8586 measured reflections
1263 independent reflections (plus 892 Friedel-related reflections)
3 standard reflections every 150 reflections intensity decay: < 2.6%, corrected

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.080$
$S = 1.040$
2155 reflections
259 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.042$
$\Delta\rho_{\max} = 0.193$ e Å^{-3}
$\Delta\rho_{\min} = -0.171$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0004 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.10 (2)

Table 1. *Selected geometric parameters (Å, °)*

C9—C8	1.393 (3)	C1—C11	1.521 (3)
C9—C1	1.515 (3)	C11—C12	1.508 (4)
C8—C3	1.509 (3)	C12—O12	1.418 (3)
C3—C2	1.519 (4)	C12—C13	1.515 (4)
C2—N1	1.488 (3)	O12—C14	1.429 (3)
N1—C1	1.512 (3)		
C8—C9—C1	123.0 (2)	C9—C1—C11	111.9 (2)
C9—C8—C3	121.4 (2)	C12—C11—C1	116.1 (2)
C8—C3—C2	112.6 (2)	O12—C12—C11	107.3 (2)
N1—C2—C3	110.0 (2)	O12—C12—C13	113.1 (2)
C2—N1—C1	113.6 (2)	C11—C12—C13	109.4 (2)
N1—C1—C9	109.8 (2)	C12—O12—C14	113.0 (2)
N1—C1—C11	110.6 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6···O8	0.78 (3)	1.88 (3)	2.647 (3)	168 (3)
N1—H100···O12	0.92 (3)	2.06 (3)	2.813 (3)	138 (2)
O8—H82···Cl	0.93 (3)	2.29 (3)	3.211 (2)	172 (3)
O5—H5···Cl$^{\mathrm{i}}$	1.01 (4)	1.98 (4)	2.989 (2)	174 (3)
N1—H100···O8$^{\mathrm{ii}}$	0.92 (3)	2.61 (3)	3.268 (3)	129 (2)

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y, 1 + z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEX* (McArdle, 1995). Software used to prepare material for publication: *PARST*97 (Nardelli, 1983*b*).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1043). Services for accessing these data are described at the back of the journal.

References

Brzezińska, E. (1994). *Acta Pol. Pharm.* **51**, 137–141.
Brzezińska, E., Venter, D. & Glinka, R. (1996). *Pharmazie*, **51**, 397–399.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1418.
Molecular Structure Corporation (1989*a*). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1989*b*). *TEXSAN. TEXRAY Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Nardelli, M. (1983*a*). *Acta Cryst.* C**39**, 1141–1142.
Nardelli, M. (1983*b*). *Comput. Chem.* **7**, 95–98.
Olszak, T. A. (1998). *Acta Cryst.* C**54**, 1456–1459.
Olszak, T. A., Grabowski, M. J. & Brzezińska, E. (1994). *Acta Cryst.* C**50**, 283–284.
Olszak, T. A., Stępień, A., Grabowski, M. J. & Brzezińska, E. (1996). *Acta Cryst.* C**52**, 1038–1040.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1999). C**55**, 1005–1008

(2*S*,3*S*)- and (2*R*,3*S*)-2-[2-(benzyloxy)ethyl]-3-(6-chloro-9*H*-purin-9-yl)oxolane†

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Abstract

The title diastereomeric compounds, $C_{18}H_{19}ClN_4O_2$, are the products formed when the (2*S*,3*S*)- and (2*R*,3*S*)-3-(5-amino-6-chloropyrimidinyl)amino-2-(2-benzyloxy)ethyloxolanes are treated with triethyl orthoformate in the presence of 4-toluenesulfonic acid. The crystal structure determination unambiguously shows the *cis* and *trans* orientations, respectively, of the 2-benzyloxyethyl and the 6-chloropurinyl substituents of the oxolanyl ring.

