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exo-Dithio and monothio carborane derivatives: a mechanism for their partial degradation. Molecular structure of tetramethylammonium 7,8-(3′,6′,9′-trioxaundecane-1′,11′-dithiolato-*SS*′)-7,8-dicarba-*nido*-undecaborate

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Abstract

The reaction of 1,2-dithiol-*o*-carborane, under basic conditions, with appropriate organic dihalogenated compounds results in the formation of macrocycles incorporating 7,8-dicarba-*nido*-undecaborate or 1,2-dicarba-*closo*-dodecaborane units. The synthesis of some non-cyclic dicarborane compounds containing only one sulfur per cage directly bonded to the cluster is described. On the basis of the different behaviour of the dithiolato compounds versus the monothiolato, a mechanism that explains the formation of partially degraded and non-degraded compounds is proposed. The molecular structure of tetramethylammonium 7,8-(3′,6′,9′-trioxaundecane-1′,11′-dithiolato-*SS*′)-dicarba-*nido*-undecaborate has been determined. It crystallizes in space group $P2_1/c$ with 4 formula units per cell. The cell dimensions are $a=14.058(7)$, $b=7.536(2)$, $c=22.980(9)$ Å, $\beta=99.41°$.

Introduction

One of the most peculiar characteristics of macrocycles is the existence of a cavity, which causes most of their distinctive properties. We have developped a new type of macrocycle that combines a 'soft' 7,8-dicarba-*nido*-undecaborate moiety with an external chain, usually of the $S_2(CH_2)_n$, O_2S_2 or O_3S_2 type [1–5]. These partially degraded molecules were obtained together with the corresponding non-degraded species in a process that, *a priori*, should only produce the latter. Here, some newly synthesized macrocycles of this type are presented and a mechanism that explains this unexpected partial degradation reaction is proposed. In addition, the synthesis of some carborane derivatives with only one sulfur atom directly connected to the cluster is described. Although this last type of compound is not one of the macrocycles, their bulky and rigid nature should permit the formation of spatially intricate metal complexes, favouring a selectivity comparable to that expected for macrocycles. The molecular structure of tetramethylammonium 7,8-(3′,6′,9′-trioxaundecane-1′,11′-dithiolato-*SS*′)-7,8-dicarba-*nido*-undecaborate is also reported. This compound presents a *syn* disposition of one sulfur lone pair versus the cluster's open face.

Experimental

Materials

o-Carborane and 1-methyl-1,2-dicarba-*closo*-dodecaborane were purchased from Dexil Chemical Corporation and sublimed before use. From this, 1,2-dithiol-*o*-carborane was synthesized according to the method described by Smith *et al.* [6].

All chemicals used in this work were Fluka or Aldrich analytical reagent grade and were used as supplied. Solvents were purified and dried before use. All reactions were carried out under a dinitrogen atmosphere.

Chemical analysis of C, H and N were performed with a Perkin-Elmer 240B microanalyzer in our analytical laboratory. Infrared spectra were recorded in the region 4000–400 cm^{-1}, using a Perkin-Elmer 240

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FT spectrophotometer, in KBr pellets. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400WB spectrometer.

Preparation

Synthesis of tetramethylammonium 7,8-(3′,6′,9′-trioxaundecane-1′,11′-dithiolato-SS′)-7,8-dicarba-nido-undecaborate (I)

This compound was synthesized as described elsewhere [5]. Repeated acetone/ethyl acetate recrystallizations gave colourless needles with identical analytical data (elemental analysis and IR spectrum) to the non-crystalline product.

Synthesis of caesium (II) and tetramethylammonium (III) 7,8-(3′,6′,9′-trithiaundecane-1′,11′-dithiolato-SS′)-7,8-dicarba-nido-undecaborate

1,11-Dichloro-3,6,9-trithiaundecane was synthesized following a reported procedure [7].

