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Synthesis and characterization of a new dicage *ortho*-carborane with a supramolecular structure directed by intermolecular C-$H_{carborane}$···O bonds

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Abstract

Reaction between $[HC{\equiv}CCH_2SCH(CO_2CH_3)]_2$ (**1**) and the *N*,*N*-dimethylaniline adduct of decaborane(14), $[\{C_6H_5(CH_3)_2N\}_2B_{10}H_{12}]$, in refluxing toluene, affords *meso*-2,3-bis-(1,2-dicarba-*closo*-dodecaboran-1-yl-methylenethio)-dimethylsuccinate, $[C_2B_{10}H_{11}CH_2SCH(CO_2CH_3)]_2$ (**2**). The species was characterized by spectroscopic methods and a single crystal X-ray diffraction study. The crystal structure of **2** reveals intermolecular hydrogen bonding involving the C–H unit of the carborane and the C=O group of the ester function, leading to a supramolecular assembly: one-dimensional ribbons packed in zigzag fashion on the *bc* plane of the unit cell. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carboranes; Hydrogen bonding; Supramolecular; Crystal engineering

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1. Introduction

Polyhedral borane chemistry has developed substantially since its beginnings in the 1960s. Contributing to this area was the discovery of the *closo*-borane anions [1] and the icosahedral carboranes [2]. The latter were prepared by the reaction of decaborane(14) adducts, $B_{10}H_{12}L_2$, with acetylenic compounds. Such reactions have been used extensively to prepare high boron content species for applications in BNCT, carborane-based polymeric materials, macromolecules and electronic materials [3]. The reaction between a decaborane(12) adduct and a molecule containing more than one acetylenic moiety is clearly a potential synthetic route to the preparation of new species with interesting applications [4]. Although applications of icosahedral carboranes have expanded, identification of supramolecular assemblies of polyhedral boron containing compounds through weak intermolecular interactions such as van der Waals forces or hydrogen bonding is quite limited. Linked cyclic arrays of C_2B_{10} cages function as 'anti-crown' ethers [5]; others, so-called 'carboracyles' [6], are potential hosts for guest–host chemistry. Carboranes or their metalladerivatives function as guests in guest–host complexes with cyclodextrins [7,8] and also are complexed by crown ethers and related molecules in systems in which the carboranyl C–H groups form H-bonds with electron donors of the host molecule [9,10]. These latter interactions portend well for the involvement of carboranes in supramolecular chemistry and this is emphasized by the observation that hexamethyl phosphoramide (hmpa), forms three different C–H···O hydrogren-bonded structures involving the carborane cage and hmpa [11]. In our contribution to this area, herein we give an account of attempts to incorporate several cages into a complex organic substrate and describe the synthesis and characterization of a new dicage *o*-carborane, $[o\text{-}C_2B_{10}H_{11}CH_2SCHCO_2CH_3]_2$, that exhibits supramolecular organized structure directed by intermolecular C–$H_{carborane}$···O hydrogen bonds involving functional groups connected to the carborane cage [12].

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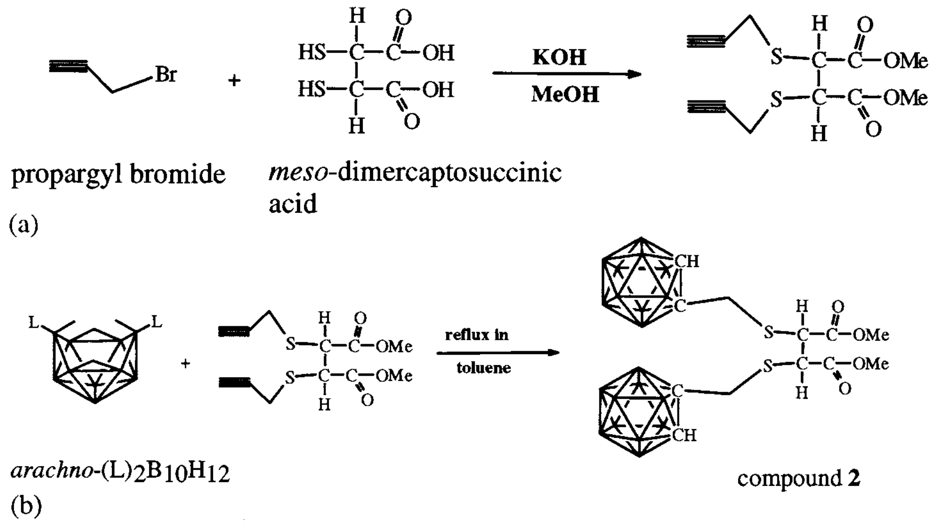
2. Results and discussion

