temperature* (*symmetry codes given in Fig.* 1)

Cl1—P2	1.943 (5)	I1—Cl4	2.535 (3)
Cl2—P2	1.929 (5)	Cl5—C1	1.696 (15)
Cl3—P2	1.937 (6)	Cl6—C1	1.674 (16)
P1···P2	2.928 (4)		
N1—P1—N1$^{\text{i}}$	108.7 (9)	P2···P1···P2$^{\text{i}}$	107.4 (1)
N1—P1—N1$^{\text{ii}}$	111.0 (10)	P2···P1···P2$^{\text{ii}}$	113.6 (1)
Cl1—P2—Cl2	104.4 (3)	Cl4—I1—Cl4$^{\text{iv}}$	180
Cl1—P2—Cl3	104.5 (3)	Cl5—C1—Cl5$^{\text{v}}$	116.4 (14)
Cl2—P2—Cl3	105.7 (3)	Cl5—C1—Cl6	107.8 (3)
Cl1—P2—N1	115.2 (7)	Cl5—C1—Cl6$^{\text{v}}$	106.4 (3)
Cl2—P2—N1	113.4 (6)	Cl6—C1—Cl6$^{\text{v}}$	112.3 (15)
Cl3—P2—N1	112.7 (7)		
P2$^{\text{i}}$···P1···P2—Cl1	119.2 (2)	P2$^{\text{iii}}$···P1···P2—Cl2	123.2 (2)
P2$^{\text{ii}}$···P1···P2—Cl1	0.5 (5)	P2$^{\text{i}}$···P1···P2—Cl3	− 118.3 (2)
P2$^{\text{iii}}$···P1···P2—Cl1	− 118.2 (2)	P2$^{\text{ii}}$···P1···P2—Cl3	123.0 (2)
P2$^{\text{i}}$···P1···P2—Cl2	0.6 (5)	P2$^{\text{iii}}$···P1···P2—Cl3	4.3 (3)
P2$^{\text{ii}}$···P1···P2—Cl2	− 118.1 (2)		

shown in Fig. 1. The main differences between the two structures determined at 295 and 105 K are the following: In the space group $I4_1/acd$, the central P atom of the cation and the atoms of the anion are constrained to $z = 0.125$, whilst in $Ibca$ the z coordinates are refined to 0.1364 (7), 0.1306 (2) and 0.1311 (5) for the P1, I1 and Cl4 atoms, respectively. Therefore, the ions lying at $x + y = \frac{1}{4} + n$, with n an integer, are displaced downwards whilst the ions at $x + y = \frac{3}{4} + n$ are displaced upwards with respect to the positions of the room-temperature structure. At the solvent molecules, the positions of the C atoms do not differ significantly and the orientation of the $CCl_4/CHCl_3$ molecules is almost equal in the two structure determinations. The packing diagram (see Fig. 2) exhibits a close resemblance of the orthorhombic low-temperature structure with the tetragonal room-temperature structure. The reversibility of the phase transition between the two structures, the space groups of which are connected by a subgroup–supergroup relationship, is obvious. In the following, the discussion is dealing with the more accurate room-temperature structure determination unless stated otherwise.

The $[P(NPCl_3)_4]^+$ cations are located on fourfold roto-inversion axes, $\bar{4}$ (S_4). Within the precision of the measurement, the central PN_4 group is a regular tetrahedron. The P—N—P bond angles are almost linear [173.3 (11)°], as in the linear compound tetraphenylimidobis(phosphinic acid) (Nöth, 1982) or in some cases of the bis(triphenylphosphino)iminium cation (Belaj, 1993). As observed in $[Cl_3PNPCl_3][PCl_6]$ (Faggiani, Gillespie, Sawyer & Tyrer, 1980), $Cl_3PNP(O)Cl_2$ (Belaj, 1993), $[ClP(NPCl_3)_3]Cl$ and $[ClP(NPCl_3)_3][PCl_6]0.5C_2H_2Cl_4$ (Belaj, 1992), the N—P—Cl angles in the $NPCl_3$ tetrahedron are clearly larger than the Cl—P—Cl bond angles and the Cl—P2···P1···P2 torsion angles and the Cl—P2···P2—Cl torsion angles are close to 0 or ±120°.

