ORGANIC COMPOUNDS

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Crystal and Molecular Structure of 1,12-Dicarboxy-1,12-dicarba-*closo*-dodecaborane(12), $C_4H_{12}B_{10}O_4$

R. Centore, M. R. Ciajolo and A. Tuzi

Dipartimento di Chimica, Università di Napoli
'Federico II', Via Mezzocannone 4, 80134 Napoli, Italy

L. G. Komarova, A. L. Rusanov and V. A. Vasnev

INEOS Russian Academy of Sciences,
28 Vavilov Street, 117812 Moscow, Russia

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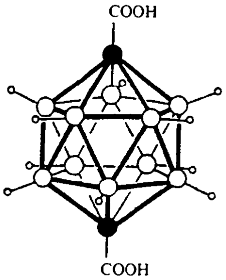
Abstract

The fivefold symmetry of the carborane cage is slightly distorted because of small differences between the basal B—B bond lengths. The C···C diameter of the cage is *ca* 0.3 Å shorter than the diameters involving *para*-boron atoms. Molecules of the title compound are bonded along extended rows through hydrogen bonds between carboxylic groups. The rows are parallel to the $-\mathbf{a}+\mathbf{b}-\mathbf{c}$ axis. Molecules are repeated along the rows by inversion centres.

Comment

The accuracy of structural investigations on molecules containing the carborane cage, based on X-ray crystallography, is often reduced due to disorder in the crystals, caused by the almost spherical shape of the cage. Therefore, structural information on these compounds has often been obtained by other techniques, such as electron diffraction in the vapor phase (Bohn & Bohn, 1971; Mastryukov *et al.*, 1982). The title compound has been known for several years (Zakharkin, Kalinin & Podvisotskaya, 1970). It may be synthesized from *para*-carborane, following the route of Gratfsein & Dvorak (1963). We are currently using this compound as a monomer for the synthesis of liquid crystalline polyesters with high thermal stability. The presumptive expectation that, as largely reported for dicarboxylic acids (Leiserowitz, 1976), the title compound (I) might pack forming extended rows through hydrogen bonds between carboxylic groups and, consequently, might have a non-disordered crystal phase, prompted us to study its crystal and molecular structure by single-crystal X-ray diffractometry. Suitable single crystals (m.p. 629–631 K) were obtained by evaporation from methanol/water solutions.



(I)

The fivefold symmetry of the carborane cage is slightly distorted; this is mainly due to a spread of the basal B—B distances, which vary from a maximum of 1.795 (2) Å, for B1—B5, to a minimum of 1.771 (2) Å, for B1—B2, with a mean value of 1.784 (5) Å [*c.f.* 1.792 (7) Å found for *para*-carborane by electron diffraction measurements in the vapor phase (Bohn & Bohn, 1971)]. The longitudinal B—B distances vary from a maximum of 1.761 (2) Å, for B3—B5′, to a minimum of 1.753 (2) Å, for B1—B4′, with a mean value of 1.758 (1) Å [*c.f.* 1.772 (13) Å for *para*-carborane]. The finding that basal B—B distances are longer than longitudinal ones is very significant in the present study and is most likely a real effect, having been observed in several structures containing the carborane cage (Bohn & Bohn, 1971; Kirillova, Klimova, Struchkov & Stanko, 1976). The C—C bond length, C1—C2 = 1.515 (1) Å, is close to that observed for an sp^3-C atom bonded to a carbonyl group (Kennard, 1968). The mean value of the B—H distance, 1.09 Å, is in good agreement with that reported in a previous X-ray study of a similar compound (Kirillova, Klimova, Struchkov & Stanko, 1976).

The pattern of the bond angles between B and C atoms is also in good agreement with values reported by Kirillova, Klimova, Struchkov & Stanko (1976). In fact, bond angles at the B atoms lie in the ranges 58.24 (6)–61.31 (7)° and 107.79 (8)–108.15 (8)°, while those at the C atoms are somewhat enlarged, being in the ranges 62.37 (7)–63.36 (7)° and 115.00 (8)–115.43 (8)°. This effect is consistent with a shrinking of the ideal icosahedral geometry of the cage along the C1···C1′ diameter, due to the C—B bond lengths being shorter than the B—B ones. Accordingly, the C1···C1′ diameter is 3.065 (2) Å, while the diameters of the cage involving *para*-B atoms are in the range 3.373 (3)–3.388 (3) Å. The approximate volume of the carborane cage, assuming icosahedral symmetry,

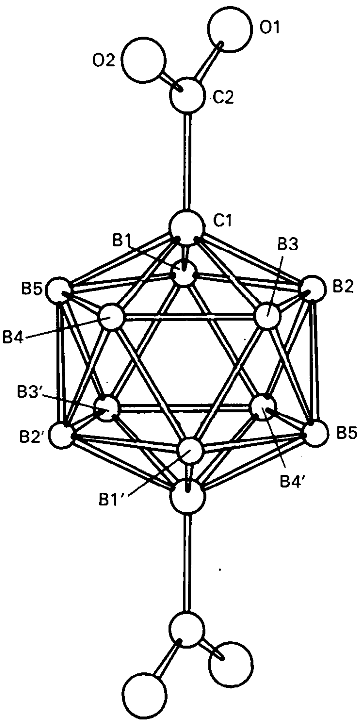


Fig. 1. Molecular drawing of the title compound showing the labelling of the non-H atoms. H atoms are omitted for clarity.