Comment

Lithium aluminium hydride reduction of (2*S*,3*S*)- and (2*R*,3*S*)-2-methoxycarbonyl-3-(tritylamino)oxolanes (Papaioannou *et al.*, 1991) followed by *O*-benzylation ($PhCH_2Br/NaH$) and detritylation with 4-toluenesulfonic acid, produced unexceptionally the corresponding (2*S*,3*S*)- and (2*R*,3*S*)-3-amino-2-(2-benzyloxy)ethyloxolanes (Papaioannou, 1998). Treatment of these amines with 4,6-dichloro-5-nitropyrimidine, followed by

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† Alternative names: 9-{(2*S*,3*S*)- and (2*R*,3*S*)-2-[(2-benzyloxy)ethyl]oxolan-3-yl}-6-chloro-9*H*-purine.

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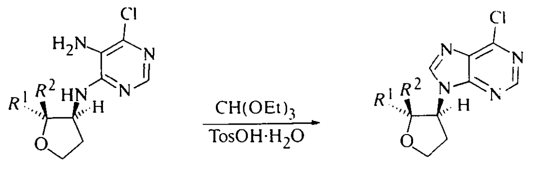
the catalytic hydrogenation of the nitro group in the presence of Raney Ni, produced the pyrimidinyl derivatives, (1*a*) and (1*b*), respectively. Finally, reaction of (1*a*) and (1*b*) with triethyl orthoformate in the presence of 4-toluenesulfonic acid hydrate (TosOH·H_2O) produced the purinyl derivatives, (2*a*) and (2*b*), respectively (Papaioannou *et al.*, 1998). As these compounds were projected as key-intermediates in the synthesis of a series of novel nucleosides of the 2,3-dideoxyribose type, we decided to establish unambiguously the mode of orientation of the oxygenated side-chain and the substituted purinyl ring around the central oxolanyl ring by determining their structure using X-ray analysis.



(1*a*) R^1=H
R^2=$CH_2CH_2OCH_2Ph$
(1*b*) R^1=$CH_2CH_2OCH_2Ph$
R^2=H

(2*a*) R^1=H
R^2=$CH_2CH_2OCH_2Ph$
(2*b*) R^1=$CH_2CH_2OCH_2Ph$
R^2=H

The crystal structure determination of the title compounds, (2*a*) and (2*b*), unambiguously shows that the 2-benzyloxyethyl group and the purinyl ring are indeed attached to the oxolanyl ring in the *cis* and *trans* mode, respectively. Moreover, a comparison of the two crystal structures reveals the following structural differences. Although the oxolanyl ring adopts the envelope conformation in both structures, different atoms deviate from the plane defined by the other four atoms. Thus, in the *cis* compound, (2*a*), the C14 atom is out of the plane by 0.557 (4) Å, whereas in the *trans* compound, (2*b*), it is the C10 atom which is out of the plane by 0.518 (4) Å. Moreover, the plane of the purinyl ring is oriented differently in relation to the plane defined by the four atoms of the oxolanyl ring in the two isomers. Thus, in (2*a*) the C4—N9—C10—C11 torsion angle is 136.9 (3)°, whereas the same angle in (2*b*) is 100.1 (3)°. In addition, the two molecules exhibit different conformations in their 2-benzyloxyethyl side-chains. Thus, in (2*a*) this chain adopts an extended 'zig-zag' conformation, whereas in (2*b*) the C14—C15—C16—O17 segment adopts a bent conformation. An unexpected result of this bending is that the calculated through-space distance between atoms N9 and O17 is 4.917 (3) Å in the *trans* isomer, (2*b*), which is shorter than the same distance [5.250 (3) Å] in the *cis* isomer, (2*a*). The absolute configurations of atoms C14 and C10, which were chosen to agree with the established chirality of the corresponding (2*S*,3*S*)- and (2*R*,3*S*)-2-methoxycarbonyl-3-(tritylamino)oxolanes from which (2*a*) and (2*b*) were synthesized, are depicted in Figs. 1(*a*) and 1(*b*).

