Acta Cryst. (1994). C**50**, 1296–1299

Monohydrates of Two Isomers of Aminotoluenesulfonic Acid

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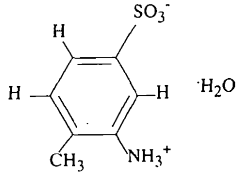
(*Received* 25 *June* 1993; *accepted* 29 *October* 1993)

Abstract

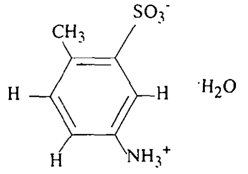
The structures of 2-aminotoluene-4-sulfonic acid monohydrate, $C_7H_9NO_3S.H_2O$ (I), and 4-aminotoluene-2-sulfonic acid monohydrate, $C_7H_9NO_3S.H_2O$ (II), have been determined. The compounds crystallize as zwitterions (ammoniotoluenesulfonate). Both structures consist of layers of nearly planar molecules oriented parallel to one another with the sulfonate and ammonium groups directed towards the adjacent layers. The water molecules lie between the layers. There are hydrogen bonds between the water molecule, sulfonate O atoms and ammonium H atoms in each structure. The structures differ in the stacking pattern of the layers. The layers in (I) are identical, so that molecules in adjacent layers are parallel, while the adjacent layers in (II) are rotated at approximately 90° with respect to one another.

Comment

As part of a continuing study of layered metal arylsulfonate compounds (Kosnic, McClymont, Hodder & Squattrito, 1992), it is of interest to determine if the arylsulfonic acids also have similar layered structures. In addition, we wanted to know how the molecular-packing patterns would differ for the two isomeric sulfonic acids, (I) and (II), used in this experiment.



(I)



(II)

The structural diagrams of the two isomers, Figs. 1 and 2, show that they differ only in the placement of the methyl group on the phenyl ring. This difference is sufficient to result in substantially different packing schemes, shown in Figs. 3 and 4. For both isomers, the molecules in a given layer are parallel to one another, with the sulfonate and ammonium groups directed towards the outer surfaces of the layers. Half the molecules are oriented with the sulfonate group 'up' and half with the sulfonate group 'down'. The structure of 2-aminotoluene-4-sulfonic acid, (I), is formed by the stacking of identical layers 'in register' while the layers in 4-aminotoluene-2-sulfonic acid, (II), stack in a more complicated pattern in which the molecules in alternate layers are nearly orthogonal.

The layers in both structures are held together by hydrogen bonds involving the ionic groups and water molecules of crystallization (Tables 2 and 4). In both cases, the H atoms of each ammonium group interact with two sulfonate O atoms and a water O atom, while both H atoms of each water molecule interact with sulfonate O atoms.

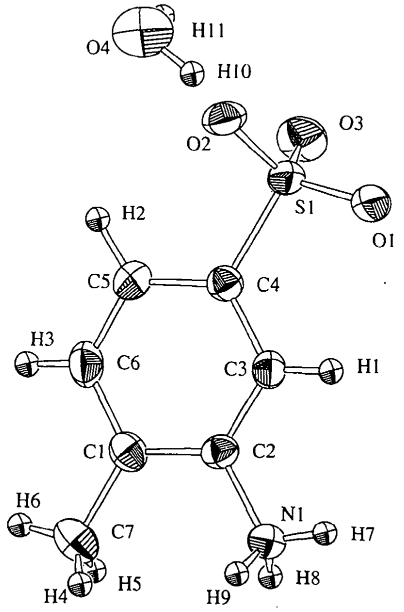


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of (I) showing atomic labeling scheme. In this and subsequent figures, the displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

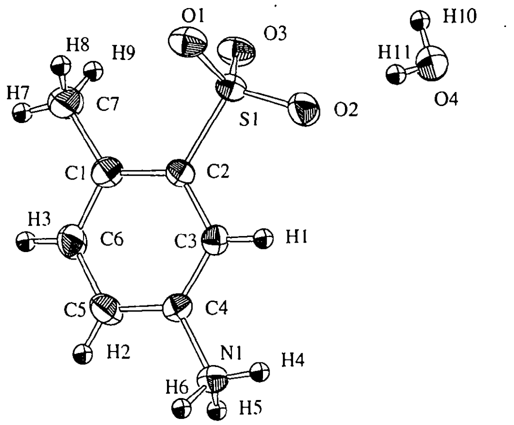


Fig. 2. *ORTEP*II diagram of (II) showing atomic labeling scheme.