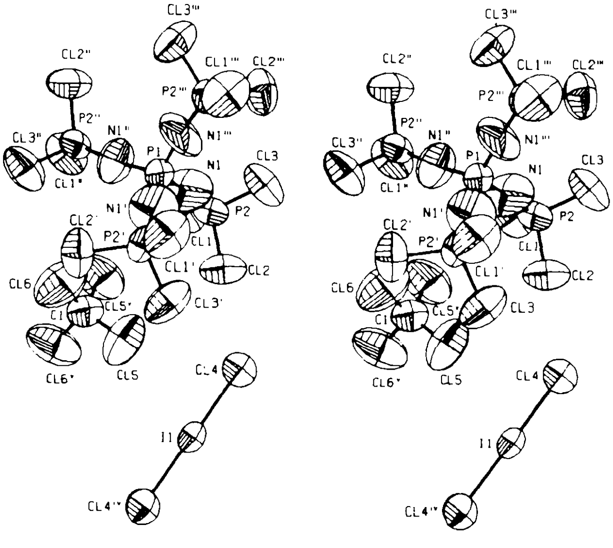

Fig. 1. Stereoscopic *ORTEP* (Johnson, 1965) plot showing the atomic labelling scheme of the $[P(NPCl_3)_4]^+$ cation, the ICl_2^- anion and one CCl_4 solvent molecule. The equiprobability ellipsoids are drawn at the 50% level. Symmetry codes: (i) $\frac{1}{4} + y, \frac{3}{4} - x, \frac{1}{4} - z$; (ii) $1 - x, \frac{1}{2} - y, z$; (iii) $\frac{3}{4} - y, x - \frac{1}{4}, \frac{1}{4} - z$; (iv) $-x, \frac{1}{2} - y, z$; (v) $\frac{1}{2} - x, y, -z$.

In contrast to the compounds mentioned above, the P—N distances of 1.452 (17) and 1.481 (17) Å are extremely short, shorter than could be found in any other acyclic compound containing the P—N—P structural fragment. Short P—N distances [1.43 (5) and 1.55 (5) Å] and almost linear P—N—P angles [169 (3) and 157 (4)°] are also observed in the structure determination at 105 K. From a search of the Cambridge Structural Database (CSD, Version 5.1, release date 3 May 1994; Allen, Kennard & Taylor, 1983), the mean value for the P—N bond length is 1.576 (1) Å.

Due to the lower number of electrons, the position of the N atom is less accurately determined than the positions of the P and Cl atoms. Assuming the mean P—N distances to be nearly constant in the PNP fragment, the P···P distance may be taken as a measure of the P—N—P angle, namely $\alpha_{PNP} = 2 \arcsin [d_{P\cdots P}/(2d_{P-N})]$, even if the position of the N atom is not or not exactly determined. This assumption is tested with the help of the data from the CSD: Fig. 3 shows the correlation between the P···P distance and the P—N—P bond angle for all acyclic P—N—P structural fragments (449 hits, *R* factors restricted to be less than 0.1). For P—N—P angles between 130 and 160°, a slight decrease in the P—N distance with increasing P—N—P angle is very probable, as indicated by the smaller slope of the regression line compared with the slope of the function mentioned above. This effect is to be expected considering the transition from sp^2 hybridization of nitrogen in the bent form to *sp* hybridization in the linear form (Wilson & Bau, 1974).

The compounds with linear P—N—P geometries show P···P distances not larger than 3.11 Å (P—N 1.523–1.555 Å). They all lie on centres of symmetry ($\bar{1}$ or $\bar{3}$). The linearity has been interpreted in terms of a disorder of nitrogen around the centre of symmetry by Müller, Ha-Eierdanz, Kräuter & Dehnicke (1991) for $[(Ph_3P)_2N]_3[Co_3Se_{24}]$.2DMF. The compound $[(Ph_3P)_2N]_3\{Na[Mo_3(CO)_6(NO)_3(\mu_2\text{-}OCH_3)_3(\mu_3\text{-}O)]_2\}$ (Kirtley *et al.*, 1980) contains a bent $[(Ph_3P)_2N]^+$ cation [139.1 (12)°, P···P 2.953 Å] lying on a general position and a linear one [P···P 3.062 Å] occupying an inversion centre (no disorder stated for the N atom). This demonstrates that, due to the low PNP bending force constant (Bougeard, Brémard, De Jaeger & Lemmouchi, 1993), small packing effects may force a P—N—P angle up to 180°, while the electronic situation around the N atom is changed.