The dialkyne starting material, $[HC{\equiv}CCH_2SCH(CO_2CH_3)]_2$ (compound **1**), is obtained from the reaction of propargyl bromide with *meso*-dimercaptosuccinic acid in KOH/MeOH. The compound is characterized by IR and NMR spectroscopies, and elemental analysis. The synthetic route and the proposed structure of **1** are illustrated in Scheme 1(a). The ^{1}H-NMR spectrum consists of four resonances of relative intensity 1:3:2:1. The peak at the highest frequency is a singlet that corresponds to the proton of the chiral carbon, $-SCHCO_2CH_3$; the resonance of the acetylenic proton occurs at + 2.31 ppm, showing a triplet pattern arising from the four-bond coupling with the aliphatic protons, $-CH_2S-$. The ^{13}C-NMR spectrum of **1** shows the expected six resonances, assigned to the proposed molecular structure by means of the attached proton test, and by comparison with the *o*-carborane (see below) and published data.

The substrate **1** contains four potential sites for incorporation of polyhedral borane cages. The two acetylenic moieties should afford carboranes on reaction with $B_{10}H_{14}$ in the presence of base and the two thio-functionalities can potentially coordinate to a $B_{10}H_{14}$ unit. Thus, we first investigated the reaction between **1** and $B_{10}H_{14}$, and noted the formation of relatively low yields of a substance that we later identified as **2** (see below). Apparently decaborane(12) adducts with the S function in **1** were interacting with the acetylenic moiety, forming **2**, but the steric requirements of the acetylenic species **1** precluded good yields. Thus, we decided to use a preformed decaborane(12) adduct, $B_{10}H_{12}L_2$. The reaction of the *N*,*N*-dimethylaniline adduct of decaborane(12), $[\{C_6H_5(CH_3)_2N\}_2B_{10}H_{12}]$, with the acetylenic compound, **1**, at reflux temperature in toluene, results in the formation of the new *meso*-2,3-bis-(1,2-dicarba-*closo*-dodecaboran-1-ylmethylenethio)dimethylsuccinate, $[C_2B_{10}H_{11}CH_2SCH(CO_2CH_3)]_2$ (**2**), crystallized from $MeOH/CH_2Cl_2$/pentane as an air-stable white crystalline solid (Scheme 1(b)). **2** is characterized by IR and NMR spectroscopies, mass spectrometry, as well as single crystal X-ray diffraction analysis.

2.1. Crystallographic results for $[C_2B_{10}H_{11}CH_2SCH(CO_2CH_3)]_2$ (2)

Crystals were obtained from pentane/dichloro-methane. All measurements were made on a Siemens CCD area detector single crystal X-ray diffractometer using ω scans and the double pass method. Data reduction and structure solutions were carried out using the SAINT and SHELXTL software packages, respectively. Least square refinements were achieved using SHELXL-97. Absorption correction was applied to the data using equivalent reflections (SADABS). **2**, $C_{12}H_{34}B_{20}O_4S_2$, $M = 522.71$, monoclinic space group $P2_1/n$, $a = 7.3736(1)$, $b = 20.0598(3)$, $c = 9.8051(1)$ Å, $\alpha = \gamma = 90°$, $\beta = 99.108(1)°$, $U = 1432.02(3)$ Å^3, $D_c = 1.212$ mg m^{-3}, $Z = 2$, $\mu(\text{Mo–K}_\alpha) = 0.207$ mm^{-1}, $F(000) = 540$, $T = 293(2)$ K. A total of 10 929 reflections were collected, 2805 ($R_{int} = 0.0695$) independent reflections, to $2\theta_{max} = 55.0°$. The final $\omega R(F^2)$ for all unique reflections was 0.1511 with a conventional $R(F)$ of 0.0649 [for 2792 reflections with $I > 2\sigma(I)$] for 221 parameters. The molecule contains a crystallographic center of symmetry relating to the two halves of the molecule. One of the carbons [C(4)] shows a positional disorder, which was resolved. All H atoms on the cages were located and refined freely. The other H atoms were treated using appropriate riding models. Selected interatomic distances and angles are given in Table 1.