Acta Crystallographica Section C
ISSN 0108-2701 © 1994

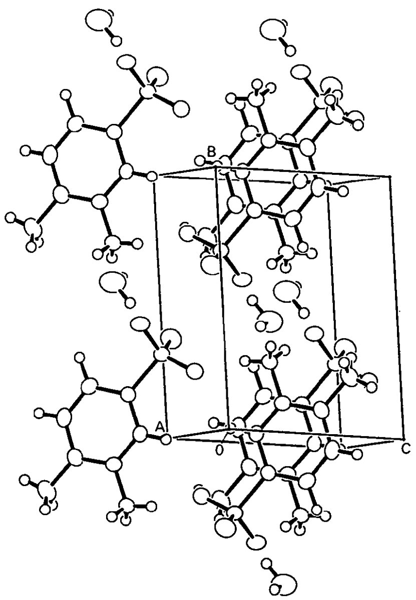


Fig. 3. *ORTEP*II packing diagram of (I) showing the outline of the unit cell.

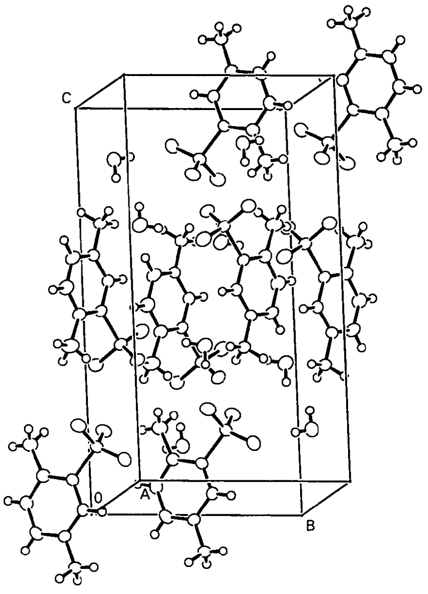


Fig. 4. *ORTEP*II packing diagram of (II) showing the outline of the unit cell.

Experimental

Crystals of both compounds were obtained by dissolving about 1 g of powdered reagent grade material (Eastman Kodak) in 100 ml of warm distilled water. Crystals grew upon cooling and partial evaporation of the solvent. Crystals of the triclinic compound, (I), formed as long prismatic rods, while crystals of the monoclinic compound, (II), were parallelogram-shaped slabs.

Compound (I)

Crystal data

$C_7H_9NO_3S.H_2O$
$M_r = 205.23$
Triclinic
$P\overline{1}$
$a = 8.514\ (1)$ Å
$b = 8.817\ (1)$ Å
$c = 6.028\ (1)$ Å
$\alpha = 96.66\ (1)°$
$\beta = 93.35\ (1)°$
$\gamma = 93.83\ (1)°$
$V = 447.5\ (1)$ Å^3
$Z = 2$
$D_x = 1.523$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 22.3–24.8°$
$\mu = 0.328$ mm^{-1}
$T = 296$ K
Rod
0.35 × 0.15 × 0.15 mm
Colorless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega–2\theta$ scans
Absorption correction: none
1680 measured reflections
1564 independent reflections
1323 observed reflections $[I > 3\sigma(I)]$
$R_{\text{int}} = 0.017$

$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -7 \rightarrow 7$
3 standard reflections monitored every 150 reflections
intensity variation: none within intensity statistics

Refinement

Refinement on F
$R = 0.036$
$wR = 0.039$
$S = 3.08$
1323 reflections
155 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: $C = 0.67\ (7) \times 10^{-5}$
Atomic scattering factors from Cromer & Waber (1974); Cromer (1974)

Compound (II)

Crystal data

$C_7H_9NO_3S.H_2O$
$M_r = 205.23$
Monoclinic
$C2/c$
$a = 11.365\ (3)$ Å
$b = 9.142\ (2)$ Å
$c = 17.671\ (1)$ Å
$\beta = 96.93\ (1)°$
$V = 1822.6\ (5)$ Å^3
$Z = 8$
$D_x = 1.496$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 18 reflections
$\theta = 23.6–24.9°$
$\mu = 0.322$ mm^{-1}
$T = 296$ K
Parallelepiped
0.30 × 0.20 × 0.20 mm
Colorless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega–2\theta$ scans
Absorption correction: none
1800 measured reflections
1703 independent reflections
1249 observed reflections $[I > 3\sigma(I)]$
$R_{\text{int}} = 0.017$

