DUNITZ, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules*, pp. 207–209. Ithaca and London: Cornell Univ. Press.

FRANKLIN, J. D. & MARSH, R. E. (1982). *Acta Cryst.* B**38**, 1681–1682.

KROON, J. (1982). *Molecular Structure and Biological Activity*, edited by J. F. GRIFFIN & W. L. DUAX, pp. 151–163. New York: Elsevier Biomedical.

KROON, J., DUISENBERG, A. J. M. & PEERDEMAN, A. F. (1984). *Acta Cryst.* C**40**, 645–647.

KROON-BATENBURG, L. M. J., DE VRIES, A. J. & KROON, J. (1985). To be published.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

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

SPEK, A. L. (1982). *The EUCLID package.* In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1985). C**41**, 1208–1212

Structures of Two Crystalline Modifications of Bis(triphenylphosphoranediyl)ammonium 3-Isothiocyanato-4,7; 4,8; 5,6-tri-μ-hydro-3,4,5,5,6,7,8,9,10,11-decahydro-1,2-didebor[C_{2v}-($1v^6 2v^4 422$)-Δ^{18}-*closo*]undecaborate(1−) Dichloromethane Solvate (2/1),* $C_{36}H_{30}NP_2^+.B_9H_{13}(NCS)^-.0{\cdot}5CH_2Cl_2$

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Abstract. $M_r = 749{\cdot}5$, $\bar{\lambda}(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å. α-Form: monoclinic, $P2_1/a$, $a = 15{\cdot}405\,(3)$, $b = 16{\cdot}129\,(2)$, $c = 17{\cdot}811\,(1)$ Å, $\beta = 108{\cdot}523\,(12)°$, $U = 4196$ Å^3, $Z = 4$, $D_x = 1{\cdot}186$ Mg m^{-3}, $\mu = 0{\cdot}207$ mm^{-1}, $F(000) = 1564$, $T = 295$ K, final $R = 0{\cdot}0836$ for 3793 observed reflections. β-Form: triclinic, $P\bar{1}$, $a = 11{\cdot}385\,(7)$, $b = 13{\cdot}960\,(3)$, $c = 15{\cdot}228\,(4)$ Å, $\alpha = 65{\cdot}06\,(2)$, $\beta = 69{\cdot}73\,(3)$, $\gamma = 75{\cdot}52\,(3)°$, $U = 2043$ Å^3, $Z = 2$, $D_x = 1{\cdot}218$ Mg m^{-3}, $\mu = 0{\cdot}212$ mm^{-1}, $F(000) = 782$, $T = 185$ K, final $R = 0{\cdot}0690$ for 5137 observed reflections. The title compound exists in both monoclinic (α) and triclinic (β) modifications. The substituted borane anion has a 1,2-didebor-undecaborate architecture with the isothiocyanato ligand at the 3 position and μ-H functions in 4–7, 4–8 and 5–6 locations (as determined by a low-temperature study of the β form). Between the two crystal forms the cations are effectively superimposable, and are bent at nitrogen, P—N—P *ca* 137°.

Introduction. The structure of the $[B_9H_{13}(NCS)]^-$ ion, (1), has been inferred from high-field, variable-temperature NMR studies (Jacobsen, Morris & Reed, 1984); these suggested that the arrangement of borane H atoms is similar to that in $B_9H_{13}(NCMe)$, (2) (Wang, Simpson & Lipscomb, 1961) in which there are μ-4,7 and μ-5,6 H atoms, in contrast to that in the parent species $[B_9H_{14}]^-$, (3) (Greenwood, McGinnety & Owen, 1972) which has μ-3,6 and μ-3,7 H atoms. In view of our interest in the effects of bridging H atoms on the lengths of B—B connectivities in borane and substituted borane polyhedra, we have determined the structure of $[B_9H_{13}(NCS)]^-$ as its $[(Ph_3P)_2N]^+$ salt in the solid state. Initially the structure was determined from a room-temperature data set, but this study failed to locate all the borane H atoms. In repeating the experiment with a different crystal at low temperature we unexpectedly encountered a second crystalline modification. Results of both determinations are presented herein.

