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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.

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An *m*-Carboranedicarboxylic Acid Dianilide

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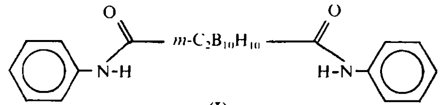
Abstract

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), [—$OCCB_{10}H_{10}CCOHNC_6H_4$-$C_6H_4NH$—]$_n$. 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*).

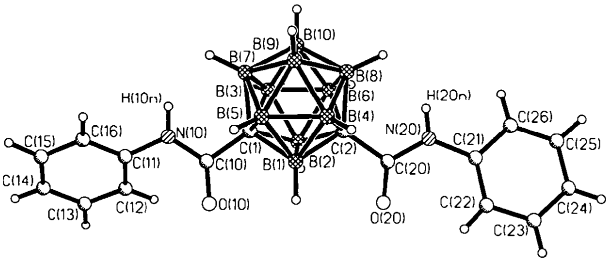


Fig. 1. Perspective view of the structure of the title compound showing the atomic labelling.

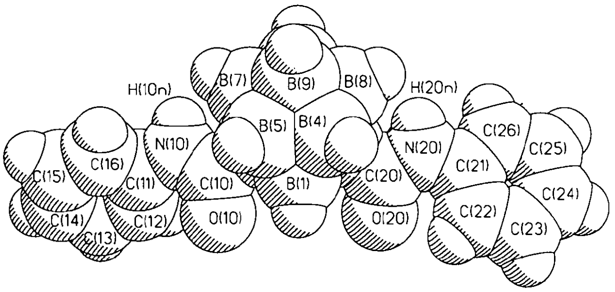


Fig. 2. Space-filling projection of the title compound indicating the spatial shielding of the amide H atoms.

In the case of the *E* configuration of the amide groups, the H atoms of these groups would be *exo*-oriented and therefore more accessible to a hydrogen-bond acceptor. However, such a configuration would be much more strained due to the steric repulsion between the *syn*-oriented carborane nucleus and phenyl groups. These steric hindrances may be the cause of the metastability of the 'hydrogen-bonded' form (I*b*), assuming that the structure of the latter is indeed built up from molecules of (I) in the *E* configuration.

Experimental

Crystal data

$C_{16}H_{22}B_{10}N_2O_2$
$M_r = 382.46$
Triclinic
$P\overline{1}$
$a = 9.727\ (3)$ Å
$b = 10.366\ (4)$ Å
$c = 10.727\ (3)$ Å
$\alpha = 106.36\ (3)°$
$\beta = 96.08\ (3)°$
$\gamma = 95.87\ (3)°$
$V = 1022.0\ (6)$ Å^3
$Z = 2$
$D_x = 1.243$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 12–12.5°$
$\mu = 0.072$ mm^{-1}
$T = 293\ (2)$ K
Well formed prisms
0.4 × 0.3 × 0.25 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3775 measured reflections
3772 independent reflections
3009 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.1131$