Scheme 1. (a) Synthesis of the dialkyne starting material (**1**). (b) Synthesis of the dicage *o*-carborane (**2**).

Table 1
Selected interatomic distances (Å) and angles (°) for compound **2**

Distances			
C(1)–C(2)	1.629(5)	B(3)–B(4)	1.720(7)
C(1)–C(3)	1.529(5)	B(3)–B(8)	1.708(8)
C(3)–S(1)	1.780(4)	B(3)–B(7)	1.752(7)
S(1)–C(4)	1.988(14)	B(4)–B(5)	1.738(8)
C(4)–C(5)	1.553(9)	B(6)–B(10)	1.727(10)
C(5)–O(1)	1.175(5)	B(8)–B(12)	1.726(8)
C(5)–O(2)	1.302(5)	B(9)–B(10)	1.760(11)
O(2)–C(6)	1.420(5)	B(11)–B(12)	1.728(10)
Angles			
C(1)–B(3)–C(2)	58.0(3)	C(2)–C(1)–C(3)	121.4(3)
C(1)–B(4)–B(3)	60.2(3)	C(1)–C(3)–S(1)	116.9(3)
C(2)–B(3)–B(7)	59.2(3)	C(3)–S(1)–C(4)	91.9(5)
C(1)–B(6)–B(10)	104.2(4)	S(1)–C(4)–C(5)	108.7(5)
B(11)–B(12)–B(9)	109.0(4)	O(1)–C(5)–C(4)	107.5(6)
B(10)–B(12)–B(9)	60.5(4)	O(1)–C(5)–O(2)	125.8(4)
B(6)–B(10)–B(12)	108.5(5)	C(5)–O(2)–C(6)	117.1(3)

Compound **2** has the molecular structure depicted in Fig. 1, which can be described as two *o*-carborane clusters linked through a bis(methylenethio)dimethylsuccinate, $\{CH_2SCH(CO_2CH_3)\}_2$, fragment. In the solid state, viewed along the bond between the two chiral carbons, the molecule adopts a staggered conformation of C_i point symmetry; however, the eclipsed conformation has a plane of symmetry across the same bond, and **2** must, therefore, be described as the achiral *meso*-diastereosomer. The interatomic distances and angles are within the normal ranges found in other monosubstituted *o*-carboranes; thus, the distance between the cluster carbon atoms, C(1)–C(2) in **2** is 1.629(5) Å, comparable to the values of 1.637(4) and 1.620(4) Å found for the related species 1-$C_6H_4(CO)_2NCH_2CH_2CH_2$-1,2-$C_2B_{10}H_{11}$ and 1-$(C_6H_5)_2$-C=NCH_2-1,2-$C_2B_{10}H_{11}$ [13]. The boron–boron distances range from the longest B(9)–B(10) value of 1.760(11) to the B(3)–B(8) shortest of 1.708(8); this last value is significantly shorter than the lengths normally found in this kind of cluster. The bond between the polyhedral carbon atom, C(1), and the exopolyhedral carbon C(3) is found to be 1.529(5) Å, close to the values found for related bonds in the species described in Ref. [13]. The disymmetric carbon atoms of the dimethylsuccinate fragment show a positional disorder with respect to the inversion center of the staggered conformation of **2**; this circumstance leads to a short interatomic length between them, when compared to the corresponding distances found on the D,L-2,3-bis(phenylthio)- and *meso*-2,3-bis-(methylthio)-dimethylsuccinate [14]. This disorder may also be the cause of the short B(3)–B(8) interatomic distance.