Experimental. Preparation and recrystallization from CH_2Cl_2/*n*-hexane (Jacobsen, Morris & Reed, 1984) yields the title compound as its dichloromethane solvate (2:1). Data are given for the α-form, with differences in respect of the β-form in curly brackets. Clear, colourless blocks, 0·03 × 0·02 × 0·04 {0·07 × 0·05 × 0·03} cm, mounted on glass fibre; preliminary Weissenberg photography; CAD-4 diffractometer; lattice parameters from 25 centred reflections, $13 < \theta < 14{\cdot}5°$ $\{12 < \theta < 16°\}$; graphite-monochromated Mo $K\alpha$; for data collection $\theta_{\max} = 25°$; ω–2θ scan in 96 steps; ω-scan width $0{\cdot}85° + 0{\cdot}35°\tan\theta$ $\{0{\cdot}8° + 0{\cdot}35°\tan\theta\}$; rapid prescan after which reflections with $I \geq \sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to a maximum measuring time of 60 s; no significant crystal decay or movement; 7292 {7186}

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* Nomenclature according to Casey, Evans & Powell (1983).

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unique reflections over 125 {120} X-ray hours; no absorption or extinction corrections; for structure solution and refinement 3793 {5137} amplitudes $[F \geq 2\cdot0\sigma(F)]$; automatic centrosymmetric direct methods (Sheldrick, 1976 {Sheldrick, 1984}); full-matrix least squares (F); $w^{-1} = [\sigma^2(F) + x(F)^2]$ ($x = 1\cdot121361$ {0·092157}); anisotropic thermal parameters for all non-H atoms, phenyl groups idealized (C—C 1·395, C—H 1·08 Å); dichloromethane H atoms idealized and allowed to ride on C (H—C—H 109·5°, C—H 1·08 Å); anion H atoms positionally refined, U_H* = 0·10 {0·05} Å^2; R 0·0836 {0·0690}, wR 0·1522 {0·1336}; data:variable ratio 9:1 {11·5:1}; max. Δ/σ in final cycle 0·08 {0·16}; max. peak and min. trough in final ΔF synthesis 0·62 {0·40} and −0·54 {−0·29} e Å^{-3}; neutral-atom scattering factors for C, N, Cl, B, P (Cromer & Liberman, 1970) and H (Stewart, Davidson & Simpson, 1965); computer programs: *SHELX76* (Sheldrick, 1976), *SHELX84* (Sheldrick, 1984), *XANADU* (Roberts & Sheldrick, 1976), *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *ORTEP*II (Johnson, 1976).

Loss of crystallinity of the specimen initially used during solution and refinement of its structure (presumably due to loss of CH_2Cl_2 solvate) necessitated a second synthesis and recrystallization for a low-temperature study. A different lattice was suggested by preliminary (room-temperature) X-ray photography, and the existence of a second modification was confirmed by subsequent successful solution and refinement of the structure. Exhaustive attempts to interrelate the lattices of the two modifications were unsuccessful.

Discussion. Tables 1 and 2 list derived fractional coordinates.† Fig. 1 shows a perspective view of the 3-NCS-$\mu_{4,7},\mu_{4,8},\mu_{5,6}$-$H_3$-$B_9H_{11}$ anion (1) using coordinates and thermal parameters determined from the β-form (low-temperature study). In Tables 3 and 4 are listed internuclear separations.

The α-form of (1).PPN.0·5CH_2Cl_2 [PPN is bis(triphenylphosphoranediyl)ammonium] was studied at room temperature. Although we have been able to locate and successfully refine all non-hydrogen atoms and (positionally) HB(3), we could not establish unequivocal positions for any other borane H atoms. For this reason data collection was repeated at low temperature (185 K), but because of intervening loss of