$\theta_{\rm max} = 28.03°$
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 12$
$l = 0 \rightarrow 14$
2 standard reflections monitored every 98 reflections
intensity variation: 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0505$
$wR(F^2) = 0.1296$
$S = 1.077$
3758 reflections
359 parameters
All H-atom parameters refined
Calculated weights
$w = 1/[\sigma^2(F_o^2) + (0.0841P)^2 + 0.1539P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.018$
$\Delta\rho_{\rm max} = 0.257$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.180$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.2504 (2)	0.8640 (2)	0.62916 (15)	0.0345 (4)
C10	0.2887 (2)	0.9598 (2)	0.7688 (2)	0.0422 (4)
O10	0.4087 (2)	1.0038 (2)	0.81282 (15)	0.0799 (6)
N10	0.1807 (2)	0.9875 (2)	0.8334 (2)	0.0530 (4)
C11	0.1899 (2)	1.0698 (2)	0.9667 (2)	0.0433 (4)
C12	0.2838 (2)	1.0530 (2)	1.0639 (2)	0.0529 (5)
C13	0.2833 (3)	1.1295 (2)	1.1931 (2)	0.0588 (6)
C14	0.1916 (3)	1.2216 (2)	1.2229 (2)	0.0592 (6)
C15	0.1012 (3)	1.2401 (2)	1.1256 (2)	0.0669 (6)
C16	0.0988 (3)	1.1633 (2)	0.9962 (2)	0.0594 (6)
C2	0.3471 (2)	0.7028 (2)	0.43101 (15)	0.0360 (4)
C20	0.4791 (2)	0.6483 (2)	0.3831 (2)	0.0447 (4)
O20	0.5901 (2)	0.6855 (2)	0.4519 (2)	0.0911 (7)
N20	0.4583 (2)	0.5612 (2)	0.2625 (2)	0.0504 (4)
C21	0.5594 (2)	0.4998 (2)	0.1885 (2)	0.0437 (4)
C22	0.6964 (2)	0.5560 (3)	0.2076 (2)	0.0572 (5)
C23	0.7868 (3)	0.4907 (3)	0.1270 (2)	0.0681 (7)
C24	0.7400 (3)	0.3705 (3)	0.0302 (2)	0.0671 (7)
C25	0.6027 (3)	0.3153 (2)	0.0112 (2)	0.0606 (6)
C26	0.5115 (3)	0.3788 (2)	0.0901 (2)	0.0510 (5)
B1	0.3762 (2)	0.8657 (2)	0.5309 (2)	0.0370 (4)
B2	0.3357 (2)	0.7252 (2)	0.5928 (2)	0.0356 (4)
B3	0.1551 (2)	0.7069 (2)	0.6030 (2)	0.0404 (4)
B4	0.2850 (2)	0.8261 (2)	0.3703 (2)	0.0427 (5)
B5	0.2207 (2)	0.9339 (2)	0.5030 (2)	0.0435 (5)
B6	0.2203 (2)	0.5992 (2)	0.4709 (2)	0.0408 (4)
B7	0.0837 (2)	0.8349 (2)	0.5470 (2)	0.0416 (5)
B8	0.1873 (2)	0.6617 (2)	0.3339 (2)	0.0417 (5)
B9	0.1032 (2)	0.8068 (2)	0.3802 (2)	0.0456 (5)
B10	0.0627 (2)	0.6669 (2)	0.4427 (2)	0.0432 (5)

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

C1—C10	1.529 (2)	C2—C20	1.535 (2)
C1—B1	1.700 (3)	C2—B2	1.702 (2)
C1—B2	1.705 (3)	C2—B1	1.702 (3)
C1—B7	1.716 (3)	C2—B8	1.719 (3)
C1—B5	1.718 (3)	C2—B6	1.720 (3)
C1—B3	1.723 (3)	C2—B4	1.722 (3)
C10—O10	1.203 (2)	C20—O20	1.202 (2)
C10—N10	1.331 (2)	C20—N20	1.334 (2)
N10—C11	1.432 (2)	N20—C21	1.419 (2)
C11—C12	1.373 (3)	C21—C22	1.369 (3)
C11—C16	1.374 (3)	C21—C26	1.391 (3)

C10—C1—B1	114.93 (14)	C20—C2—B2	115.73 (14)
C10—C1—B2	115.81 (14)	C20—C2—B1	113.97 (14)
C10—C1—B7	121.77 (14)	C20—C2—B8	122.67 (14)
C10—C1—B5	118.18 (14)	C20—C2—B6	120.46 (15)
C10—C1—B3	119.68 (14)	C20—C2—B4	117.71 (14)
O10—C10—N10	124.8 (2)	O20—C20—N20	125.1 (2)
O10—C10—C1	120.4 (2)	O20—C20—C2	120.4 (2)
N10—C10—C1	114.8 (2)	N20—C20—C2	114.5 (2)
C10—N10—C11	125.3 (2)	C20—N20—C21	128.0 (2)
C12—C11—C16	120.5 (2)	C22—C21—C26	120.5 (2)
C12—C11—N10	121.1 (2)	C22—C21—N20	123.2 (2)
C16—C11—N10	118.3 (2)	C26—C21—N20	116.4 (2)
B1—C1—C10—O10	−18.3 (4)	B1—C2—C20—O20	32.6 (4)
B2—C1—C10—O10	52.8 (4)	B2—C2—C20—O20	−38.1 (4)
C11—N10—C10—O10	−2.3 (5)	C21—N20—C20—O20	−3.0 (5)