Under a dinitrogen atmosphere, 1.0 g (4.80 mmol) of 1,2-dithiol-1,2-dicarba-*closo*-dodecaborane and 0.384 g (9.60 mmol) of sodium hydroxide were dissolved in 50 ml of degassed absolute ethanol. Similarly, 1.339 g (4.80 mmol) of dichlorotetraethylentrisulfur were dissolved in 50 ml of dimethylformamide.

By means of a syringe pump the dichloride and the sodium 1,2-dithiolate-1,2-dicarba-*closo*-dodecaborane were added simultaneously from syringes at a rate of 4 ml/h into 250 ml of refluxing degassed absolute ethanol, contained in a round bottom flask equipped with three condensers. To avoid a fast contact of the two reacting solutions, the syringe tubes discharged into the lateral condensers. At the end of the addition, the NaCl formed was separated by filtration and the bulk of the solvent evaporated. Water and diethyl ether were added and, after separation of the two layers, caesium carbonate or tetramethylammonium chloride (in excess) was added to the aqueous solution. As a result a white precipitate was obtained with Cs^{+}, while a gelatinous solid was obtained with $(CH_3)_4N^{+}$. The latter was dissolved in acetone and precipitated with water to yield a white solid. Both were filtered, washed with hexane and dried under vacuum overnight. Yield: 1.1. g (42.8% of **II**) and 0.5 g (30.2% of **III**). *Anal.* Calc. for $C_{10}H_{26}B_9CsS_5$: C, 22.37; H, 4.88. Found: C, 22.62; H, 5.07%. Calc. for $C_{14}H_{38}B_9S_5N$: C, 35.17; H, 8.01; N, 2.93. Found: C, 34.86; H, 8.09; N, 2.92%. ^{1}H NMR (ppm) (III-Cs) (d$_6$-acetone): 2.18 (C*H*$_2$). ^{1}H NMR (ppm) (III-$(CH_3)_4N^{+}$) (d$_6$-acetone): 2.7–2.9 (C*H*$_2$); 3.44 [$N(CH_3)_4$]. ^{13}C NMR(ppm)(III)-$(CH_3)_4N^{+}$)(d$_6$-acetone): 31.3; 32.31; 32.73; 37.62 (*C*H$_2$); 55.87 [$N(CH_3)_4$]. IR (KBr pellets): ν(C–H), 2910 and 2834 cm^{-1}; ν(B–H), 2525 cm^{-1}; ν(C–H), 1415 cm^{-1}.

Synthesis of 1-methyl-2-thiol-1,2-dicarba-closo-dodecaborane (IV)

Under a dinitrogen atmosphere 1-methyl-1,2-dicarba-closo-dodecaborane (2 g, 12.6 mmol) was dissolved in thf (40 ml) and the solution cooled (0 °C). Butyllithium (12.8 mmol) was added dropwise (10 min). The mixture was kept at 0 °C for a further 30 min and then was stirred at r.t. for 12 h. After cooling to 0 °C, sulfur (0.4 g, 12.5 mmol) was added slowly (2 h) and the resulting suspension stirred (r.t.) for an additional 4 h period. The thf was evaporated and diethyl ether (40 ml) was added. The working up procedure is analogous to that described in the synthesis of 1,2-dithiol-*o*-carborane. The resulting solid was chromatographed over alumina with hexane to afford a white solid. Yield: 1.66 g (70%). *Anal.* Calc. for $C_3H_{14}B_{10}S$: C, 18.93; H, 7.41. Found: C, 19.49; H, 7.70%. ^{1}H NMR (ppm) (d-chloroform): 2.166 (C*H*$_3$); 3.616(S*H*). IR (KBr): ν(C–H), 2936 cm^{-1}; ν(B–H), 2595 cm^{-1}.