Table 1. *Fractional coordinates of refined atoms for* (1α)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
P(1)	0·44004 (11)	0·31142 (10)	0·12846 (9)	0·0323
P(2)	0·43439 (11)	0·31044 (10)	0·29221 (9)	0·0348
N(1)	0·4386 (4)	0·3465 (3)	0·2106 (3)	0·0395
C(12)	0·32084 (25)	0·3048 (3)	−0·02518 (22)	0·0465
C(13)	0·23623 (25)	0·3159 (3)	−0·08333 (22)	0·0501
C(14)	0·16194 (25)	0·3459 (3)	−0·06268 (22)	0·0530
C(15)	0·17226 (25)	0·3648 (3)	0·01612 (22)	0·0522
C(16)	0·25687 (25)	0·3537 (3)	0·07427 (22)	0·0402
C(11)	0·33116 (25)	0·3237 (3)	0·05362 (22)	0·0330
C(22)	0·5612 (3)	0·1840 (3)	0·1773 (3)	0·0562
C(23)	0·5900 (3)	0·1015 (3)	0·1831 (3)	0·0666
C(24)	0·5307 (3)	0·0400 (3)	0·1410 (3)	0·0783
C(25)	0·4427 (3)	0·0609 (3)	0·0930 (3)	0·0782
C(26)	0·4140 (3)	0·1434 (3)	0·0871 (3)	0·0514
C(21)	0·4732 (3)	0·2049 (3)	0·1292 (3)	0·0393
C(32)	0·5347 (3)	0·45368 (23)	0·11695 (24)	0·0445
C(33)	0·5937 (3)	0·50169 (23)	0·08955 (24)	0·0521
C(34)	0·6386 (3)	0·46641 (23)	0·04063 (24)	0·0623
C(35)	0·6246 (3)	0·38311 (23)	0·01911 (24)	0·0571
C(36)	0·5656 (3)	0·33510 (23)	0·04651 (24)	0·0532
C(31)	0·5206 (3)	0·37038 (23)	0·09543 (24)	0·0409
C(42)	0·3107 (4)	0·33813 (25)	0·3747 (3)	0·0649
C(43)	0·2553 (4)	0·38858 (25)	0·4040 (3)	0·0806
C(44)	0·2459 (4)	0·47256 (25)	0·3844 (3)	0·0801
C(45)	0·2918 (4)	0·50611 (25)	0·3355 (3)	0·0777
C(46)	0·3472 (4)	0·45566 (25)	0·3061 (3)	0·0676
C(41)	0·3566 (4)	0·37168 (25)	0·3257 (3)	0·0396
C(52)	0·3045 (3)	0·1890 (3)	0·2448 (3)	0·0549
C(53)	0·2735 (3)	0·1073 (3)	0·2318 (3)	0·0793
C(54)	0·3345 (3)	0·0419 (3)	0·2595 (3)	0·0848
C(55)	0·4264 (3)	0·0580 (3)	0·3003 (3)	0·0809
C(56)	0·4573 (3)	0·1397 (3)	0·3133 (3)	0·0568
C(51)	0·3964 (3)	0·2052 (3)	0·2856 (3)	0·0415
C(62)	0·6161 (3)	0·3549 (3)	0·34870 (21)	0·0496
C(63)	0·7011 (3)	0·3628 (3)	0·40692 (21)	0·0598
C(64)	0·7135 (3)	0·3340 (3)	0·48347 (21)	0·0692
C(65)	0·6407 (3)	0·2973 (3)	0·50180 (21)	0·0753
C(66)	0·5557 (3)	0·2893 (3)	0·44359 (21)	0·0666
C(61)	0·5433 (3)	0·3181 (3)	0·36704 (21)	0·0412
S(1)	0·2515 (3)	0·07483 (16)	−0·11689 (18)	0·1054
C(1)	0·3079 (9)	0·1332 (6)	−0·1544 (6)	0·0937
N(2)	0·3555 (7)	0·1769 (5)	−0·1776 (6)	0·1030
B(3)	0·4141 (10)	0·2339 (11)	−0·2107 (8)	0·1077
B(4)	0·4354 (17)	0·3992 (12)	−0·2877 (11)	0·1802
B(5)	0·5538 (14)	0·2613 (22)	−0·2996 (16)	0·2057
B(6)	0·4712 (11)	0·1840 (10)	−0·2772 (9)	0·1134
B(7)	0·3532 (11)	0·3272 (7)	−0·2659 (8)	0·0948
B(8)	0·4861 (12)	0·3409 (9)	−0·3541 (9)	0·1123
B(9)	0·3687 (9)	0·2321 (8)	−0·3101 (7)	0·0855
B(10)	0·3704 (11)	0·3304 (9)	−0·3619 (9)	0·1086
B(11)	0·4501 (11)	0·2419 (9)	−0·3663 (7)	0·0986
Cl(1)	0·9104 (4)	0·5326 (6)	0·4869 (4)	0·2476
C(2)	0·9651 (24)	0·4469 (11)	0·5107 (12)	0·1400
HB(3)	0·465 (5)	0·275 (4)	−0·226 (4)	

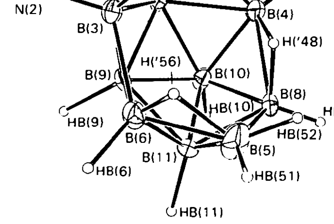

Fig. 1. A perspective view of the anion.