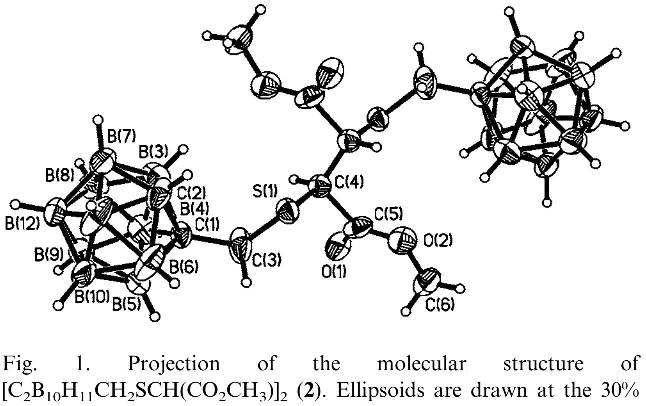


Fig. 1. Projection of the molecular structure of $[C_2B_{10}H_{11}CH_2SCH(CO_2CH_3)]_2$ (**2**). Ellipsoids are drawn at the 30% probability level.

The crystal structure of **2** shows an intermolecular interaction through hydrogen bonding, involving the C–H unit of the carborane, as proton donor, and the C=O group of the ester function as acceptor; the $C–H_{carborane}\cdots O_{ester}$ distance at 3.338(5) Å is toward the upper end of the range reported for the *o*- *m*- and *p*-dicarbadodecaborane adducts with hmpa [11], and for the recently reported system [9,12-bis-(4-acetophenyl)-1,2-dicarbadodecaborane(12)] [12] for which H-bonding is also proposed. These crystal lattice interactions in **2** lead to the formation of one-dimensional tapes along the *a* axis (Fig. 2); these ribbons pack in a zigzag fashion along on the *bc* plane (Fig. 3). The individual molecular blocks within the infinite columns use the two acidic C–H groups of the carborane cages and the two carboxylic units of the ester functions to form four equivalent hydrogen bonds with two other molecules; the detail of the complementarity between the proton donors and the proton acceptors of this system can be seen in Fig. 2.

The NMR data for compound **2** conform to the molecular structure described above. The ^{11}B-NMR spectrum consists of five resonances of relative intensity 1:1:2:2:4, ranging from −1.9 to −12.4 ppm. In the ^1H-NMR spectrum, the C–H unit of the carborane cage gives rise to a broad singlet at +3.96 ppm; the resonances of the hydrogen atoms directly bound to boron atoms appear in the region from +2.30 to +2.19 ppm. Interestingly, the $-SCH_2-$ group affords a singlet, when the spectrum is run in $CDCl_3$; however, in CD_2Cl_2 two close signals signals are observed. As the temperature is decreased, the proton signal of the carborane C–H group shifts significantly to higher frequencies [δ (^1H) (CH_{carb}) +4.24 ppm at 183 K; +4.07 ppm at 300 K in CD_2Cl_2]. The solid state IR spectrum of **2** exhibits ν_{CH} at 3060 cm^{-1}, representing a shift to lower wavenumbers from the value found for the *o*-carborane, 1,2-$C_2B_{10}H_{12}$ (3077 cm^{-1}) [15]. These shifts are consistent with the involvement of the $C–H_{carborane}$ group in hydrogen bonds. Thus the NMR and IR spectroscopic data conform to the X-ray structure, leading to the conclusion that the CH units of the dicage carborane, **2**, are involved in hydrogen bonding. The ^{13}C-NMR spec-