Synthesis of 1-methyl-2-methylthiolato-S-1,2-dicarba-closo-dodecaborane (V)

Compound **IV** (0.3 g, 1.58 mmol) was dissolved in 50 ml of a solution containing KOH (0.1 g, 1.7 mmol) in degassed absolute ethanol. Dimethyl sulfate (0.3 g, 2.38 mmol) was added dropwise with stirring during 2 h and the system was brought to reflux for 2 h. The solvent was eliminated by rotary evaporation and diethyl ether and aqueous KOH (1 M) were added. The layers were separated and the ethereal one dried over $MgSO_4$. The diethyl ether was evaporated to yield a product which was purified by chromatography over alumina with hexane and sublimated at 40 °C and 0.1 atm. Yield: 193 mg (60%) *Anal.* Calc. for $C_4H_{16}B_{10}S$: C, 23.51; H, 7.89. Found: C, 23.20; H, 8.10%. ^{1}H NMR(ppm)(d-chloroform): 2.132 (C*H*$_3$); 2.446 (S-C*H*$_3$). IR (KBr): ν(C–H), 2928 cm^{-1}; ν(B–H), 2588 cm^{-1}.

Synthesis of tetramethylammonium 7-methyl-8-methylthiolato-S-7,8-dicarba-nido-undecaborate (VI)

Compound **V** (0.5 g, 2.45 mmol) and KOH (0.5 g, 8.9 mmol) were dissolved in degassed absolute ethanol and refluxed for 2 h. The ethanol was eliminated and the residue was dissolved in water. Upon the addition of tetramethylammonium chloride, compound **VI** separated which was filtered and recrystallized in a EtOH–H_2O mixture to afford the pure white product. Yield: 0.64 g (98%). *Anal.* Calc.

for $C_8H_{28}B_9NS$: C, 35.90; H, 10.54; N, 5.23. Found: C, 36.48; H, 11.07; N, 5.26%. ^1H NMR(ppm)(d_6-acetone): 1.50 (CH_3); 2.11 (S-CH_3); 3.39 [$N(CH_3)_4$]. IR (KBr): ν(C–H), 2920 cm^{-1}; ν(B–H), 2526 cm^{-1}.

Synthesis of 1,4-bis(1′-methyl-2′-methylenethiolato-S-1′,2′-dicarba-closo-dodecaborane)benzene (VII)

The preparation of this compound is analogous to that reported for **V**, using α,α'-dichloro-*p*-xylene and increasing the refluxing time to 3.5 h. The product was recrystallized in hexane. Yield: 60%. *Anal.* Calc. for $C_{14}H_{34}B_{20}S_2$: C, 34.83; H, 7.10. Found: C, 34.39; H, 7.36%. ^1H NMR(ppm)(d_1-chloroform): 2.068 (CH_3); 4.044 (S-CH_2-Ar); 7.27 (Ar-H). IR (KBr): ν(Ar–H), 3031 cm^{-1}; ν(C–H), 2935 cm^{-1}; ν(B–H), 2577 cm^{-1}.

Synthesis of tetramethylammonium 1,4-bis(7′-methyl-8′-methylenethiolato-S-7′,8′-dicarba-nido-undecaborate)benzene (VIII)

The method is analogous to the preparation of **VI**, but using **VII**. Yield: 96%. *Anal.* Calc. for $C_{22}H_{58}B_{18}N_2S_2$: C, 43.36; H, 9.59; N, 4.60. Found: C, 44.00; H, 10.44; N, 4.85%. ^1H NMR(ppm)(d_1-chloroform): 1.56 (CH_3); 3.38 [$N(CH_3)_4$]; 4.0 (S-CH_2-Ar); 7.47 (Ar-H). IR (KBr): ν(Ar–H) 3030 cm^{-1}; ν(C–H), 2923, 2864 cm^{-1}; ν(B–H), 2518 cm^{-1}.