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

† Lists of structure factors, anisotropic thermal parameters, phenyl and CH_2Cl_2 H atom coordinates, relevant interbond angles, and parameters used in the EHMO study have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42186 (64 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

crystallinity of the original sample, this was performed on a freshly resynthesized specimen. This was recrystallized from the same solvent mixture as a different modification (*β*-form). Solution and refinement of this form allowed all borane H atoms to be located. Thus, in the cage of anion (1) (*β*-form), which has the *arachno* (didebor) architecture of its *closo* octadecahedral parent, H atoms bridge the 4–7, 4–8 and 5–6 B—B connectivities and there is a BH_2 group at position 5. B(3) also carries two terminal functions, *exo*-polyhedral NCS and *endo*-polyhedral HB(3).

Table 2. *Fractional coordinates of refined atoms for* (1*β*)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}(Å^2)
P(1)	0·13341 (10)	0·52927 (8)	0·67651 (8)	0·0228
P(2)	−0·01142 (10)	0·36117 (8)	0·84346 (8)	0·0238
N(1)	0·1071 (3)	0·4176 (3)	0·7649 (3)	0·0272
C(12)	0·2595 (3)	0·69519 (20)	0·63442 (17)	0·0347
C(13)	0·3332 (3)	0·74581 (20)	0·65424 (17)	0·0385
C(14)	0·3637 (3)	0·70071 (20)	0·74578 (17)	0·0448
C(15)	0·3205 (3)	0·60499 (20)	0·81751 (17)	0·0393
C(16)	0·2468 (3)	0·55437 (20)	0·79769 (17)	0·0314
C(11)	0·2163 (3)	0·59946 (20)	0·70615 (17)	0·0285
C(22)	0·23743 (25)	0·58583 (19)	0·46970 (19)	0·0350
C(23)	0·32971 (25)	0·57463 (19)	0·38483 (19)	0·0406
C(24)	0·42302 (25)	0·48730 (19)	0·39544 (19)	0·0394
C(25)	0·42405 (25)	0·41116 (19)	0·49092 (19)	0·0383
C(26)	0·33177 (25)	0·42237 (19)	0·57579 (19)	0·0305
C(21)	0·23846 (25)	0·50970 (19)	0·56518 (19)	0·0242
C(32)	−0·0677 (3)	0·59021 (21)	0·59612 (24)	0·0374
C(33)	−0·1786 (3)	0·65261 (21)	0·57531 (24)	0·0482
C(34)	−0·2258 (3)	0·74076 (21)	0·60366 (24)	0·0521
C(35)	−0·1623 (3)	0·76651 (21)	0·65282 (24)	0·0499
C(36)	−0·0514 (3)	0·70411 (21)	0·67363 (24)	0·0404
C(31)	−0·0042 (3)	0·61596 (21)	0·64528 (24)	0·0259
C(42)	0·0041 (3)	0·27938 (21)	0·70270 (19)	0·0326
C(43)	−0·0309 (3)	0·21539 (21)	0·66835 (19)	0·0420
C(44)	−0·1245 (3)	0·14932 (21)	0·73174 (19)	0·0482
C(45)	−0·1831 (3)	0·14722 (21)	0·82948 (19)	0·0544
C(46)	−0·1481 (3)	0·21120 (21)	0·86382 (19)	0·0439
C(41)	−0·0545 (3)	0·27728 (21)	0·80043 (19)	0·0264
C(52)	0·14986 (23)	0·22651 (25)	0·95552 (17)	0·0350
C(53)	0·18031 (23)	0·15750 (25)	1·04463 (17)	0·0436
C(54)	0·08827 (23)	0·14002 (25)	1·13675 (17)	0·0433
C(55)	−0·03421 (23)	0·19156 (25)	1·13975 (17)	0·0465
C(56)	−0·06466 (23)	0·26057 (25)	1·05064 (17)	0·0394
C(51)	0·02737 (23)	0·27804 (2)	0·95853 (17)	0·0264
C(62)	−0·2607 (3)	0·4568 (3)	0·8555 (3)	0·0439
C(63)	−0·3619 (3)	0·5315 (3)	0·8767 (3)	0·0704
C(64)	−0·3491 (3)	0·6015 (3)	0·9156 (3)	0·0607
C(65)	−0·2351 (3)	0·5967 (3)	0·9333 (3)	0·0539
C(66)	−0·1339 (3)	0·5219 (3)	0·9121 (3)	0·0413
C(61)	−0·1467 (3)	0·4520 (3)	0·8732 (3)	0·0295
S(2)	0·47117 (15)	0·30531 (13)	0·85982 (11)	0·0588
C(1)	0·4992 (5)	0·2054 (5)	0·9563 (4)	0·0493
N(2)	0·5159 (5)	0·1337 (4)	1·0271 (4)	0·0438
B(3)	0·5422 (6)	0·0432 (5)	1·1175 (5)	0·0524
B(4)	0·4438 (10)	−0·1395 (6)	1·3256 (6)	0·0749
B(5)	0·7170 (10)	−0·0580 (11)	1·2667 (11)	0·1158
B(6)	0·6553 (8)	0·0608 (7)	1·1753 (7)	0·0731
B(7)	0·4075 (8)	−0·0099 (6)	1·2296 (6)	0·0594
B(8)	0·5737 (9)	−0·1130 (5)	1·3613 (7)	0·0762
B(9)	0·4950 (6)	0·0774 (4)	1·2217 (5)	0·0465
B(10)	0·4384 (7)	−0·0236 (6)	1·3411 (5)	0·0582
B(11)	0·5887 (9)	0·0212 (6)	1·3063 (7)	0·0806
Cl(1)	−0·0646 (3)	1·02143 (18)	0·42372 (16)	0·1020
C(2)	−0·0789 (15)	1·0416 (11)	0·5205 (13)	0·0820
HB(3)	0·594 (6)	−0·039 (5)	1·101 (4)	
HB(41)	0·380 (6)	−0·211 (5)	1·378 (5)	
HB(51)	0·808 (6)	−0·062 (5)	1·254 (4)	
HB(52)	0·738 (6)	−0·150 (5)	1·294 (5)	
HB(6)	0·720 (6)	0·137 (5)	1·141 (4)	
HB(7)	0·348 (6)	0·022 (5)	1·215 (5)	
HB(8)	0·593 (6)	−0·173 (5)	1·423 (5)	
HB(9)	0·445 (6)	0·185 (5)	1·217 (4)	
HB(10)	0·395 (6)	−0·002 (5)	1·412 (5)	
HB(11)	0·589 (6)	0·082 (5)	1·354 (4)	
H('47)	0·411 (6)	−0·093 (5)	1·225 (5)	
H('48)	0·596 (6)	−0·153 (5)	1·286 (4)	
H('56)	0·730 (6)	−0·010 (5)	1·151 (5)	