The title compound represents unambiguously an outlier in Fig. 3: There is no centre of symmetry near the N atom and the P···P distance is substantially smaller than in known compounds with linear P—N—P geometries. Assuming the simple relation between α_{PNP} and the P···P distance to hold approximately for the compound discussed here, a P—N—P angle of *ca* 136° is estimated from the P1···P2 distance of 2.928 (4) Å. In the structure determination at 105 K, short P···P distances [2.97 (2) and 2.92 (2) Å] were also observed.

The following paragraphs are concerned with attempts at reconciling the refinement results [α_{PNP} = 173.3 (11)°, large displacement parameters] with the conflicting chemical evidence of Fig. 3 ($\alpha_{PNP} \simeq 136°$). Firstly, it was assumed that the N atoms were disordered over two or four positions; in these models large correlations occurred between the nitrogen parameters but the *R* factor did not drop significantly (Hamilton, 1965), and the N—P—N angles around the central P atom and the N—P—Cl

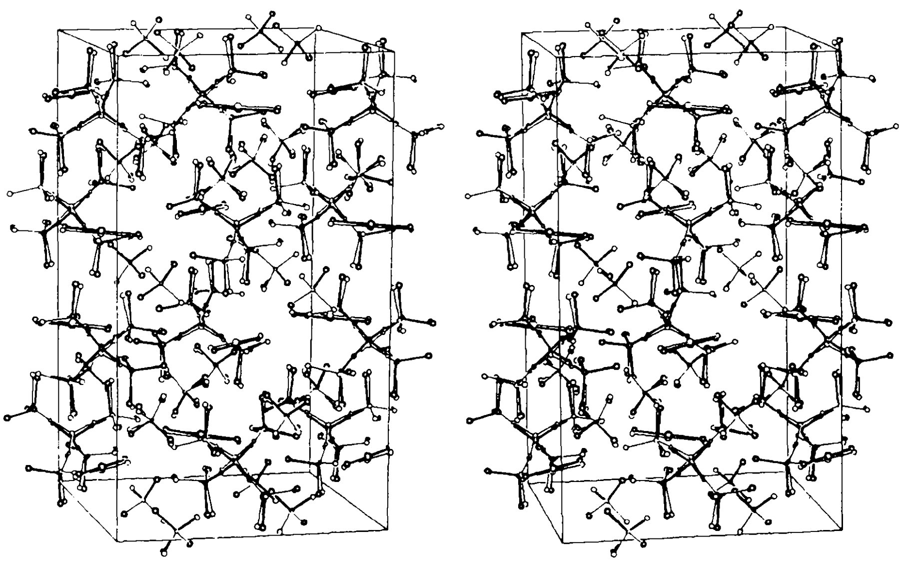

Fig. 2. Stereoscopic drawing of the packing in the unit cell at 295 K (thick lines) in comparison to the packing at 105 K (thin lines). The atoms are drawn as spheres with arbitrary radii.

angles necessarily became very different. Obviously, the Cl atoms of the $NPCl_3$ group (and eventually of the CCl_4/$CHCl_3$ solvent molecules) also have to be taken into account in a disorder model. Several computations showed that the structure cannot be modelled disregarding the thermal motion of the cation.

At room temperature, the N and Cl atoms especially show unusually large displacement parameters (see Table 1). According to the 'rigid-bond' postulate (Hirshfeld, 1976), the difference $\Delta = |z^2_{A,B} - z^2_{B,A}|$ should vanish for every covalently bonded pair of atoms A and B, where $z^2_{A,B}$ denotes the mean-square amplitude of vibration of atom A along the direction of the bond A—B. In this structure determination, the lack of high-order data ($\sin\theta/\lambda > 54°$) leads to only limited accuracy of the displacement parameters. Nevertheless, the differences Δ's for covalently bonded pairs of atoms are less than $2\sigma(\Delta)$; within the rather large σ's the 'rigid-bond' test is fulfilled.