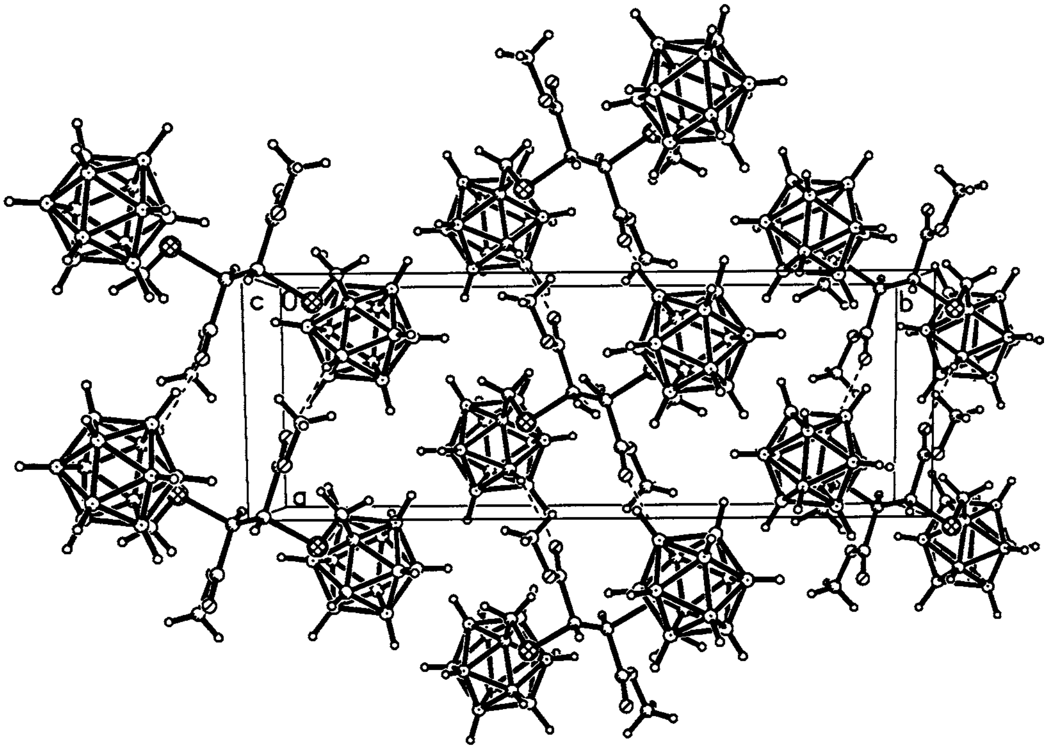


Fig. 2. View of the packing diagram for **2** along the *c* axis, illustrating the formation of infinite tapes via intermolecular hydrogen bonds: the tapes grow in the direction of *a*.

trum of **2** consists of six resonances, in agreement with the molecular structure. The hydrogen atoms of **2** were related with the directly bound carbon atoms by the means of [^{1}H-^{13}C]-HETCOR spectroscopy.

In conclusion, the formation and characterization of a new dicage *o*-carborane and of its dialkyne precursor have been described. In the new dicage species, two *o*-carborane clusters are linked through an organic chain containing ester groups and sulfur atoms. The molecule possesses two C–H groups and two C=O units that are involved in C–H···O hydrogen bonds, giving rise to a supramolecular structure of infinite columns. The individual molecules adopt a staggered configuration in the solid state, which allows intermolecular recognition and maximization of hydrogen bonds. This work demonstrates that the design of species containing C–H groups of carboranes and protons acceptors such as a carboxylic unit can lead to supramolecular assemblies. It is apparent that weak C–H$_{\text{carborane}}$···X hydrogen bonds can play an important role in the engineering of new solids.

3. Experimental

Reactions were carried out using a vacuum line, Schlenk tubes and an inert atmosphere box, employing standard methods [16]. Thin layer chromatography (TLC) of the products was performed in air using 20 × 20 cm glass plates coated with 0.1 cm of silica gel (Aldrich standard grade with gypsum binder and fluorescent indicator). Solvents used were reagent grade and were dried before use. $B_{10}H_{14}$ was obtained from laboratory stock and sublimed before use. NMR spectroscopy was carried out on a Bruker ARX 500 spectrometer at 500.1 MHz for proton, 160.5 MHz for boron-11, and at 202.5 MHz for phosphorus-31. Chemical shifts are reported in ppm for $CDCl_3$ solutions, unless otherwise stated, to low field (high frequency) of $Et_2O{\cdot}BF_3$ for ^{11}B, of $SiMe_4$ for ^{1}H and of 85% H_3PO_4 for ^{31}P. Mass spectra were recorded on a VG ZAB-HF using FAB. IR spectra were measured on a Perkin-Elmer Series 1600 FT-IR using KBr pellets. Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA.