Our finding of a *third* H bridge [between B(4) and B(8)] in (1) (*β*-form) was unexpected, although such an arrangement has been observed (Barton, 1982; Huffman & Schaeffer, 1984) in *commo*-$B_{15}H_{23}$ which contains a similar B_9H_{13} fragment. This apart, comparison of (1*β*) with other structurally characterized *arachno* B_9 species shows that the overall stereochemistry is similar to that in B_9H_{13}(NCMe), (2) (Wang, Simpson & Lipscomb, 1961), but different from that in $[B_9H_{14}]^-$, (3) (Greenwood, McGinnety & Owen, 1972) where the 3–6 and 3–7 connectivities are bridged and BH_2 units occur at positions 4, 5 and 8. In an attempt to establish if the reasons for these differences are electronic in origin, we have carried out Extended Hückel Molecular Orbital (EHMO) calculations (*ICON*8; Howell, Rossi, Wallace, Haraki & Hoffmann, 1977) on non-idealized models of B_9H_{13} derived from the crystal structures of (1*β*) and $[B_9H_{14}]^-$ by removal of the *exo*-polyhedral B(3) ligand (NCS^- and H^- respectively). Parameters used in this study have been deposited.

Table 3. *Internuclear distances* (Å) *for* (1α)

Cl(1′) is related to Cl(1) by the operator 1−*x*, 1−*y*, 1−*z*.

P(1)—N(1)	1·575 (6)	B(4)—B(8)	1·87 (3)
P(1)—C(11)	1·791 (4)	B(4)—B(10)	1·77 (3)
P(1)—C(21)	1·791 (5)	B(5)—B(6)	1·91 (3)
P(1)—C(31)	1·804 (5)	B(5)—B(8)	1·74 (3)
P(2)—N(1)	1·587 (6)	B(5)—B(11)	1·69 (3)
P(2)—C(41)	1·795 (5)	B(6)—B(9)	1·689 (21)
P(2)—C(51)	1·788 (5)	B(6)—B(11)	1·780 (22)
P(2)—C(61)	1·785 (5)	B(7)—B(9)	1·774 (19)
S(1)—C(1)	1·568 (12)	B(7)—B(10)	1·812 (21)
C(1)—N(2)	1·182 (15)	B(8)—B(10)	1·750 (23)
N(2)—B(3)	1·531 (19)	B(8)—B(11)	1·682 (22)
B(3)—B(6)	1·868 (23)	B(9)—B(10)	1·839 (21)
B(3)—B(7)	1·878 (21)	B(9)—B(11)	1·844 (20)
B(3)—B(9)	1·684 (21)	B(10)—B(11)	1·901 (22)
B(3)—HB(3)	1·13 (7)	Cl(1)—C(2)	1·61 (3)
B(4)—B(7)	1·85 (3)	Cl(1′)—C(2)	1·93 (3)