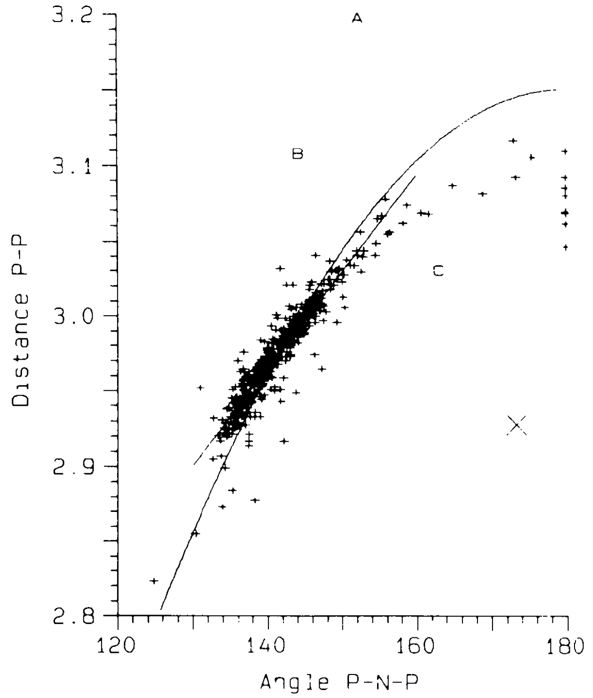

Fig. 3. Plot of the P···P distance (Å) *versus* the P—N—P bond angle (°) in acyclic P—N—P fragments found at the CSD (+, *A*, *B*, *C*) and in the cation of the title compound (*X*). The solid curve shows the geometrical correlation between the two quantities if the P—N distance is fixed at the mean value of all the P—N distances in acyclic P—N—P fragments found at the CSD [1.576 (1) Å]. The regression line is computed for all data with $130 < \alpha_{PNP} < 160°$, neglecting the outliers *A*, *B*, *C*. Outlier *A* (Bogdan, Sabat, Sunshine, Woodcock & Shriver, 1988) is due to a wrong coordinate [assuming 0.4792 instead of 0.4892 for *x* of P1, the two $N[P(C_6H_5)_3]_2^+$ cations in the asymmetric unit show comparable geometric parameters, *e.g.* P—N—P 149.7 and 152.8°, P···P 3.030 and 3.040 Å, respectively]; the structure determination of the outliers *B* (Abu-Salah, Hussain & Schlemper, 1988) and *C* (Braga *et al.*, 1982) resulted in large *R*-factors of 0.092 and 0.097, respectively.

The analysis of the atomic displacement parameters in terms of rigid-body motions (Schomaker & Trueblood, 1968) establishes that the $[P(NPCl_3)_4]^+$ cation is not a rigid body: the residual index R_u, defined as $R_u = [\sum w(\Delta U)^2/\sum w(U_{obs})^2]^{1/2}$, with $w = 1/\sigma^2$, is 0.327, the maximum difference Δ between non-bonded pairs of atoms being 0.174 (7) Å^2. This high value of R_u is not caused by ill-determined parameters for the N atom: omission of N1 from the rigid-body calculation resulted in $R_u = 0.312$. On the other hand, the PN_4 [$R_u = 0.028$, $\Delta_{max} = 0.022$ (16) Å^2] and the $NPCl_3$ tetrahedra [$R_u = 0.050$, $\Delta_{max} = 0.027$ (16) Å^2] behave as rigid bodies within the precision of the U_{ij} values. The rigid-body calculation of these two tetrahedra resulted in P—N bond lengths corrected for libration (Schomaker & Trueblood, 1968), of 1.629 and 1.510 Å for P(1)—N(1) and N(1)—P(2), respectively. Estimates of the lower and upper limits of the P—N bond lengths (Johnson, 1970) resulted in data of little value (1.529, 1.489, 1.946 and 1.970 Å, respectively).

In order to determine the nature of internal motion in the cation, the analysis was continued with allowance for intramolecular torsion (Trueblood, 1978; Dunitz, Maverick & Trueblood, 1988): Several models of a rigid PN_4 core with four attached rigid PCl_3 groups, each participating in the motion of the core but also librating relative to the core about an axis, were tested for the following axes: bond P1—N1, bond N1—P2, line through N1 normal to the P1—N1—P2 plane, and the line bisecting the P1—N1—P2 angle. All these tests failed: in the best case, R_u dropped from 0.327 to only 0.291.