3.1. Synthesis of [$HC{\equiv}CCH_2SCH(CO_2CH_3)]_2$ (1)

1 was obtained from Dr Wesley Harris. It was prepared by adding *meso*-dimercaptosuccinic acid to a suspension of KOH in methanol in a round-bottom flask. This mixture was stirred under nitrogen until the potassium hydroxide dissolved; then, propargyl bromide was added, and the resulting solution heated to the reflux temperature under a nitrogen atmosphere. A yellow solution was obtained and it was filtered and the filtrate evaporated to dryness. The pale yellow residue was crystallized from CH_2Cl_2: pentane, giving rise to a pale yellow crystalline product in quantitative yield. IR: $\nu_{CH(alkyne)}$ 3280 cm^{-1}, $\nu_{CH(aliphatic)}$ 2944 cm^{-1}, $\nu_{C=O}$(ester) 1733 cm^{-1}, ν_{C-O}(ester) 1299 cm^{-1}. ^{1}H-NMR (CDCl$_3$, 300 MHz, 300 K) δ +3.93 (s, SC*H*CO$_2$CH$_3$); +3.79 (s, ester OC*H*$_3$); +3.43 (m, 2.7 Hz, CC*H*$_2$S); +2.31 (apparent t, 2.7 Hz, alkyne CC*H*). ^{13}C{^{1}H}-NMR (CDCl$_3$, 75.42 MHz, 300 K) δ +170.07 (carboxy *C*O$_2$CH$_3$); +79.02 (*C*CH); +72.37 (C*C*H); +52.85 (methoxy CO$_2$*C*H$_3$); +47.41 (S*C*HCO$_2$CH$_3$); +20.49 (C*C*H$_2$S). Elemental analysis: Calc.: C, 50.33, H, 4.93; Found: C, 50.11, H, 4.93.

3.2. Synthesis of [$C_2B_{10}H_{11}CH_2SCH(CO_2CH_3)]_2$ (**2**)

A 50 ml two-necked round-bottomed flask, fitted with a reflux condenser, nitrogen inlet, and a rubber septum, was loaded with decaborane, B$_{10}$H$_{14}$, (0.2 g, 1.6 mmol) and the acetylenic compound, [HCCCH$_2$SCH(CO$_2$CH$_3$)]$_2$, (0.15 g, 0.54 mmol); the two reactants were dissolved in 50 ml of toluene, giving rise to a pale yellow solution. The vessel was evacuated and filled with nitrogen; then, *N*,*N*-dimethylaniline, C$_6$H$_5$N-(CH$_3$)$_2$, (0.39 g 3.2 mmol) was added via the septum into the reaction flask. The resulting bright yellow solution was stirred under nitrogen atmosphere at reflux temperature for three days. After this time, a pale yellow solution and orange precipitate were formed. The reaction mixture was filtered through silica gel and the silica gel washed with CH$_2$Cl$_2$; the solvent was evaporated and the oily-yellow residue applied to TLC plates, using CH$_2$Cl$_2$:pentane 60:40 as mobile phase. The major component of the chromatogram at R_f 0.1 was removed from the silica gel using CH$_2$Cl$_2$, giving rise, after evaporation of the solvent, to a yellow oily product. Crystallization of the oily product from MeOH/CH$_2$Cl$_2$/pentane resulted in the isolation of an air-stable white solid, which was characterized as the new *ortho*-carborane, [C$_2$B$_{10}$H$_{11}$CH$_2$SCH(CO$_2$CH$_3$)]$_2$ (67 mg, 0.13 mmol, 24%). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of pentane into a solution of the *ortho*-carborane in CH$_2$Cl$_2$. Mass spectrometry (FAB in thioglycerol matrix): envelope with a base peak at *m*/*z* 522 and cutoff at *m*/*z* 525, showing the isotopic distribution of the molecular ion [M−H]$^+$, which correlates well with the calculated profile for ^{12}C$_{12}$^{1}H$_{33}$^{11}B$_{20}$^{16}O$_4$^{32}S$_2$; IR: ν_{CH}(carbo-

