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# An *m*-Carboranedicarboxylic Acid Dianilide

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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.

## 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., Parthasarathi, V., Bruins Slot, H. J. & Hiltwanger, 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*. 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.* **A24**, 212–216.

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### Abstract

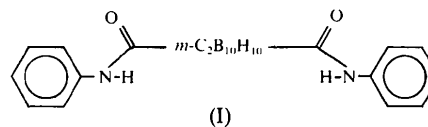
The crystal structure of the 'non hydrogen-bonded' (according to IR data) polymorph of 1,7-bis(phenyl-carbamoyl)-1,7-dicarba-*closo*-dodecaborane(12),  $C_{16}$ -

$H_{22}B_{10}N_2O_2$ , has been determined. The two phenylamide groups have a *Z* configuration [the torsion angles O—C—N—C are  $-2.3(5)$  and  $-3.0(5)^\circ$ ]. 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 inter-chain 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 spectroscopy 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 (Ia) is formed, whereas fast crystallization leads to a metastable 'hydrogen-bonded' form (Ib) 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 (Ia) form for this study.



The molecule of (I) in form (Ia) 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  $46.9(7)^\circ$  for the C11–C16 phenyl group and  $26.2(4)^\circ$  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 (Ia).

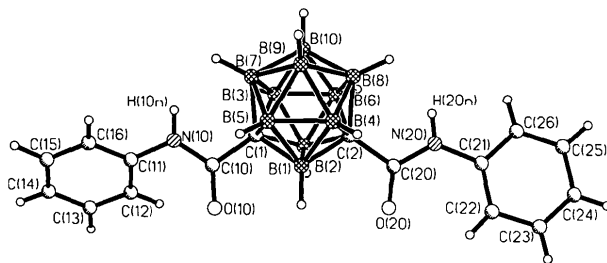


Fig. 1. Perspective view of the structure of the title compound showing the atomic labelling.

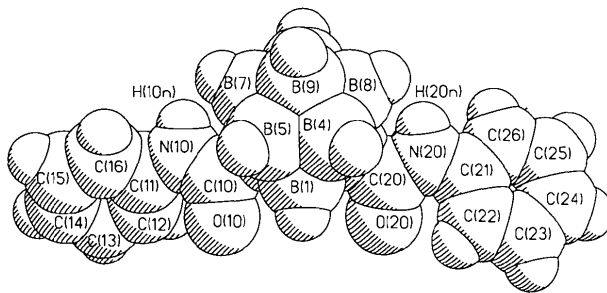


Fig. 2. Space-filling projection of the title compound indicating the spatial shielding of the amide H atoms.

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 (*Ib*), assuming that the structure of the latter is indeed built up from molecules of (*I*) in the *E* configuration.

## Experimental

### Crystal data

C<sub>16</sub>H<sub>22</sub>B<sub>10</sub>N<sub>2</sub>O<sub>2</sub>

*M<sub>r</sub>* = 382.46

Triclinic

*P* $\bar{1}$

*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<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.243 Mg m<sup>-3</sup>

### Data collection

Syntex *P*<sub>2</sub> diffractometer

$\theta/2\theta$  scans

Absorption correction:  
none

Mo *K* $\alpha$  radiation

$\lambda$  = 0.71069 Å

Cell parameters from 24  
reflections

$\theta$  = 12–12.5°

$\mu$  = 0.072 mm<sup>-1</sup>

*T* = 293 (2) K

Well formed prisms

0.4 × 0.3 × 0.25 mm

Colourless

3775 measured reflections  
3772 independent reflections  
3009 observed reflections  
[*I* > 2 $\sigma$ (*I*)]  
*R*<sub>int</sub> = 0.1131

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.0505$   
 $wR(F^2) = 0.1296$   
*S* = 1.077

3758 reflections  
359 parameters  
All H-atom parameters  
refined

Calculated weights

$$w = 1/[\sigma^2(F_o^2) + (0.0841P)^2 + 0.1539P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

2 standard reflections  
monitored every 98  
reflections  
intensity variation: 2.5%

$(\Delta/\sigma)_{\max} = 0.018$   
 $\Delta\rho_{\max} = 0.257 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.180 \text{ e } \text{Å}^{-3}$   
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<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
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: *SHELXL93* (Sheldrick, 1993).

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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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## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- Brisson, J. & Brisse, F. (1985). *Can. J. Chem.* **63** 3390–3397.
- Brisson, J. & Brisse, F. (1986). *Macromolecules*, **19**, 2632–2639.
- Leites, L. A., Kats, G. A., Bukalov S. S. & Komarova, L. G. (1991). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 371–376.
- Ruede, D. R. & Fayos, J. (1982). *Eur. Polym. J.* **18**, 1–4.
- Sheldrick, G. M. (1989). *SHELXTL-Plus*. PC version. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.