Table 4. *Internuclear distances* (Å) *for* (1*β*)

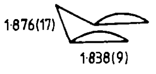
Cl(1′) is related to Cl(1) by the operator −*x*, 1−*y*, 1−*z*.

P(1)—N(1)	1·586 (4)	B(5)—HB(51)	0·97 (7)
P(1)—C(11)	1·785 (3)	B(5)—HB(52)	1·16 (7)
P(1)—C(21)	1·789 (3)	B(5)—H('56)	1·56 (7)
P(1)—C(31)	1·796 (4)	B(6)—B(9)	1·708 (12)
P(2)—N(1)	1·578 (4)	B(6)—B(11)	1·759 (14)
P(2)—C(41)	1·788 (3)	B(6)—HB(6)	1·27 (7)
P(2)—C(51)	1·782 (3)	B(6)—H('56)	1·22 (7)
P(2)—C(61)	1·791 (4)	B(7)—B(9)	1·701 (11)
S(1)—C(1)	1·606 (6)	B(7)—B(10)	1·775 (12)
C(1)—N(2)	1·157 (8)	B(7)—HB(7)	0·76 (7)
N(2)—B(3)	1·487 (10)	B(7)—H('47)	1·18 (7)
B(3)—B(6)	1·901 (12)	B(8)—B(10)	1·752 (13)
B(3)—B(7)	1·872 (12)	B(8)—B(11)	1·726 (14)
B(3)—B(9)	1·718 (10)	B(8)—HB(8)	1·01 (7)
B(3)—HB(3)	1·23 (7)	B(8)—H('48)	1·39 (7)
B(4)—B(7)	1·842 (13)	B(9)—B(10)	1·786 (11)
B(4)—B(8)	1·902 (14)	B(9)—B(11)	1·759 (12)
B(4)—B(10)	1·715 (13)	B(9)—HB(9)	1·45 (7)
B(4)—HB(41)	1·21 (7)	B(10)—B(11)	1·796 (13)
B(4)—H('47)	1·53 (7)	B(10)—HB(10)	1·16 (7)
B(4)—H('48)	1·61 (7)	B(11)—HB(11)	1·33 (7)
B(5)—B(6)	1·825 (17)	C(2)—Cl(1)	1·562 (18)
B(5)—B(8)	1·842 (17)	C(2)—Cl(1′)	1·943 (18)
B(5)—B(11)	1·692 (17)		

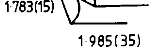
These calculations show that there are major differences between the form of the highest occupied molecular orbitals (HOMO's), and between calculated atomic charges, in the two B_9H_{13} structure types. With H bridges along the 3–6 and 3–7 connectivities the HOMO is delocalized between β atoms 4–9 inclusive, but resides hardly at all (<4%) on B(3) (charge on this atom +0·473). In marked contrast, B(3) of B_9H_{13} derived from (1β) is more negative (+0·304) since the HOMO is quite strongly localized on it (>23%), is B 2*p* in character, and is orientated tangentially to the polyhedral surface such that its nodal plane contains HB(3), B(3) and B(9). This orbital is therefore ideally suited for overlap with empty π orbitals of an *exo*-polyhedral ligand bound to B(3). This is consistent with our observation that, apart from H('48), the arrangement of μ-H atoms in (1β) parallels that in (2) (both substituents are π-acceptor ligands), whilst in (3) it is quite different. The possibility that π-acceptor ligands discourage (relative to pure σ donors) adjacent bridging H atoms in nonaboranes is of interest in view of recent studies of substitution effects on adjacent H bridges in the triangular boranes $[B_3H_8]^-$ (Peters & Nordman, 1960) and $[B_3H_6(Cl_2)]^-$ (Arunchaiya, Morris, Andrews, Welch & Welch, 1984) (2 μ-H) and derivatives such as $B_3H_7(CO)$ (Glore, Rathke & Schaeffer, 1973), $[B_3H_7(NCS)]^-$ (Andrews & Welch, 1984), *etc.* (1 μ-H, not involving the substituted β). In these triangular species it appears (Brown & Lipscomb, 1977; Andrews & Welch, 1984) that the σ-donor character of the substituent is predominantly important in influencing μ-H positions.