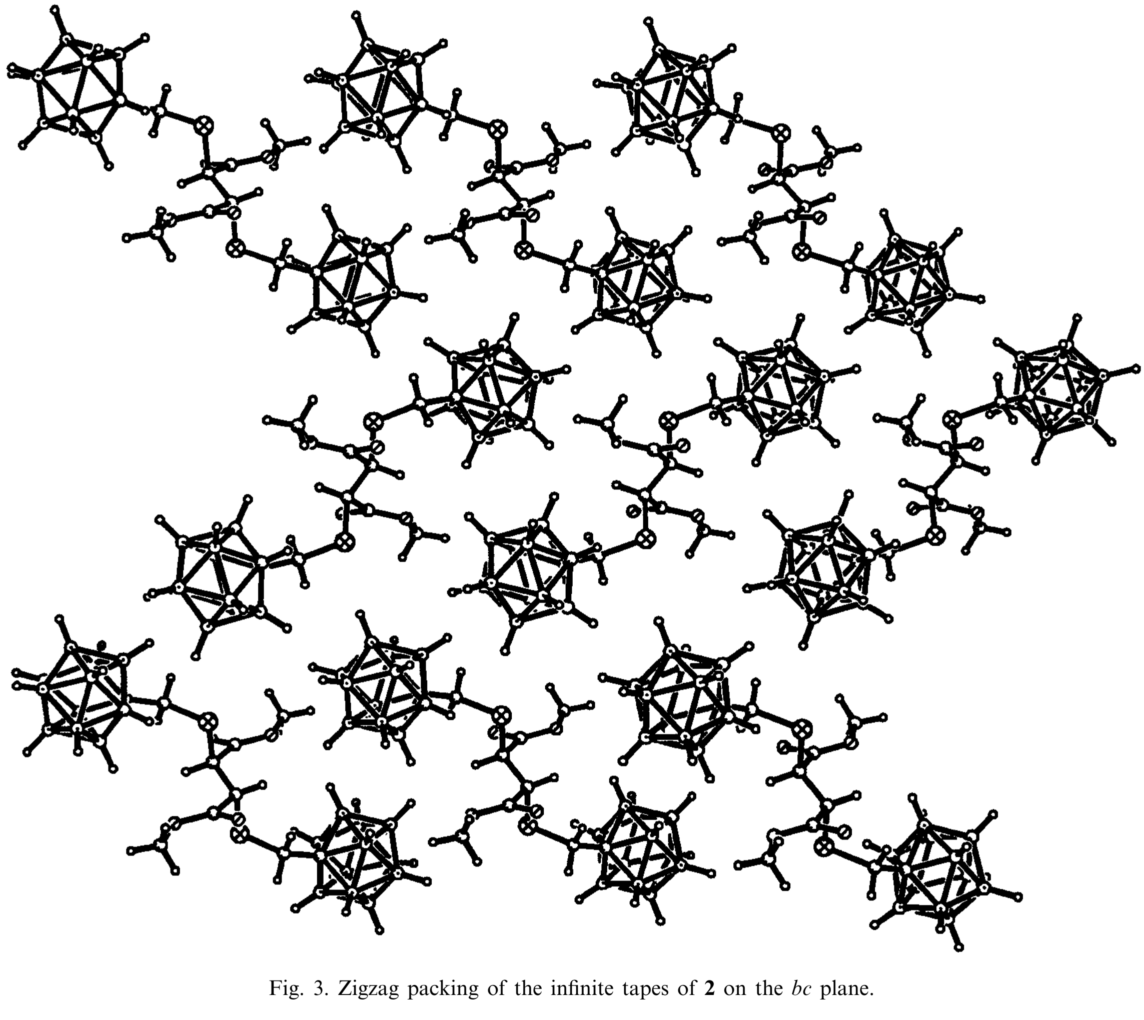


Fig. 3. Zigzag packing of the infinite tapes of **2** on the *bc* plane.

rane) 3060 cm^{-1}, ν_{BH} 2591 cm^{-1}, $\nu_{C=O}$(ester) 1728 cm^{-1}, ν_{C-O}(ester) 1299 cm^{-1}. ^{11}B-NMR ($CDCl_3$, 96.23 MHz, 300 K) ordered as relative intensity $\delta(^{11}B)$ (rel. BF_3OEt_2) [$^{1}J(^{11}B-^{1}H)$ in Hz]: 1B -1.9 [155]; 1B -4.6 [155]; 2B -8.30 [ca. 160]; 2B -10.40 [ca. 160]; 4B -12.4 [ca. 178] [overlapping of boron resonances precludes accurate determination of coupling constants]. $^{1}H\{^{11}B\}$-NMR ($CDCl_3$, 300 MHz, 300 K) δ $+3.96$ (broad s, carborane C*H*); $+3.85$ (s, ester OCH_3); $+3.58$ (s, SC*H*CO_2CH_3); $+3.54$ (s, CCH_2S); $+2.30$ to $+2.19$ (overlap of cage B*H* resonances). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 75.42 MHz, 300 K) δ $+169.53$ (carboxy *C*O_2CH_3); $+72.85$ (carborane *C*CH_2S); $+60.13$ (carborane *C*H); $+53.51$(methoxy CO_2*C*H_3); $+48.95$ (S*C*HCO_2CH_3); $+38.73$ (C*C*H_2S). Assignments made on the basis of attached proton test ^{13}C-NMR and [^{1}H-^{13}C]-HETCOR experiments.

