Acta Cryst. (1983). C39, 880–882

Structure of Bis(triphenylphosphoranediyl)ammonium Chloride–Boric Acid Adduct (1:1), $C_{36}H_{30}NP_2^+.Cl^-.BH_3O_3$

BY STEVEN J. ANDREWS,* DOROTHY A. ROBB† AND ALAN J. WELCH

Dewar Crystallographic Laboratory, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

(*Received* 19 *January* 1983; *accepted* 18 *February* 1983)

Abstract. $M_r = 635·9$, orthorhombic, *Pbca*, $a = 19·010\,(3)$, $b = 18·869\,(4)$, $c = 18·432\,(6)$ Å, $U = 6611\,(4)$ Å^3, $Z = 8$, $D_x = 1·277$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 0·205$ mm^{-1}, $F(000) = 2656$, $T = 291$ K. Final $R = 0·0611$ for 4372 observed reflections. The chloride anion is associated in the crystal with the $B(OH)_3$ molecule *via* strong bifurcated hydrogen bonds, Cl···H 1·94 (6) and 2·14 (6) Å, and two Cl···$(HO)_3B$ units are hydrogen-bonded across a centre of symmetry in a manner similar to that found in boric acid itself. The cation is non-linear, P—N—P 137·4 (2)°, and adopts a staggered conformation.

Introduction. As part of our continuing interest (Andrews, Welch, Jacobsen & Morris, 1982) in the stereochemistries of substituted derivatives of the $[B_3H_8]^-$ anion, we recently sought to study the salt $[(Ph_3P)_2N]^+[B_3H_6(Cl)(NCS)]^-$, given by reaction between $[(Ph_3P)_2N]^+]B_3H_7(NCS)]^-$ and HCl (Arunchaiya & Morris, 1983).

Crystallization of the reaction product (dichloromethane/*n*-hexane) afforded two distinct crystalline samples. The major component, subsequently shown to be the dichloromethane solvate of the target material (Andrews, Robb & Welch, 1983) turned opaque upon standing due to loss of solvent, whilst the minor component remained clear and crystalline. In aticipation that this minor product might be a second, atmospherically stable, modification of the required species, crystallographic study was pursued and the results are presented herein.

Experimental. Clear, colourless blocks, 0·5 × 0·4 × 0·3 mm; CAD-4 diffractometer, 25 reflections ($14 < \theta < 15°$) centred, graphite-monochromated Mo $K\alpha$; space group identified by rapid measurement of zonal reflections *hk*0, *h*0*l* and 0*kl* to maximum index of 4; for data collection $\theta_{max} = 27°$, ω–2θ scan in 96 steps, ω-scan width 0·8° + 0·35° tan θ, rapid prescan after which reflections with $I \geq 0·5\sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to maximum measuring time of 75s, no significant crystal decay or movement, 7182 unique reflections over 143 X-ray hours, no absorption correction; for structure solution and refinement 4372 amplitudes $[F \geq 2·0\sigma(F)]$, automatic centrosymmetric direct methods (Sheldrick, 1976); full-matrix least squares (F), $w^{-1} = [\sigma^2(F) + 0·00379\,(F)^2]^{1/2}$; anisotropic thermal parameters for all non-H atoms, phenyl groups idealized (C—C 1·395, C—H 1·08 Å), $B(OH)_3$ H atoms positionally refined (U_H‡ = 0·10 Å^2); *R* 0·0611, *wR* 0·0829; data:variable ratio 13:1; max. shift:error in final cycle < 0·03; max. peak and min. trough in final ΔF synthesis 0·33 and −0·31 e Å^{-3}; neutral-atom scattering factors for C,N,Cl,B,O,P (Cromer & Liberman, 1970) and H (Stewart, Davidson & Simpson, 1965); computer programs: *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1976), XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), and *ORTEP* II (Johnson, 1976).

The species was identified crystallographically with supportive evidence subsequently supplied by microanalysis (found, C67·7, H 5·0, N 2·7%; theoretical, C 68·1, H 5·2, N 2·2%) and ^{11}B NMR spectroscopy [21·92 p.p.m. (*s*) relative to $F_3B.OEt_2$ as external standard, 115·5 MHz spectrum, Brucker WH-360 spectrometer] on crystals of the minor component hand-picked from the bulk product.

Discussion. Table 1 lists derived fractional coordinates, those of the phenyl H atoms having been deposited as Table 2.§ Fig. 1 shows a view of the bis(triphenylphosphoranediyl)ammonium (PPN) cation along the P···P vector, and the nearest chloride anion and $B(OH)_3$ molecule. Thus the crystalline minor component is $[(Ph_3P)_2N]Cl.B(OH)_3$, the boric acid presumably formed by HCl degradation of the $[B_3H_7(NCS)]^-$ ion in the atmosphere.