With the establishment of H('47) and H('56) in (1β), a comparison of the bridged and unbridged B—B distances in its open polyhedral face with those in similar species is appropriate.

μ-4,7 and μ-5,6 arrangements are found in (1β) and in (2), and μ-3,6 and μ-3,7 in, for example, (3) (*arachno* 9-vertex), $B_{10}H_{14}$ (Tippe & Hamilton, 1969), $THF(CO)_3MnB_9H_{12}$ (Lott & Gaines, 1974), $(Et)_3N(CH_2)_4O(CO)_3MnB_9H_{12}$ (Gaines, Lott & Calabrese, 1974) and $(\eta\text{-}C_5H_5)CoB_9H_{13}$ (Pipal & Grimes, 1977) (*nido* 10-vertex). Average B—B distances for these two classes are shown in (4) and (5) respectively.



(4)



(5)

Clearly the effect of H bridging is to *decrease* significantly the appropriate B—B distance. Similar observations have been made for derivatives of $[B_3H_8]^-$. In contrast, H bridging of B—B connectivities in $[B_{11}H_{13}]^{2-}$ causes *lengthening* (Fritchie, 1967). These different effects of B—B edge-bridging will be discussed in a separate publication (Mitchell & Welch, 1985).

In (1β) all the bridging H atoms are asymmetrically bonded to their respective B—B edges with H—B (3-connected) greater than H—B (4-connected). HB(52) is clearly dissimilar to H('48) since the contact distance HB(52)···B(8) is non-bonding at 1·86 (7) Å. The relatively high errors in molecular parameters of (1α) preclude reliable comparison with (1β), but the established presence of HB(3) in (1α) would appear to exclude the possibility of $\mu_{3,6}$ and $\mu_{3,7}$ H bridging.

The cations from both (1α) and (1β) are superimposable and are bent at the central N atom, 137·3 (3)° (β-form), and adopt a semi-eclipsed conformation about the P···P vector, having a 'mean torsion angle' (Glidewell & Liles, 1981) of 31·5 (2)° (β-form). In both crystallographic modifications of (1).PPN.0·5CH_2Cl_2 the CH_2Cl_2 solvate molecules are disordered about inversion centres located midway between Cl(1) and Cl(1').

Figs. 2 and 3 reproduce the contents of one unit cell for the α-form and β-form respectively.

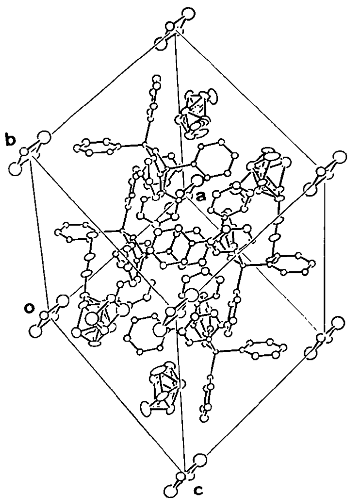


Fig. 2. Unit-cell contents for (1α).

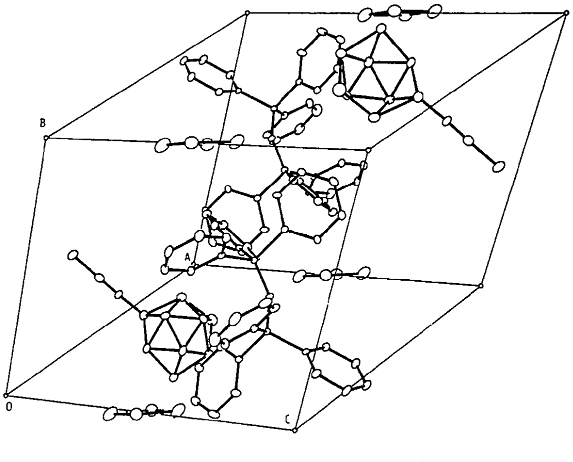


Fig. 3. Unit-cell contents for (1β).