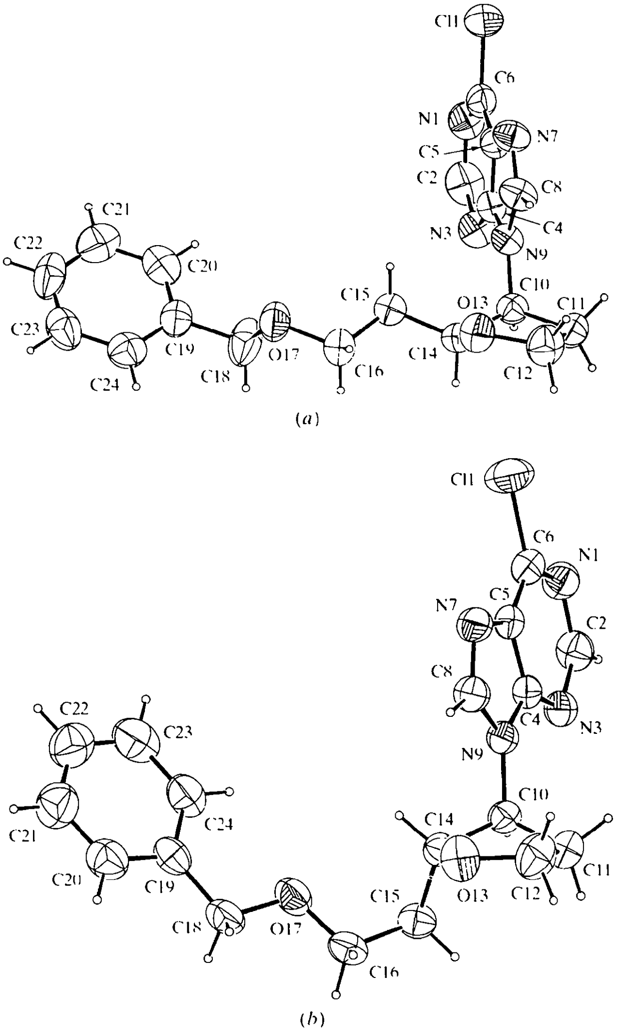


Fig. 1. View of (*a*) molecule (2*a*) and (*b*) molecule (2*b*) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

Experimental

TosOH·H_2O (0.24 g, 1.25 mmol) was added to a solution of the pyrimidinyl derivative (1) (1.74 g, 5 mmol) in triethyl orthoformate (10 ml, 60 mmol) and the resulting reaction mixture was stirred at ambient temperature for 3 h under argon. Excess triethyl orthoformate was then removed under high vacuum and the residue was subjected to flash column chromatography on MERCK silica gel 60 (230–400 mesh) using a toluene/ethyl acetate (8:2) solvent system for elution. The fractions with R_f 0.23 for purine (2*a*) and 0.22 for purine (2*b*), for a toluene/ethyl acetate (1:1) solvent system, were pooled and evaporated to dryness to leave oily residues, which crystallized on standing at ambient temperature to give the products, (2*a*) and (2*b*), which were obtained in 70% (1.26 g) and 45% (0.81 g) yields, respectively. Crystals of both compounds suitable for X-ray analysis were obtained by recrystallization from diethyl ether/hexane.

Compound (2*a*)

Crystal data

$C_{18}H_{19}ClN_4O_2$
$M_r = 358.82$
Orthorhombic
$C222_1$
$a = 7.7541\ (13)$ Å
$b = 14.4655\ (19)$ Å
$c = 31.108\ (5)$ Å
$V = 3489.3\ (10)$ Å^3
$Z = 8$
$D_x = 1.366$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 23 reflections
$\theta = 5.3$–$11.3°$
$\mu = 0.239$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.5 × 0.3 × 0.2 mm
Colourless

Data collection

Philips PW1100 diffractometer (updated by Stoe)
$\omega/2\theta$ scans
Absorption correction: none
2820 measured reflections
2820 independent reflections
1993 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 30°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 43$
3 standard reflections
every 120 reflections
intensity decay: 4.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.127$
$S = 1.018$
2820 reflections
226 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 1.6665P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.254$ e Å^{-3}
$\Delta\rho_{\min} = -0.251$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (2a)*