A re-examination of the displacement parameters (determined at 100 K) in the related $[Cl—P(NPCl_3)_3]^+$ cation (Belaj, 1992) or in $Cl_3PNP(O)Cl_2$ (Belaj, 1993) showed that the $NPCl_3$ groups, the $Cl—PN_3$ groups and the $NP(O)Cl_2$ groups are rigid and that the non-rigidity of the cation (respectively of the molecule) as a whole could not be explained by an intramolecular torsion about a bond, either. Instead it is assumed that the P—N—P bond angle is highly flexible, and correspondingly that the motion in these compounds can be described as almost independent motions of rigid tetrahedra, coupled by a 'ball joint'.

It is surprising that the P(2) atom in the title compound, although more distant from the centre of the cation than N1, it is not appreciably affected by the high flexibility of N1. Furthermore, the almost regular $P(\cdots P)_4$ tetrahedron [P···P···P angles of 107.4 (1) and 113.6 (1)°] behaves as a rigid body [$R_u = 0.016$, $\Delta_{max} = 0.002$ (4) Å^2]. In order to reconcile all these facts, there are three possible explanations: firstly a non-rigid body motion of the cation analogous to the motion postulated in the $[Cl—P(NPCl_3)_3]^+$ cation or in $Cl_3PNP(O)Cl_2$, but consisting to a larger extent of a vibration of N1 through the centre of the P···P connecting line; secondly, a model in which N1 precesses around about the P···P line with a fixed P—N—P bond angle of *ca* 136°; thirdly, a similar model of disordered N atoms (and hence disordered $NPCl_3$ groups) with P—N—P bond angles of *ca* 136° must be considered. The second and third model are not distinguishable, considering the 'time-scale' of the X-ray experiment. The second model (see Fig. 4) reproduces well the orientation of the equiprobability ellipsoids of the N and Cl atoms (*cf.* Fig. 1), if τ is the torsion angle *X*—P1···P2—N1 [*X* has the fractional coordinates $(\frac{1}{2},\frac{1}{4},0)$] and if the three torsion angles Cl—P2—N1—P1 are constrained to be $180 - \tau$ and $\pm 60 - \tau$. Evidently, in such a precession motion this cation does not have at any time the $\bar{4}$ symmetry as observed for the time-averaged electron-density distribution.

A section normal to the P···P connecting line through N1 of the difference Fourier map after omission of N1 does not show a circular electron-density distribution, but a single peak near the centre of the P···P connecting line. However, the second model cannot be excluded by this fact, since the section through a Fourier synthesis map calculated with four or eight circularly arranged N atoms (diameter 1.07 Å corresponding to a P—N—P angle of 136°, $U_{iso} = 0.08$, site occupation factors of 0.25 or 0.125, respectively) shows that the peaks of the contributing atoms are too broad to be resolved into single peaks or even a ring-like electron-density distribution. In order to study the structure of this cation more precisely, particularly at low temperature, the structure determination of the salt with the Cl^- anion or the larger PCl_6^- anion is planned. However, no disorder was observed in the crystal structure determinations of the related compounds $A(—N{=}X)_4$ [$X = C(C_6H_5)_2$, A = Si, Ge, Sn (Alcock & Pierce-Butler, 1975) and $X = —C—C(CF_3)_2—S—C(CF_3)_2—S—$, A = Ge (Roesky, Dhathathreyan, Noltemeyer & Sheldrick, 1985)] at room temperature. The *A*—N=C angles in these four compounds are 128.4–140.2, 124.0–130.0, 121.6 and 123.6–130.7°, respectively.

The three atoms of the ICl_2^- anions lie on twofold axes parallel to [110] or [$\bar{1}$10]. The ions show 222 (D_2) symmetry and are, therefore, linear and symmetric (trigonal bipyramidal arrangement of the five electron pairs around the I atom), as commonly observed: A search of the CSD yielded 13 hits (*R*-factor less than 0.05): mean (I—Cl) = 2.552 (12) Å, mean (Cl—I—Cl) = 179.2 (3)°. The anions show thermal vibration amplitudes of the same magnitude as those of the P atoms of the cations. The solvent molecules are placed on twofold rotation axes parallel to [100] or [010] and behave as rigid bodies ($R_u = 0.037$) with very high thermal vibration amplitudes.