is 11.7 Å^3. With regard to the B—B—H angles, these may be grouped in two classes. In fact, the angles between B—H and basal B—B bonds (*e.g.* B2—B1—H1) are near 120°, while those between B—H and longitudinal B—B bonds (*e.g.* B3′—B1—H1) are near 126°. Bond angles of the type C—B—H are also close to 120°.

The orientation of the carboxy group with respect to the carborane cage is determined by the torsion angles O1—C2—C1—B1 = −27.7 (2) and O2—C2—C1—B4 = 7.9 (2)°. The O1—C2 bond is thus staggered with respect to C1—B1 and C1—B2, while the O2—C2 bond is almost eclipsed by the C1—B4 bond.

Crystal packing is shown in Fig. 2. Molecules are bonded along extended and strictly linear rows through hydrogen bonds between carboxylic groups. The linear symmetry of the rows, which are parallel to the $-\mathbf{a}+\mathbf{b}-\mathbf{c}$ axis, is *ti* (Corradini, 1968), *i.e.* molecules are repeated along the rows only by inversion centres. The distance between the O atoms involved in the hydrogen bond, O1···O2^{i}, is 2.639 Å [symmetry code: (i) $-x$, $-y+1$, $-z$]. The cyclic hydrogen-bonded dimer (C2, O1, O2, C2^{i}, O1^{i}, O2^{i}) is planar to within 0.01 Å. Lattice translations along **a** generate layers of hydrogen-bonded rows, which are piled up along $\mathbf{b}+\mathbf{c}$. Adjacent layers are shifted to $(\mathbf{b}-\mathbf{c})/2$. The lateral packing of the hydrogen-bonded rows includes O···H—B contacts, the shortest being O1···B2^{ii} = 3.656 (3) Å [symmetry code: (ii) $-x+1$, $-y+1$, $-z+1$].

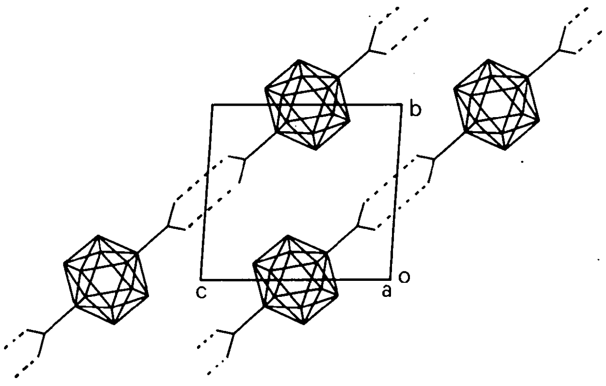


Fig. 2. Crystal packing viewed down (100). H atoms are omitted for clarity.

Experimental

Crystal data

$C_4H_{12}B_{10}O_4$
$M_r = 232.25$
Triclinic
$P\bar{1}$
$a = 6.706$ (1) Å
$b = 7.159$ (1) Å
$c = 7.216$ (1) Å
$\alpha = 100.64$ (1)°
$\beta = 105.40$ (1)°
$\gamma = 62.66$ (1)°
$V = 296$ (2) Å^3
$Z = 1$

$D_x = 1.303$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 24 reflections
$\theta = 14.19$-24.15°
$\mu = 0.643$ mm^{-1}
$T = 293$ K
Prism
0.53 × 0.34 × 0.20 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: none
1221 measured reflections
1221 independent reflections
1066 observed reflections [$I > 3\sigma(I)$]

$\theta_{max} = 76.86$°
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 9$
2 standard reflections
frequency: 60 min
intensity variation: <1.5%

Refinement

Refinement on F
$R = 0.046$
$wR = 0.060$
$S = 2.856$
1066 reflections
103 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.182$ e Å^{-3}
$\Delta\rho_{min} = -0.204$ e Å^{-3}
Extinction correction: Stout & Jensen (1989)
Extinction coefficient: 1.9 (2) × 10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
O1	0.2393 (2)	0.4422 (2)	0.1670 (2)	0.0663 (4)
O2	0.0070 (2)	0.2891 (2)	0.1023 (2)	0.0860 (5)
C1	0.3402 (2)	0.1541 (2)	0.3451 (2)	0.0370 (4)
C2	0.1858 (3)	0.3089 (2)	0.1932 (2)	0.0404 (5)
B1	0.6253 (3)	0.0983 (3)	0.3941 (3)	0.0435 (5)
B2	0.4480 (3)	0.2554 (3)	0.5596 (3)	0.0419 (5)
B3	0.2349 (3)	0.1632 (3)	0.5394 (3)	0.0429 (5)
B4	0.2813 (3)	−0.0511 (3)	0.3608 (3)	0.0434 (5)
B5	0.5225 (3)	−0.0924 (3)	0.2703 (3)	0.0433 (5)