N1—C6	1.313 (4)	N7—C8	1.309 (4)
N1—C2	1.334 (5)	C8—N9	1.361 (3)
C2—N3	1.340 (4)	N9—C10	1.471 (3)
N3—C4	1.325 (3)	C12—O13	1.424 (4)
C4—N9	1.367 (3)	O13—C14	1.425 (4)
C4—C5	1.400 (4)	C16—O17	1.436 (4)
C5—N7	1.375 (3)	O17—C18	1.394 (4)
C5—C6	1.377 (4)		
C6—N1—C2	116.9 (3)	N1—C6—C5	122.1 (3)
N1—C2—N3	128.4 (3)	C8—N7—C5	103.4 (2)
C4—N3—C2	111.6 (3)	N7—C8—N9	114.9 (2)
N3—C4—N9	128.3 (3)	C4—N9—C8	105.5 (2)
N3—C4—C5	126.2 (2)	C4—N9—C10	125.0 (2)
N9—C4—C5	105.5 (2)	C8—N9—C10	129.4 (2)
C6—C5—N7	134.6 (3)	C12—O13—C14	106.9 (2)
C6—C5—C4	114.7 (2)	C18—O17—C16	113.1 (3)
N7—C5—C4	110.7 (2)		
C4—N9—C10—C14	−107.8 (3)	C12—O13—C14—C10	−38.7 (3)
C8—N9—C10—C14	74.1 (4)	C12—O13—C14—C15	−165.5 (3)
C4—N9—C10—C11	136.9 (3)	C11—C10—C14—O13	37.1 (3)
C8—N9—C10—C11	−41.2 (4)	C14—C15—C16—O17	−178.0 (3)

Compound (2*b*)

Crystal data

$C_{18}H_{19}ClN_4O_2$
$M_r = 358.82$
Orthorhombic
$P2_12_12_1$
$a = 7.5238\ (5)$ Å
$b = 10.9972\ (8)$ Å
$c = 20.9169\ (19)$ Å
$V = 1730.7\ (2)$ Å^3
$Z = 4$
$D_x = 1.377$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 150 reflections
$\theta = 10.1$–$18.9°$
$\mu = 0.240$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.6 × 0.3 × 0.2 mm
Colourless

Data collection

Philips PW1100 diffractometer (updated by Stoe)
$\omega/2\theta$ scans
Absorption correction: none
2890 measured reflections
2890 independent reflections
1740 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 30°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 29$
3 standard reflections
frequency: 120 min
intensity decay: 4.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.137$
$S = 1.027$
2890 reflections
226 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0796P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.218$ e Å^{-3}
$\Delta\rho_{\min} = -0.356$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (2b)*

N1—C6	1.316 (4)	N7—C8	1.305 (4)
N1—C2	1.341 (4)	C8—N9	1.375 (4)
C2—N3	1.329 (4)	N9—C10	1.472 (3)
N3—C4	1.329 (3)	C12—O13	1.415 (4)
C4—N9	1.367 (3)	O13—C14	1.435 (3)
C4—C5	1.398 (4)	C16—O17	1.415 (3)
C5—C6	1.381 (4)	O17—C18	1.404 (3)
C5—N7	1.382 (4)		
C6—N1—C2	117.2 (3)	N1—C6—C5	121.9 (3)
N1—C2—N3	128.1 (3)	C8—N7—C5	103.6 (2)
C4—N3—C2	111.9 (2)	N7—C8—N9	114.7 (3)
N3—C4—N9	127.7 (2)	C4—N9—C8	105.3 (2)
N3—C4—C5	126.4 (2)	C4—N9—C10	125.6 (2)
N9—C4—C5	105.8 (2)	C8—N9—C10	128.9 (2)
C6—C5—N7	135.0 (3)	C12—O13—C14	109.8 (2)
C6—C5—C4	114.4 (2)	C18—O17—C16	113.2 (2)
N7—C5—C4	110.6 (2)		
C4—N9—C10—C14	−145.6 (3)	C12—O13—C14—C10	18.1 (3)
C8—N9—C10—C14	28.8 (4)	C12—O13—C14—C15	104.2 (3)
C4—N9—C10—C11	100.1 (3)	C11—C10—C14—O13	31.4 (3)
C8—N9—C10—C11	−85.5 (3)	C14—C15—C16—O17	60.6 (3)

The data have not been corrected for absorption effects. No extinction correction was applied. H atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1988*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1988*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1035). Services for accessing these data are described at the back of the journal.