---

* To whom correspondence should be addressed.

† Present address: University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

‡ The isotropic thermal parameter defined as exp[$-8\pi^2U(\sin^2\theta)/\lambda^2$].

§ Lists of structure factors, anisotropic thermal parameters, and Tables 2, 4, 5 and 6 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38428 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/070880-03$01.50

Table 1. *Fractional atomic coordinates with e.s.d.'s and isotropic thermal parameters*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_{ii} U_{ii}.$$

	x	y	z	$U_{\rm eq}$(Å^2)
B(1)	0·4362 (3)	0·0241 (3)	0·0854 (4)	0·063
Cl(1)	0·44846 (7)	−0·08764 (6)	0·23793 (7)	0·067
O(1)	0·42787 (18)	0·06228 (21)	0·02312 (22)	0·074
O(2)	0·48961 (17)	−0·02432 (20)	0·09078 (20)	0·071
O(3)	0·39185 (20)	0·03722 (23)	0·14073 (22)	0·085
P(1)	0·27692 (5)	0·02820 (5)	0·41950 (5)	0·031
P(2)	0·37157 (5)	0·14985 (5)	0·39748 (5)	0·032
N(1)	0·34637 (16)	0·07001 (16)	0·40018 (17)	0·040
C(12)	0·36836 (11)	−0·06751 (14)	0·48335 (16)	0·055
C(13)	0·38564	−0·12333	0·52968	0·073
C(14)	0·33370	−0·15485	0·57230	0·066
C(15)	0·26448	−0·13057	0·56860	0·061
C(16)	0·24721	−0·07476	0·52227	0·047
C(11)	0·29915	−0·04323	0·47965	0·036
C(22)	0·17828 (13)	−0·05115 (15)	0·34385 (12)	0·049
C(23)	0·14663	−0·07556	0·28030	0·063
C(24)	0·17475	−0·05725	0·21296	0·075
C(25)	0·23453	−0·01453	0·20916	0·079
C(26)	0·26618	0·00988	0·27271	0·058
C(21)	0·23806	−0·00843	0·34005	0·038
C(32)	0·15014 (14)	0·10172 (15)	0·42544 (12)	0·049
C(33)	0·09992	0·14400	0·45967	0·067
C(34)	0·10939	0·16436	0·53177	0·075
C(35)	0·16908	0·14243	0·56964	0·070
C(36)	0·21930	0·10014	0·53541	0·050
C(31)	0·20983	0·07978	0·46331	0·035
C(42)	0·42513 (16)	0·12856 (13)	0·53254 (15)	0·056
C(43)	0·45055	0·14788	0·60072	0·075
C(44)	0·44875	0·21869	0·62240	0·087
C(45)	0·42152	0·27017	0·57590	0·075
C(46)	0·39610	0·25084	0·50772	0·057
C(41)	0·39790	0·18004	0·48604	0·040
C(52)	0·25856 (14)	0·24411 (15)	0·39944 (12)	0·051
C(53)	0·20842	0·28726	0·36624	0·061
C(54)	0·20940	0·29663	0·29117	0·068
C(55)	0·26052	0·26286	0·24931	0·068
C(56)	0·31067	0·21971	0·28251	0·052
C(51)	0·30968	0·21033	0·35758	0·038
C(62)	0·48302 (13)	0·21817 (10)	0·33186 (14)	0·042
C(63)	0·54380	0·22144	0·28959	0·050
C(64)	0·57072	0·15996	0·25803	0·062
C(65)	0·53685	0·09522	0·26873	0·064
C(66)	0·47607	0·09195	0·31099	0·050
C(61)	0·44915	0·15343	0·34256	0·033
H(1)	0·461 (3)	0·049 (3)	−0·017 (3)	
H(2)	0·488 (3)	−0·057 (3)	0·146 (3)	
H(3)	0·411 (3)	0·002 (3)	0·178 (3)	

Table 3. *Bond lengths* (Å) *and angles* (°)