$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 10$
$l = -20 \rightarrow 20$
3 standard reflections monitored every 150 reflections
intensity variation: none within intensity statistics

Refinement

Refinement on F
$R = 0.036$
$wR = 0.038$
$S = 2.65$
1249 reflections
152 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.08$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: $C = 0.142\ (8) \times 10^{-5}$
Atomic scattering factors from Cromer & Waber (1974); Cromer (1974)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2) *for compound* (I)

$B_{\rm iso}$ for H; $B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	y	z	$B_{\rm iso}/B_{\rm eq}$
S(1)	0.64162 (8)	0.30206 (8)	0.8640 (1)	2.39 (3)
O(1)	0.5339 (2)	0.2389 (2)	1.0120 (3)	3.38 (9)
O(2)	0.5703 (2)	0.4072 (2)	0.7242 (3)	3.06 (8)
O(3)	0.7904 (2)	0.3685 (2)	0.9768 (3)	3.67 (9)
O(4)	0.9345 (2)	0.5796 (2)	0.7089 (4)	4.7 (1)
N(1)	0.6555 (3)	−0.2823 (3)	0.6218 (4)	2.5 (1)
C(1)	0.7789 (3)	−0.1035 (3)	0.3849 (4)	2.5 (1)
C(2)	0.6981 (3)	−0.1255 (3)	0.5748 (4)	2.2 (1)
C(3)	0.6552 (3)	−0.0051 (3)	0.7210 (4)	2.2 (1)
C(4)	0.6907 (3)	0.1437 (3)	0.6763 (4)	2.2 (1)
C(5)	0.7660 (3)	0.1702 (3)	0.4842 (5)	2.8 (1)
C(6)	0.8102 (4)	0.0472 (3)	0.3446 (5)	3.0 (1)
C(7)	0.8304 (5)	−0.2348 (4)	0.2312 (6)	3.5 (1)
H(1)	0.598 (3)	−0.023 (3)	0.846 (4)	2.1 (5)
H(2)	0.791 (3)	0.279 (3)	0.445 (4)	2.6 (6)
H(3)	0.863 (3)	0.061 (3)	0.223 (4)	2.6 (6)
H(4)	0.744 (4)	−0.311 (4)	0.185 (6)	6 (1)
H(5)	0.918 (4)	−0.283 (4)	0.288 (6)	6 (1)
H(6)	0.889 (5)	−0.196 (4)	0.127 (6)	7 (1)
H(7)	0.595 (4)	−0.283 (4)	0.742 (6)	4.9 (8)
H(8)	0.753 (4)	−0.335 (3)	0.646 (5)	4.4 (8)
H(9)	0.595 (4)	−0.332 (4)	0.511 (6)	4.7 (8)
H(10)	0.8910	0.5001	0.7875	5.4
H(11)	1.0273	0.6043	0.7973	5.4

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

S(1)—O(1)	1.446 (2)	C(1)—C(6)	1.389 (4)
S(1)—O(2)	1.461 (2)	C(1)—C(7)	1.503 (4)
S(1)—O(3)	1.456 (2)	C(2)—C(3)	1.382 (3)
S(1)—C(4)	1.780 (3)	C(3)—C(4)	1.387 (3)
N(1)—C(2)	1.470 (3)	C(4)—C(5)	1.392 (4)
C(1)—C(2)	1.395 (4)	C(5)—C(6)	1.381 (4)
O(1)—S(1)—O(2)	113.5 (1)	O(2)—S(1)—O(3)	111.6 (1)
O(1)—S(1)—O(3)	113.6 (1)	O(2)—S(1)—C(4)	105.9 (1)
O(1)—S(1)—C(4)	105.7 (1)		

D	H	A	D—H	H···A	D—H···A
N1	H7	$O1^{i}$	0.92 (3)	1.91 (4)	168 (3)
N1	H8	$O4^{ii}$	0.99 (3)	1.81 (3)	176 (3)
N1	H9	$O2^{iii}$	0.87 (3)	1.96 (3)	167 (3)
O4	H10	O3	0.96	1.92	170
O4	H11	$O3^{iv}$	0.93	1.99	170

Symmetry codes: (i) $1-x, -y, 2-z$; (ii) $x, y-1, z$; (iii) $1-x, -y, 1-z$; (iv) $2-x, 1-y, 2-z$.