Synthesis of 1,2-bis-(1′-methyl-2′-thiolato-1′,2′-dicarba-closo-dodecaborane)ethane (IX)

Compound **IV** (0.3 g, 1.57 mmol) was dissolved in 50 ml of a solution containing KOH (0.1 g, 1.78 mmol) in degassed absolute ethanol. 1,2-Dibromoethane (0.068 ml, 0.7 mmol) was slowly added and the system was stirred for 1 h at room temperature and 2 h at reflux. After elimination of the KBr and evaporation of the solvent, diethyl ether (50 ml) and aqueous KOH (100 ml) were added. The two layers were separated and benzene (50 ml) was added to the organic phase. The mixture was evaporated at the rotary evaporator almost to dryness (about 5 ml were left) and 5 ml of diethyl ether and 5 ml of benzene were added. The mixture was fully evaporated and the solid residue was extracted with hot hexane. After elimination of the solvent the pure product was obtained. Yield: 178 mg (56%). *Anal.* Calc. for $C_8H_{30}B_{20}S_2$: C, 23.63; H, 7.44. Found: C, 23.41; H, 7.72%. ^1H NMR(ppm)(d_1-chloroform): 2.11 (CH_3); 3.17 (S-CH_2-CH_2-S). IR (KBr): ν(C–H), 2934 cm^{-1}; ν(B–H), 2578, 2563, 2552 cm^{-1}.

Synthesis of 1,3-bis(1′-methyl-2′-thiolato-1′,2′-dicarba-closo-dodecaborane)propane (X)

The preparation was done in a manner similar to that described for **IX**, using 1,3-bis(tosyloxy)propane. Yield: 55%. *Anal.* Calc. for $C_9H_{32}B_{20}S_2$: C, 25.70; H, 7.67. Found: C, 26.44; H, 7.77%. IR (KBr): ν(C–H), 2936 cm^{-1}; ν(B–H) 2593 cm^{-1}. ^1H NMR(ppm)(d_1-chloroform): 2.11 (CH_2-CH_2-CH_2); 2.17 (carborane-CH_3); 3.16 (CH_2-CH_2-CH_2). ^{13}C NMR(ppm)(d_1-chloroform): 23.47 (carborane-CH_3); 28.03 (S-CH_2CH_2-CH_2-S); 36.27 (S-CH_2-CH_2-CH_2-S); 81.42 (carborane's C-CH_3); 82.84 (carborane's C-S).

Partial degradation of 1,3-bis-(1′-methyl-2′-thiolato-1′,2′-dicarba-closo-dodecaborane)propane (XI)

Degradation of **X** was achieved by refluxing the product for 12 h in a procedure analogous to the preparation of *VI*. Yield: 90%. *Anal.* Calc. for $C_{17}H_{56}B_{18}N_2S_2$: C, 37.31; H, 10.31; N, 5.12. Found: C, 37.08; H, 10.54; N, 5.0%. IR (KBr): ν(B–H), 2520 cm^{-1}.

Synthesis of 1,2-(α,α′-dithiolato-p-xylene-SS′)-1,2-dicarba-closo-dodecaborane (XII) and potassium 7,8(α,α′-dithiolato-p-xylene-SS′)dithia-p-xylene)-7,8-dicarba-nido-undecaborate monoaquo (XIII)

In a synthesis analogous to the preparation of **III**, α,α-dichloro-*p*-xylene (0.294 g, 1.68 mmol), potassium hydroxide (0.189 g, 3.37 mmol) and 1,2-dithiol-*o*-carborane (0.35 g, 1.68 mmol) were mixed. The white precipitate (KCl and a polymer?) was filtered and discarded. The filtrate was evaporated and water and methylene chloride were added. An emulsion was formed which was destroyed upon the addition of saturated KCl/water yielding an intermediate layer. All three layers were separated. The organic one was evaporated and the solid residue chromatographed with diethyl ether over alumina to afford compound **XII**. Yield 156 mg (30%). *Anal.* Calc. for $C_{10}H_{18}B_{10}S_2$: C, 38.69; H, 5.84. Found: C, 37.75; H, 5.51%. IR (KBr): ν(B–H), 2571 cm^{-1}. From the intermediate layer a crystalline product **XIII** was obtained after 4 days at room temperature and with the vessel opened. Yield 240 mg (40%). *Anal.* Calc. for $C_{10}H_{20}B_9OKS_2$: C, 33.67; H, 5.65. Found: C, 33.19; H, 5.39%. IR (KBr): ν(O–H), 3431 cm^{-1}; ν(Ar–H), 3027 cm^{-1}; ν(C–H), 2927 cm^{-1}; ν(B–H), 2540 cm^{-1}. A very small amount of solid was obtained upon the addition of tetramethylammonium chloride to the aqueous layer. Compounds **XIII** and **XIV** were washed with hexane and dried in vacuum overnight.