References

Papaioannou, D. (1998). Unpublished results.

Papaioannou, D., Stavropoulos, G., Sivas, M., Barlos, K., Francis, G. W., Aksnes, D. W. & Maartmann-Moe, K. (1991). *Acta Chem. Scand.* **45**, 99–104.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Stoe & Cie (1988*a*). *DIF4. Diffractometer Control Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1988*b*). *REDU4. Data Reduction Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1999). C**55**, 1008-1009

$(PMePh_3)(7,8\text{-}Et_2\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_{10})$

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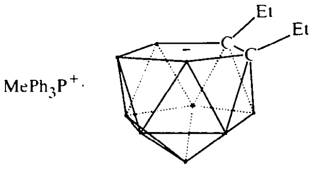
(*Received 2 June 1998; accepted 8 February 1999*)

Abstract

Methyltriphenylphosphonium 7,8-diethyl-7,8-dicarba-*nido*-undecaborate(1−), $C_{19}H_{18}P^+\cdot C_6H_{20}B_9^-$, is a salt which is formed from the cationic phosphonium ion and anionic *nido* carborane cage. The C—C distance in the boron cage is 1.567 (4) Å.

Comment

Our studies concerning *closo*-1,2-dicarbadodecaborane(12)s have led us to conclude that the C—C distance in the cage can be modified (Sillanpää *et al.*, 1996). In the case of relevant *nido* cages, the elongation seems to be less striking. For example, in *nido*-$(7,8\text{-}C_2B_9H_{12})^-$ the C—C distance is 1.542 (3) Å (Buchanan *et al.*, 1990) and in *nido*-$(7,8\text{-}Ph_2\text{-}7,8\text{-}C_2B_9H_{10})^-$ ($NHEt_3^+$ salt) 1.590 (5) Å and for $[NMe_3(CH_2Ph)]^+$ salt 1.602 (3) Å (Cowie *et al.*, 1993). In order to get more information on the dependence of the C—C distance as a function of the C substituent, the crystal structure of $(PMePh_3)(7,8\text{-}Et_2\text{-}7,8\text{-}C_2B_9H_{10})$, (I), is now reported.



(I)

An anionic structural unit of the salt is shown in Fig. 1. The methyl group of one ethyl arm bonded to the cage C atom is orientated up from the upper belt (atoms C7, C8, B9, B10 and B11) of the boron cage. The methyl group of the other ethyl group is approximately in the same plane of the upper-belt atoms. The bond angles and distances in the anion and cation are normal, but some distortions are found in the anion.

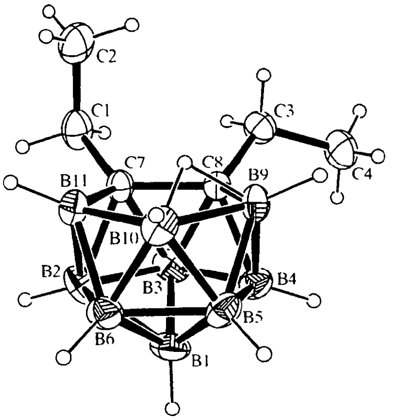


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the anionic part of (I) in the asymmetric unit. Only the heavy atoms have been labelled. Displacement ellipsoids are drawn at the 20% probability level.

In the lower belt (B2, B3, B4, B5 and B6), the B—B distances are in the range 1.730 (7)–1.806 (7) Å (Table 1), while in the upper belt the C7—C8 bond length is 1.567 (4) (the shortest bond) and the B9—B10 bond length is 1.843 (7) Å (the longest bond). Bond angles in the lower belt range from 106.0 (3) to 109.8 (3)° and in the upper belt from 101.5 (3) to 114.5 (3)°.

Alkyl substituents on C atoms in 7,8-dicarbaboranes seem to have quite a small effect on the C—C bond distance. Aromatic substituents, compared with H substituents, lengthen the C—C distance by about 0.05 Å. Generally this follows with that which has been found for relevant *closo* cages, but in the *nido* case this effect is much weaker.