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

O1—C2	1.221 (1)	B1—B5	1.795 (2)
O2—C2	1.262 (1)	B1—B3′	1.759 (2)
C2—C1	1.515 (1)	B1—B4′	1.753 (2)
C1—B1	1.712 (2)	B2—B3	1.794 (2)
C1—B2	1.708 (2)	B2—B4′	1.756 (2)
C1—B3	1.709 (2)	B2—B5′	1.760 (2)
C1—B4	1.716 (2)	B3—B4	1.777 (2)
C1—B5	1.708 (2)	B3—B5′	1.761 (2)
B1—B2	1.771 (2)	B4—B5	1.784 (2)
O1—C2—O2	124.7 (1)	C1—B2—B5′	103.99 (8)
O1—C2—C1	119.34 (9)	B1—B2—B3	108.10 (8)
O2—C2—C1	115.92 (9)	B1—B2—B4′	59.61 (7)
C2—C1—B1	116.22 (8)	B3—B2—B5′	59.40 (7)
C2—C1—B2	116.43 (8)	B4′—B2—B5′	60.98 (7)
C2—C1—B3	118.09 (8)	C1—B3—B1′	104.33 (8)
C2—C1—B4	118.77 (8)	C1—B3—B2	58.30 (6)
C2—C1—B5	117.83 (8)	C1—B3—B4	58.96 (6)
B1—C1—B2	62.37 (7)	C1—B3—B5′	103.92 (8)
B1—C1—B3	115.09 (8)	B1′—B3—B4	59.45 (7)
B1—C1—B4	115.43 (8)	B1′—B3—B5′	61.31 (7)
B1—C1—B5	63.31 (7)	B2—B3—B4	108.15 (8)
B2—C1—B3	63.36 (7)	B2—B3—B5′	59.33 (7)
B2—C1—B4	115.24 (8)	C1—B4—B1′	104.25 (8)
B2—C1—C5	115.00 (8)	C1—B4—B2′	104.01 (8)
B3—C1—B4	62.50 (7)	C1—B4—B3	58.54 (6)
B3—C1—B5	114.71 (7)	C1—B4—B5	58.38 (6)
B4—C1—B5	62.80 (7)	B1′—B4—B2′	60.62 (7)
C1—B1—B2	58.70 (7)	B1′—B4—B3	59.77 (7)
C1—B1—B3′	103.85 (8)	B2′—B4—B5	59.62 (7)
C1—B1—B4′	104.31 (8)	B3—B4—B5	107.80 (8)
C1—B1—B5	58.24 (6)	C1—B5—B1	58.45 (7)
B2—B1—B4′	59.76 (7)	C1—B5—B2′	104.18 (8)
B2—B1—B5	107.79 (8)	C1—B5—B3′	103.92 (8)
B3′—B1—B5	59.40 (7)	C1—B5—B4	58.83 (6)
B4′—B1—B3′	60.78 (7)	B1—B5—B3′	59.28 (7)
C1—B2—B1	58.92 (7)	B1—B5—B4	108.15 (9)
C1—B2—B3	58.34 (6)	B2′—B5—B3′	61.27 (7)
C1—B2—B4′	104.36 (8)	B2′—B5—B4	59.40 (7)

For the H atom of the carboxy group, two sites were found by difference Fourier synthesis, bonded to O2 and O1 (a disorder in the orientation of the carboxy group is present). The sites were given occupancies of 0.7 and 0.3, respectively, and refined using a riding model with $U_{iso}(H) = U_{eq}(O)$. Refinement was by full-matrix least squares. Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP/PDP* (Enraf-Nonius, 1985). All calculations were run on a MicroVAXII computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving H atoms, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71774 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1058]

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N-[2-(7-Methoxy-1-naphthyl)ethyl]-acetamide, a Potent Melatonin Analog

BERNARD TINANT AND JEAN-PAUL DECLERCQ

Université Catholique de Louvain,
Laboratoire de Chimie Physique et de
Cristallographie, 1 Place Louis Pasteur,
B 1348 Louvain-la-Neuve, Belgium

JACQUES H. POUPAERT

Unité de Chimie Pharmaceutique, Ecole de Pharmacie,
Université Catholique de Louvain, Avenue E. Mounier
73 (UCL 7340), B 1020 Bruxelles, Belgium

SAID YOUS AND DANIEL LESIEUR

Institut de Chimie Pharmaceutique, Université
de Lille II, Rue du Professeur Laguesse 3 BP 83,
F 59006 Lille CEDEX, France

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Abstract

The four crystallographically independent molecules present in the unit cell of *N*-[2-(7-methoxy-1-naphthyl)-ethyl]acetamide, $C_{15}H_{17}NO_2$, are very similar; the naphthalene ring is planar, the methoxy substituent is staggered

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