Data collection and reduction

Colourless crystals of $C_{14}H_{38}B_9NO_3S_2$ were grown from an acetone/ethyl acetate recrystallization of the crude compound. Crystal data are summarized in Table 1. A prismatic crystal with dimensions (mm)

TABLE 1. Crystal data and details of data collection

Molecular formula	$B_9C_{14}H_{38}NO_3S_2$
Molecular weight	429.2
Crystal system	monoclinic
a (Å)	14.058(7)
b (Å)	7.536(2)
c (Å)	22.980(9)
β (°)	99.41(2)
Space group	$P2_1/c$
V (Å^3)	2401.77
D_c (g cm^{-3})	1.189
Z	4
Crystal dimensions (mm)	0.19×0.3×0.9
Radiation (Å)	0.70926
Absorption coefficient (cm^{-1})	2.27
2θ limits	$4<2\theta<50$
Collection range, $\pm h$, $+k$, $+l$	±16, +8, +25
No. unique reflections	4221
No. observed reflections, $I>2.5\sigma(I)$	1839
R	0.0612
R_w	0.0665

0.19×0.30×0.9 was chosen. Parameters were refined from 25 reflections in the range $10<2\theta<25$. An Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation was used. Intensity variation of one standard reflection was 1.12%. A total of 4698 reflections was collected giving 4221 unique reflections. The number of unobserved reflections was 2382 with $I<2.5\sigma$ (I).

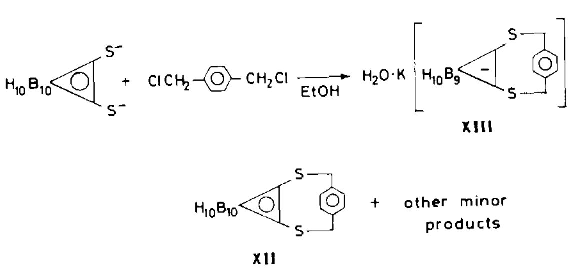
The crystal structure was determined by random phase refinement using the Ω tangent formula [8, 9]. The H atoms bound to B atoms were found in Δ Fourier maps. The remaining ones at calculated positions. All non-H atoms with the exception of the methyl C atoms of the tetramethylammonium molecule were refined anisotropically. The positional parameters of the H atoms were kept fixed and the temperature coefficients refined. Least-squares refinement using the Shelx program [10] gave $R=0.061$ and $R_w=0.066$ (weighting scheme: $w=1.1372/(\sigma^2(F)+0.0021\ F^2)$). Final $(\Delta/\sigma)_{max}$ 0.24. Max. and min. heights in final ΔF map: 0.41, -0.24 e/Å^3. Atomic scattering factors were taken from the International Tables for Crystallography [11].