P(1)–N(1)	1·579 (3)	B(1)–O(1)	1·366 (8)
P(2)–N(1)	1·582 (3)	B(1)–O(2)	1·369 (7)
P(1)–C(11)	1·796 (3)	B(1)–O(3)	1·345 (7)
P(1)–C(21)	1·780 (3)	Cl(1)–H(2)	1·94 (6)
P(1)–C(31)	1·796 (3)	Cl(1)–H(3)	2·14 (6)
P(2)–C(41)	1·800 (3)	O(1)–H(1)	1·00 (6)
P(2)–C(51)	1·797 (3)	O(2)–H(2)	1·19 (6)
P(2)–C(61)	1·790 (3)	O(3)–H(3)	1·03 (6)
		O(2)–H(1′)	1·72 (6)
P(1)–N(1)–P(2)	137·4 (2)	N(1)–P(2)–C(41)	110·9 (1)
N(1)–P(1)–C(11)	108·5 (1)	N(1)–P(2)–C(51)	114·8 (1)
N(1)–P(1)–C(21)	110·8 (1)	N(1)–P(2)–C(61)	107·7 (1)
N(1)–P(1)–C(31)	115·1 (2)	C(41)–P(2)–C(51)	110·6 (1)
C(11)–P(1)–C(21)	108·3 (1)	C(41)–P(2)–C(61)	105·8 (1)
C(11)–P(1)–C(31)	107·2 (1)	C(51)–P(2)–C(61)	106·5 (1)
C(21)–P(1)–C(31)	106·6 (1)		
O(1)–B(1)–O(2)	119·9 (5)	H(2)–Cl(1)–H(3)	56 (2)
O(1)–B(1)–O(3)	117·9 (5)	O(2)–H(2)–Cl(1)	156 (4)
O(2)–B(1)–O(3)	122·2 (5)	O(3)–H(3)–Cl(1)	168 (5)
B(1)–O(1)–H(1)	115 (4)	B(1)–O(2)–H(1′)	122 (2)
B(1)–O(2)–H(2)	113 (3)	H(2)–O(2)–H(1′)	123 (3)
B(1)–O(3)–H(3)	100 (3)	O(2)–H(1′)–O(1′)	175 (6)

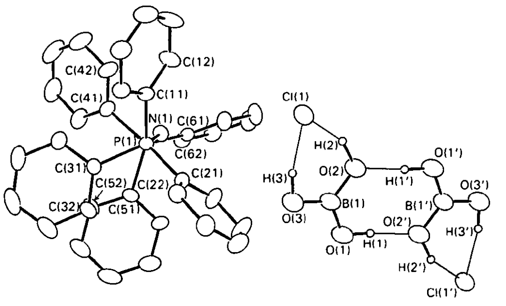

Fig. 1. View of the PPN cation along the P···P vector, and the nearest chloride anion and $B(OH)_3$ molecule.

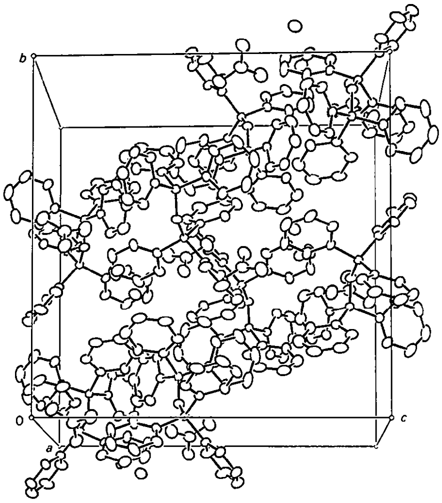

Fig. 2. Unit-cell contents in a view nearly along the *a* axis, looking towards (100).

Also shown in Fig. 1 are Cl and $B(OH)_3$ (both primed) inverted through the inversion centre at ($\frac{1}{2}$,0,0). In Table 3 are listed internuclear separations and inter-bond angles for both the covalent and strong hydrogen bonds.

The $B(OH)_3$ molecules occur pairwise, associated *via* two O(2)···H(1′) bonds in an eight-membered ring which is nearly planar (Table 4, deposited). Dimensions within this cyclic system are very similar to those in the crystal structure of boric acid itself (Craven & Sabine, 1966), in which molecules have local D_{3h} symmetry and are hydrogen-bonded into infinite sheets. In the present case the threefold symmetry of the $B(OH)_3$ molecule is destroyed by the existence of bifurcated hydrogen bonding between Cl, H(2) and H(3), these atoms lying *ca* 0·38, 0·10 and 0·01 Å, respectively, out of the BO_3 mean plane (Table 4). In addition to these strong hydrogen bonds O(1) is weakly associated with H(16) at ($\frac{1}{2}-x,-y,z-\frac{1}{2}$), and Cl with H(63) at ($1-x,y-\frac{1}{2},\frac{1}{2}-z$), relevant distances and angles having been deposited (Table 5).