Table 3. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2) *for compound* (II)

$B_{\rm iso}$ for H; $B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	y	z	$B_{\rm iso}/B_{\rm eq}$
S(1)	0.72032 (6)	0.48513 (8)	0.14838 (4)	2.21 (3)
O(1)	0.8012 (2)	0.3838 (2)	0.1927 (1)	2.9 (1)
O(2)	0.7811 (2)	0.5999 (2)	0.1119 (1)	3.2 (1)
O(3)	0.6315 (2)	0.5418 (2)	0.1942 (1)	2.7 (1)
O(4)	0.7370 (2)	0.8893 (3)	0.1498 (1)	3.8 (1)
N(1)	0.6070 (2)	0.3858 (3)	−0.1402 (1)	2.3 (1)
C(1)	0.5732 (3)	0.2612 (3)	0.0880 (2)	2.4 (1)
C(2)	0.6433 (2)	0.3810 (3)	0.0725 (2)	2.0 (1)
C(3)	0.6554 (3)	0.4227 (3)	−0.0020 (2)	2.0 (1)
C(4)	0.5960 (2)	0.3449 (3)	−0.0611 (2)	2.0 (1)
C(5)	0.5238 (3)	0.2288 (4)	−0.0482 (2)	2.8 (1)
C(6)	0.5129 (3)	0.1891 (4)	0.0260 (2)	2.9 (1)
C(7)	0.5598 (4)	0.2080 (5)	0.1666 (2)	3.6 (2)
H(1)	0.703 (2)	0.502 (3)	−0.011 (2)	2.8
H(2)	0.482 (2)	0.181 (3)	−0.088 (2)	3.1
H(3)	0.464 (3)	0.115 (3)	0.036 (2)	3.2
H(4)	0.658 (3)	0.463 (4)	−0.143 (2)	3.7
H(5)	0.536 (3)	0.410 (4)	−0.166 (2)	3.7
H(6)	0.632 (3)	0.303 (4)	−0.169 (2)	3.7
H(7)	0.507 (3)	0.137 (4)	0.166 (2)	3.9
H(8)	0.629 (3)	0.186 (4)	0.199 (2)	3.9
H(9)	0.547 (3)	0.280 (4)	0.198 (2)	3.9
H(10)	0.725 (3)	0.886 (4)	0.196 (2)	4.0
H(11)	0.756 (3)	0.807 (4)	0.141 (2)	4.0

Table 4. *Selected geometric parameters* (Å, °) *for compound* (II)

S(1)—O(1)	1.464 (2)	C(1)—C(6)	1.386 (4)
S(1)—O(2)	1.450 (2)	C(1)—C(7)	1.498 (4)
S(1)—O(3)	1.463 (2)	C(2)—C(3)	1.394 (4)
S(1)—C(2)	1.785 (3)	C(3)—C(4)	1.372 (4)
N(1)—C(4)	1.467 (4)	C(4)—C(5)	1.378 (4)
C(1)—C(2)	1.400 (4)	C(5)—C(6)	1.381 (4)
O(1)—S(1)—O(2)	113.2 (1)	O(2)—S(1)—O(3)	112.8 (1)
O(1)—S(1)—O(3)	111.0 (1)	O(2)—S(1)—C(2)	105.6 (1)
O(1)—S(1)—C(2)	106.5 (1)		

D	H	A	D—H	H···A	D—H···A
N1	H4	$O4^{i}$	0.92 (3)	1.82 (3)	177 (3)
N1	H5	$O3^{ii}$	0.91 (3)	1.96 (3)	165 (3)
N1	H6	$O1^{iii}$	0.97 (3)	1.94 (3)	161 (3)
O4	H10	$O1^{iv}$	0.85 (3)	2.01 (3)	178 (3)
O4	H11	O2	0.81 (3)	1.99 (3)	172 (4)

Symmetry codes: (i) $\frac{3}{2}-x, \frac{3}{2}-y, -z$; (ii) $1-x, 1-y, -z$; (iii) $\frac{3}{2}-x, \frac{1}{2}-y, -z$; (iv) $\frac{3}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$.