Results

Monocarborane molecules

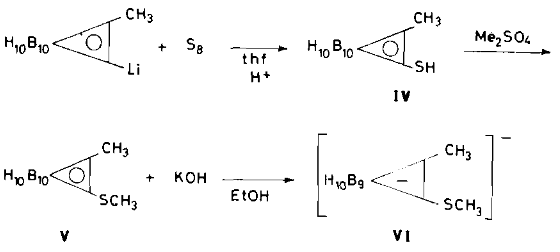
1,2- and 7,8-Dithiocarborane compounds

The reaction of $[C_2H_{10}B_{10}S_2]^{2-}$ with $Cl(CH_2CH_2S)_3CH_2CH_2Cl$ (dmf–ethanol), $ClCH_2(C_6H_4)CH_2Cl$ (ethanol) or $Cl(CH_2CH_2O)_3CH_2CH_2Cl$ (ethanol) under high dilution conditions produced macrocycles incorporating a carborane cage in the cycle. As already indicated [4, 5] with other dihalo organic compounds two types of macrocycles, one having the non-degraded carborane cage and the other having the partially degraded cage are formed and isolated in the same reaction.



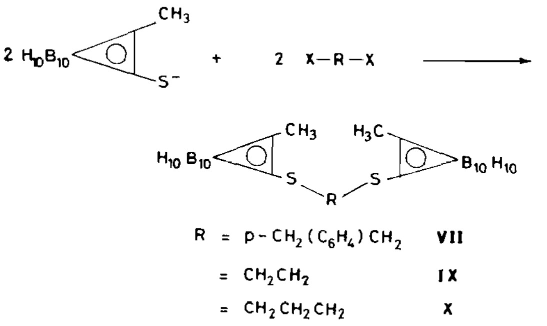
Monothiocarborane compounds

The reaction of 1-methyl-1,2-dicarba-*closo*-dodecaborane with butyllithium and sulfur in thf, followed by hydrolysis yields 1-methyl-2-thiol-1,2-dicarba-*closo*-dodecaborane (IV). This, in turn, is easily methylated to yield 1-methyl-2-methylthiolato-*S*-1,2-dicarba-*closo*-dodecaborane (V), which can be partially degraded with KOH.

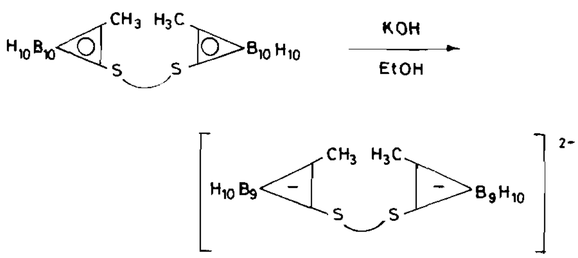


Dicarborane molecules

The reaction of 1-methyl-2-thiol-1,2-dicarba-*closo*-dodecaborane with dihalocompounds yields the dicarborane molecules indicated.



Compounds VII and X can be partially degraded with KOH to yield compounds VIII and XI, respectively. This reaction is exemplified below.



Dicarborane molecules having $(CH_3)_2Si$ bridging groups on one side and a dithioalkyl chain on the other have been unsuccessfully attempted.

It is important to notice that in the alkylation reactions of the monothiol 1-methyl-2-thiol-1,2-dicarba-*closo*-dodecaborane (IV), none or minimum amounts of the corresponding partially degraded species are obtained. In the dicarborane compounds mixed partially degraded non-degraded species have been isolated in small quantities. These mixed compounds will be the subject of future papers.

Discussion

The crystal structures of some ligands and metal complexes containing the 7,8-dicarba-*nido*-undecaborate moiety have been reported by us [2–5, 12]. Due to the observed placement of the sulfur substituents, an *anti* disposition of the sulfur lone pairs versus the cluster's open face is presumed in all cases. This led us to believe that the most stable ligand conformation would be that with an *anti* disposition of the sulfur lone pairs versus the open face. This would restrict the possibility of obtaining metal complexes with a *syn* disposition of the metal. This hypothesis prompted us to investigate the crystal structure of tetramethylammonium 7,8-(3′,6′,9′-trioxaundecane-1′,11′-dithiolato-*SS*′)-7,8-dicarba-*nido*-undecaborate. This compound was selected because it is a macrocycle with 15 members, which should be relaxed enough to allow the coexistence of several conformomers of relatively close energy, and because the molecular structure of its sodium salt was known [4]. To preclude any ligand to cation interaction and to favour a more relaxed arrangement of the *exo*-cluster-chain the $[N(CH_3)_4]$ cation was chosen. The ligand in the molecular structure of $Na[\{7,8\text{-}\mu\text{-}S(CH_2(CH_2OCH_2)_3CH_2)S\text{-}C_2B_9H_{10}\}$ [4] shows a highly symmetrical conformation as a consequence of the sodium coordination through the two sulfur and three oxygen atoms. If a tetrahedral surrounding is assumed for sulfur, the two lone pairs would adopt a clear *anti* disposition.