Program used to solve structure: *SHELXTL-Plus* (Sheldrick, 1989). Program used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1141). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(triphenylphosphine)iminium Hexafluorophosphate Dichloromethane Solvate (1/1)

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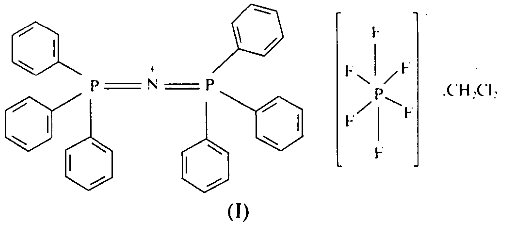
Abstract

Bis(triphenylphosphine)iminium hexafluorophosphate [or bis(phosphoranylidene)ammonium hexafluorophosphate] crystallizes from dichloromethane/hexane as a (1/1) solvate, $[C_{36}H_{30}NP_2][PF_6].CH_2Cl_2$, in which the CH_2Cl_2 molecule is extensively disordered. The cation and anion are essentially ions linked by some short intermolecular contacts.

Comment

The bis(triphenylphosphine)iminium cation $[Ph_3P{=}N^+{=}PPh_3]$ has found extensive use as a large non-interacting organic cation for the crystallization of anionic inorganic species: overwhelmingly these anions are metal carbonyl clusters (*e.g.* Bailey, Conole, Johnson, Lewis, McPartlin, Moule & Wilkinson, 1991) but there are also examples of boranes (Meyer, Muller, Paetzold & Boese, 1992), sulfur–nitrogen species (Chivers, Laidlaw, Oakley & Trsic, 1980) and chloro complexes (Fanwick, King, Tetrick & Walton, 1985).

In bis(triphenylphosphine)iminium hexafluorophosphate dichloromethane solvate, (I), the ions are essentially isolated but linked by relatively short intermolecular contacts [H216· · ·F1(at x, $1+y$, z) = 2.25 (1) Å]. Hexafluorophosphate (PF_6^-) anions typically exhibit a range of disorder modes at ambient temperature involving marked libration or free rotation of the F atoms about one or more axes passing through the P atom. A study of a large number of PF_6^- salts at temperatures below *ca* 180 K has shown that the F atoms then usu-



(I)

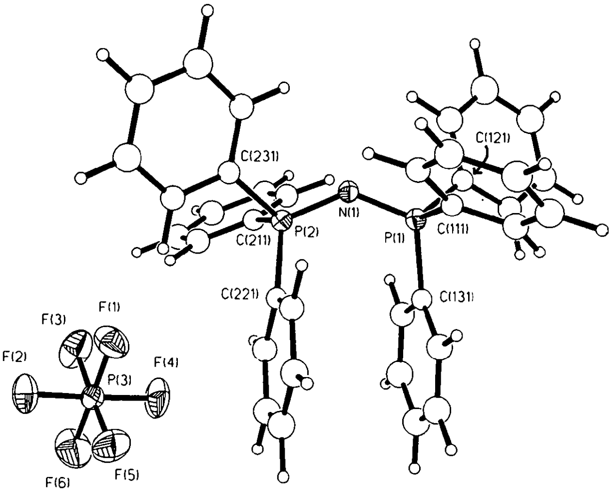


Fig. 1. A view of the ion pair with the atom-numbering scheme employed. Displacement ellipsoids for P, F and N atoms are drawn at the 30% probability level.

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