All H atoms for compound (I) were located on difference electron density maps. Atoms H(1)–H(9) were refined isotropically while atoms H(10) and H(11) were included as fixed isotropic scatterers with $B_{\rm iso}$ values of 1.2 times that of O(4) at the time of their inclusion in the model. All H atoms for compound (II) were located on difference electron density maps and were assigned isotropic displacement parameters equal to 1.2 times the B of the attached atom at their inclusion in the model. For both compounds, data collection was performed with *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988), data reduction and structure refinement with *TEXSAN* (Molecular Structure Corporation, 1991), and structure solution with *MITHRIL* (Gilmore, 1983) and *DIRDIF* (Beurskens *et al.*, 1983).

The support of the Herbert H. and Grace A. Dow Foundation, The Dow Chemical Company Foundation and Central Michigan University in the establishment of the CMU X-ray facility is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: CR1091). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, Th. E. M., Prick, P. A., Noordik, J. H., Beurskens, G., Parthasarthi, V., Bruins Slot, H. J. & Haltiwanger, R. C. (1983). *DIRDIF*. Technical Report 1983/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributors Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributors Kluwer Academic Publishers, Dordrecht.)

Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data.* Department of Chemistry, Univ. of Glasgow, Scotland.

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

Kosnic, E. J., McClymont, E. L., Hodder, R. A. & Squattrito, P. J. (1992). *Inorg. Chim. Acta*, **201**, 143–151.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. Revised edition. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1991). *TEXSAN. TEXRAY Structure Analysis Package*. Revised edition. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1994). C**50**, 1299–1301

An *m*-Carboranedicarboxylic Acid Dianilide

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(*Received* 23 *November* 1993; *accepted* 19 *January* 1994)

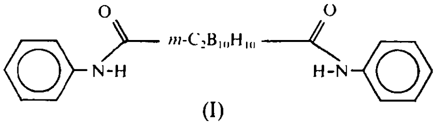
Abstract

The crystal structure of the 'non hydrogen-bonded' (according to IR data) polymorph of 1,7-bis(phenylcarbamoyl)-1,7-dicarba-*closo*-dodecaborane(12), $C_{16}H_{22}B_{10}N_2O_2$, has been determined. The two phenylamide groups have a *Z* configuration [the torsion angles O—C—N—C are −2.3 (5) and −3.0 (5)°]. As a result both 'active' protons of these groups are almost completely shielded by other H atoms of the neighbouring carborane nucleus and phenyl substituents, and, therefore, no hydrogen-bonding contacts are found.

Comment

It is widely known that the specific properties of polyamides depend strongly on the presence of interchain hydrogen-bonding interactions. The hydrogen-bonding parameters may often be predicted on the basis of the crystal structures of low molecular weight analogues of these polymers. Such studies have been carried out, in particular, for low molecular weight models of the elementary units of aliphatic (Ruede & Fayos, 1982) and aromatic (Brisson & Brisse, 1985, 1986) nylons.

The title compound (I) was synthesized as a model of the elementary unit of poly(4,4′-diphenylene-1,7-carboranyl dicarbamide), $[\text{—OCCB}_{10}\text{H}_{10}\text{CCOHNC}_6\text{H}_4\text{-C}_6\text{H}_4\text{NH—}]_n$. It has been shown by IR specroscopy that the title compound (I) has two polymorphs (Leites, Kats, Bukalov & Komarova, 1991). By using a slow crystallization method the stable 'non hydrogen-bonded' modification (I*a*) is formed, whereas fast crystallization leads to a metastable 'hydrogen-bonded' form (I*b*) in which N—H···O bonds are present. The relative amount of each form obtained depends on the particular conditions used for precipitation. Unfortunately, we were only able to prepare suitable crystals of the (I*a*) form for this study.



(I)

The molecule of (I) in form (I*a*) is elongated in shape (Fig. 1). The geometrical parameters of this molecule are in good agreement with the standard values (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). Both chemically equivalent halves of the molecule have a similar conformation: the carbonyl groups are *syn*-oriented with respect to the B1 and B2 atoms and the amide groups have a *Z* configuration and are essentially planar. The terminal phenyl groups are rotated out of the planes of the adjacent amide groups [the corresponding dihedral angles are 46.9 (7)° for the C11–C16 phenyl group and 26.2 (4)° for the C21–C26 phenyl group]. In this conformation both of the amide H atoms happen to be almost completely shielded by other H atoms of the neighbouring carborane nucleus and phenyl groups (Fig. 2). Evidently, this is the main reason for the absence of hydrogen bonds in the structure of (I*a*).