The packing of the compound (see Fig. 2) consists of layers normal to the *z*-axis, cations and anions at $z = \frac{1}{8},\frac{3}{8},\frac{5}{8},\frac{7}{8}$ with solvent molecules embedded between them at $z = 0,\frac{1}{4},\frac{1}{2},\frac{3}{4}$. The shortest intermolecular contact distances are within layers between Cl4 of the anion and two Cl2 atoms of two cations [3.354 (5) Å]. In addition, the ICl_2^- anion shows four short intermolecular Cl4···Cl1 distances [3.474 (4) Å] to the two cations lying above and below in the [001] direction. The remaining intermolecular distances [≥ 3.606 (4), ≥ 3.618 (4) and ≥ 3.626 (5) Å for the cation, anion and solvent molecule, respectively] are longer than the sum of the van der Waals' radii of two Cl atoms (3.50 Å; Bondi, 1964).

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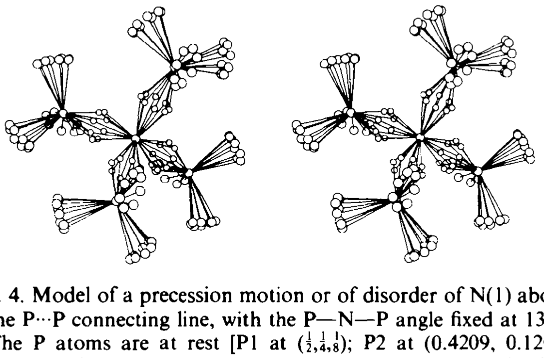

Fig. 4. Model of a precession motion or of disorder of N(1) about the P···P connecting line, with the P—N—P angle fixed at 136°. The P atoms are at rest [P1 at $(\frac{1}{2},\frac{1}{4},\frac{1}{8})$; P2 at (0.4209, 0.1201, 0.0673)], the Cl—P2—N1—P1 torsion angles are constrained to be $180 - \tau$ and $\pm 60 - \tau$, where τ is the torsion angle *X*—P1···P2—N1 [*X* at $(\frac{1}{2},\frac{1}{4},0)$]. In the stereoscopic plot, the cation is drawn with $\tau = 0, 45, \ldots, 315°$.

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The *Ab Initio* Crystal-Structure Determination of Perdeuterodimethylacetylene by High-Resolution Neutron Powder Diffraction

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Abstract

The low-temperature crystal structure of dimethylacetylene-d_6 (2-butyne-d_6, $CD_3—C{\equiv}C—CD_3$) has been solved *ab initio* from high-resolution neutron powder diffraction data. The structure is monoclinic, space group $C2/m$, with two molecules per unit cell. At 5 K, the cell dimensions are $a = 7.15889\ (4)$, $b = 6.45529\ (2)$, $c = 4.07818\ (9)$ Å and $\beta = 101.0535\ (5)^\circ$; $V = 184.97$ Å^3. The powder diffraction pattern for the material exhibits *hkl*-dependent line broadening, apparently as a result of stacking faults intrinsic to the structure. Novel analysis techniques have been used to model line broadening and enable accurate structural parameters to be obtained.

Introduction

Dimethylacetylene (2-butyne, $CH_3—C{\equiv}C—CH_3$) is a simple linear molecule composed of only two different elements. It is, therefore, a model compound for comparing the *ab initio* calculation of methyl-group rotation potentials from structural data with potentials derived from tunnelling and librational transitions [see, for example, work on *p*-xylene (Prager, David & Ibberson, 1991) and toluene (Prager, Monkenbusch, Ibberson, David & Cavagnat, 1993).] For such studies, accurate structural data are a prerequisite. The crystal structure of non-deuterated dimethylacetylene (subsequently referred to as DMA) has been solved using single-crystal X-ray diffraction (Miksic, Segerman & Post, 1959). The proposed structure is tetragonal at low temperature and only the atomic positions for C atoms were determined. On the basis of this structure, using calculated proton positions and reliable pair potentials for pure hydrocarbons (Kitaigorodskii, 1965), a full lattice dynamical calculation was carried out. However, these calculations indicate a completely unstable crystal structure, therefore suggesting incorrect structural parameters for the proton positions and possibly an erroneous