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References

Andrews, S. J. & Welch, A. J. (1984). *Inorg. Chim. Acta*, **88**, 153–160.
Arunchaiya, M., Morris, J. H., Andrews, S. J., Welch, D. A. & Welch, A. J. (1984). *J. Chem. Soc. Dalton Trans.* pp. 2525–2533.
Barton, L. (1982). *Top. Curr. Chem.* **100**, 169–206.
Brown, L. D. & Lipscomb, W. N. (1977). *Inorg. Chem.* **16**, 1–7.
Casey, J. B., Evans, W. J. & Powell, W. H. (1983). *Inorg. Chem.* **22**, 2228–2235, 2236–2245.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Fritchie, C. J. (1967). *Inorg. Chem.* **6**, 1199–1203.
Gaines, D. F., Lott, J. W. & Calabrese, J. C. (1974). *Inorg. Chem.* **13**, 2419–2423.
Glidewell, C. & Liles, D. C. (1981). *J. Organomet. Chem.* **212**, 291–300.
Glore, J. D., Rathke, J. W. & Schaeffer, R. (1973). *Inorg. Chem.* **12**, 2175–2178.
Greenwood, N. N., McGinnety, J. A. & Owen, J. D. (1972). *J. Chem. Soc. Dalton Trans.* pp. 986–989.
Howell, J., Rossi, A., Wallace, D., Haraki, K. & Hoffmann, R. (1977). *Quantum Chem. Program Exch.* **10**, 344.
Huffman, J. C. & Schaeffer, R. (1984). Personal communication to N. N. Greenwood, Liversedge Lecture of the Royal Society of Chemistry.
Jacobsen, G. B., Morris, J. H. & Reed, D. (1984). *J. Chem. Soc. Dalton Trans.* pp. 415–421.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
Lott, J. W. & Gaines, D. F. (1974). *Inorg. Chem.* **13**, 2261–2267.
Mitchell, G. F. & Welch, A. J. (1985). To be published.
Peters, C. R. & Nordman, C. E. (1960). *J. Am. Chem. Soc.* **82**, 5758.
Pipal, J. R. & Grimes, R. N., (1977). *Inorg. Chem.* **16**, 3251–3255.
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.
Sheldrick, G. M. (1984). *SHELX*84. Program for crystal structure determination. Univ. of Göttingen, FRG.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY*76 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.
Tippe, A. & Hamilton, W. C. (1969). *Inorg. Chem.* **8**, 464–470.
Wang, F. E., Simpson, P. G. & Lipscomb, W. N. (1961). *J. Chem. Phys.* **35**, 1335–1339.

Acta Cryst. (1985). C**41**, 1212–1214

Structure and Absolute Configuration of 4-(α-D-Erythrofuranosyl)-1,3-dihydro-3-methyl-1-(*p*-tolyl)-2*H*-imidazole-2-thione, $C_{15}H_{18}N_2O_3S$

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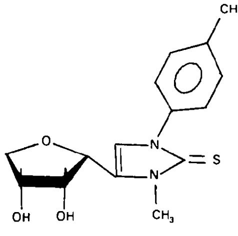
Abstract. $M_r = 306{\cdot}4$, monoclinic, $P2_1$, $a = 14{\cdot}686\ (6)$, $b = 5{\cdot}359\ (4)$, $c = 9{\cdot}439\ (3)$ Å, $\beta = 98{\cdot}68\ (3)°$, $V = 734{\cdot}4\ (7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}38$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}22$ mm^{-1}, $F(000) = 324$, $T = 300$ K, final $R = 0{\cdot}042$ ($wR = 0{\cdot}037$) for 1987 observed independent reflections. The sugar ring has a conformation intermediate between $^3T_2$ and ^3E. The configuration of the imidazole ring with respect to the furanose ring is *anti*, the glycosidic angle being −9·3 (4)°. The crystal packing is governed by hydrogen bonds involving OH groups and S atoms, forming infinite chains along [001].

Introduction. The title compound (I) was obtained (Fernández-Bolaños, Fuentes-Mota & Fernández-Bolaños Guzmán, 1983) by the catalysed formation of the anhydride of 1,3-dihydro-3-methyl-4-(D-*arabino*-1,2,3,4-tetrahydroxybutyl)-1-(*p*-tolyl)-2*H*-imidazole-2-thione. By the same process the *β* anomer was also obtained, and its structure reported by Criado, Conde & Márquez (1983). The structural study of both anomers forms part of a systematic research project dealing with D-erythrofuranosyldihydroimidazole-2-thione compounds (Conde, López-Castro & Márquez, 1978) prepared in the Organic Chemistry Department of this University.



(I)