The PPN cation is bent at the central N atom, 137·4 (2)°, and is staggered about the P···P vector, having a 'mean torsion angle' (Glidewell & Liles, 1981) of 51·9 (1)°. There is a weak intramolecular quasi-graphitic packing of rings 3 and 5 [centroid–centroid distance 4·466 (6) Å, dihedral angle 24·8 (4)°], but a much stronger intermolecular one between rings 2 and 5[4·178 (4) Å, 7·8 (4)°] with ring 5 at $(\frac{1}{2}-x, -\frac{1}{2}+y, z)$, where ring n comprises C(n1–n6) and a centroid–centroid distance ≤ 4·7 Å is considered significant (Welch, 1974). Full details of these interactions have been deposited as Table 6, and Fig. 2 reproduces the contents of one unit cell in a view nearly along the a axis, looking towards (100).

We thank the SERC for support, the Department of Chemistry, University of Edinburgh, for a vacation scholarship (DAR), and Dr D. Reed for the NMR spectrum.

References

Andrews, S. J., Robb, D. A. & Welch, A. J. (1983). To be published.

Andrews, S. J., Welch, A. J., Jacobsen, G. B. & Morris, J. H. (1982). *J. Chem. Soc. Chem. Commun.* pp. 749–750.

Arunchaiya, M. & Morris, J. H. (1983). To be published.

Craven, B. N. & Sabine, T. M. (1966). *Acta Cryst.* **20**, 214–219.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Glidewell, C. & Liles, D. C. (1981). *J. Organomet. Chem.* **212**, 291–300.

Johnson, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Roberts, P. & Sheldrick, G. M. (1976). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

Stewart, J. M., Machin, P. A., Dickinson, C., Ammon, H. L., Heck, H. & Flack, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Welch, A. J. (1974). PhD Thesis, Univ. of London, England.

Acta Cryst. (1983). C**39**, 882–887

Structural Studies of Intermediates in Antibiotic Synthesis. I. The Structures of Penicillin Sulfoxide Rearrangement Products: 2,3,5,6-Tetrahydro-5-hydroxymethyl-6,6-dimethyl-1,3-dioxo-8-[(phenylacetyl)amino]-1*H*-imidazo[5,1-*c*][1,4]thiazine (I), $C_{17}H_{19}N_3O_4S$, and 2,3,5,6-Tetrahydro-6,6-dimethyl-1,3-dioxo-8-[(phenylacetyl)amino]-1*H*-imidazo[5,1-*c*]-[1,4]thiazine-5-carboxylic Acid (II), $C_{17}H_{17}N_3O_5S$

By T. E. Haran

Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel

A. Nudelman

Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel

and Z. Shakked*

Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel

(*Received* 10 *June* 1982; *accepted* 20 *December* 1982)

Abstract. (I): $M_r = 361$, $P\bar{1}$, $a = 8{\cdot}888\,(10)$, $b = 9{\cdot}556\,(2)$, $c = 11{\cdot}483\,(7)$ Å, $\alpha = 116{\cdot}85\,(5)$, $\beta = 103{\cdot}69\,(8)$, $\gamma = 94{\cdot}27\,(6)°$, $Z = 2$, $V = 826{\cdot}8$ Å^3, $D_m = 1{\cdot}45$, $D_x = 1{\cdot}448$ g cm^{-3}, graphite-monochromated Mo $K\alpha$, $\mu = 1{\cdot}78$ cm^{-1}, $T = 83$ K, $F(000) = 380$, $R = 0{\cdot}07$ for 3172 observed reflexions. (II): $M_r = 375$, $P2_1$, $a = 7{\cdot}332\,(1)$, $b = 14{\cdot}608\,(1)$, $c = 8{\cdot}371\,(2)$ Å, $\beta = 107{\cdot}98\,(2)°$, $Z = 2$, $V = 889{\cdot}5$ Å^3, $D_m = 1{\cdot}40$, $D_x = 1{\cdot}398$ g cm^{-3}, graphite-monochromated Cu $K\alpha$, $\mu = 18{\cdot}03$ cm^{-1}, $T = 293$ K, $F(000) = 392$, $R = 0{\cdot}04$ for 1732 observed reflexions. The two compounds, obtained from a rearrangement reaction of a penicillin sulfoxide, display the novel 2,3,5,6-tetrahydro-1*H*-imidazo[5,1-*c*][1,4]thiazine bicyclic ring system. The abnormal behavior of the hydroxymethyl carbon in (I) indicates a possible chemical disorder. In both crystals the molecules are held together by means of intermolecular hydrogen bonds and van der Waals interactions.

---

* Incumbent of the Hugo Ramniceanu Career Development Chair. To whom correspondence should be addressed.

0108-2701/83/070882-06$01.50