4. Supplementary materials

Text giving experimental details and tables of bond lengths and angles, fractional coordinates, and anisotropic thermal parameters for the structure of $[C_2B_{10}H_{11}CH_2SCH(CO_2CH_3)]_2$ (**2**) are available from the authors and have been deposited with the Cambridge Crystallographic Data Centre (CCDC-116777). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) E.L. Muetterties, W.H. Knoth, Chem. Eng. News, May 9 (1966) 88. (b) E.L. Muetterties, W.H. Knoth, Polyhedral Boranes, Marcel Dekker, New York, 1968.

[2] (a) T.J. Heying, J.W. Ager, S.L. Clark, D.J. Mangold, H.L. Goldstein, M. Hillman, R.J. Polak, J.W. Szymanski, Inorg. Chem. 2 (1963) 1089. (b) M.M. Fein, J. Bobinski, N. Mayes, N. Schwartz, M.S. Cohen, Inorg. Chem. 2 (1963) 1111. (c) M.M. Fein, J.E. Paustian, J. Bobinski, B.M. Lichstein, N. Mayes, N. Schwartz, M.S. Cohen, Inorg. Chem. 2 (1963) 1115.

[3] For examples see: (a) M.F. Hawthorne, in: W. Siebert (Ed.), Advances in Boron Chemistry. Special Publication. Royal Society of Chemistry 201 (1997) 261. (b) M.F. Hawthorne, Chem. Brit. April (1996) 32. (c) P. Kaszynski, D. Lipiak, K.A. Bairamov, E. Brady, M.K. Patel, A.J. Laska, in: W. Siebert (Ed.), Advances in Boron Chemistry. Special Publication. Royal Society of Chemistry 201 (1997) 507. (d) O. Kriz, A.L. Rheingold, M. Shang, T.P. Fehlner, Inorg. Chem. 33 (1994) 3777.

[4] For example see: R. Ll. Thomas, G.M. Rosair, A.J. Welch, J. Chem. Soc. Chem. Commun. (1996) 1327.

[5] M.F. Hawthorne, Z. Zheng, Acc. Chem. Res. 30 (1997) 267.

[6] W. Jiang, I.T. Chizhevsky, M.M. Mortimer, W. Chen, C.B. Knobler, S.E. Johnson, F.A. Gomez, M.F. Hawthorne, Inorg. Chem. 35 (1996) 3056.

[7] A. Harada, S. Takahashi, J. Chem. Soc. Chem. Commun. (1988) 1352.

[8] P.A. Chetati, P. Moser, G. Ribs, Organometallics 10 (1991) 2895.

[9] P.D. Godfrey, W.J. Grigsby, P.J. Nichols, C.L. Raston, J. Am. Chem. Soc. 119 (1997) 9283.

[10] R.J. Blanch, M. Williams, G.D. Fallon, M.G. Gardiner, R. Kaddour, C.L. Raston, Angew. Chem. Int. Ed. Engl. 36 (1997) 504.

[11] M.G. Davidson, T.G. Hibbert, J.A.K. Howard, A. Mackinnon, K. Wade, J. Chem. Soc. Chem. Commun. (1996) 2285.

[12] During revision of the manuscript, the following article appeared describing intermolecular hydrogen bonding in which the functional group interacting with the carborane C–H is connected to the carborane cage: G. Harakas, T. Vu, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 120 (1998) 6405.

[13] Y. Wu, P.J. Carroll, S.O. Kang, W. Quintana, Inorg. Chem. 36 (1997) 4753.

[14] A. Parfoury, B. Tinaut, J.P. Declercq, M. van Meerssche, Bull. Soc. Chim. Belg. 92 (1983) 437.

[15] H. Schroeder, T.L. Heying, J.R. Reiner, Inorg. Chem. 2 (1963) 1093.

[16] D.F. Shriver, M.A. Drezdon, The Manipulation of Air-Sensitive Compounds, John Wiley, New York, 1986.