On the contrary, the molecular structure of $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}S(CH_2(CH_2OCH_2)_3CH_2)S\text{-}C_2B_9H_{10}\}$ is more relaxed (Fig. 1), due to the non-coordination. The most relevant feature of this molecule is the disposition of C22 which is almost coplanar (−0.1594 Å) with the plane formed by S1–C7–C8–S2*, while C12 is at a distance of 1.7035 Å comparable to that of 1.7664 Å found in $Na[\{7,8\text{-}\mu\text{-}S(CH_2(CH_2OCH_2)_3CH_2S\text{-}C_2B_9H_{10}\}$. This coplanar disposition of C22 with the plane S1–C7–C8–S2 presumes a *syn* disposition of one lone pair with regard to the open face. This is an important result since it indicates that a *syn* disposition of the electron pairs are possible, and that it can be even more stable than other allowed conformomers with an *anti* disposition, such as that observed in $Na[\{7,8\text{-}\mu\text{-}S(CH_2(CH_2OCH_2)_3CH_2)S\text{-}C_2B_9H_{10}\}$. Final atomic parameters for non-hydrogen atoms are reported in Table 2. Selected distances and angles are reported in Tables 3 and 4, respectively.

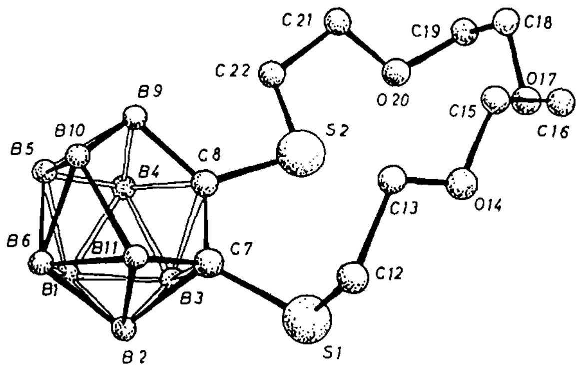


Fig. 1. Molecular structure of tetramethylammonium 7′,8′-(1,13-dithia-4,7,10-trioxatridecane)-7,8-dicarbaundecaborate.

The reaction of 1,2-dithiolato-*o*-carborane with organic dihalogenated compounds yields either larger or, at least, comparable amounts of partially degraded versus non-partially degraded species. On the contrary, the reaction of 1-methyl-2-thiolate-*o*-carborane with organic mono or dihalogenated compounds preferentially yields non-degraded species and only very small quantities of partially degraded species have been found in some cases. The main difference between both situations is the number of sulfur atoms directly connected to the carborane cluster, i.e. two and one, respectively. Next, we present a mechanism that explains this different behaviour.

From an examination of the values depicted in Table 5, the following general conclusions about the thiocarborane compounds can be reached. The non-degraded species display long C–C distances (1.84 Å av.) compared to the degraded (1.54 Å), and comparatively long with respect to *o*-carborane (1.64

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*The $-0.4498x + 0.8841y + 0.1264z = 0.2384$ plane has been used. The S1, C7, C8 and S2 distances to this plane are −0.0305, 0.0538, −0.0296 and 0.0064 Å, respectively.

TABLE 2. Final positional parameters (×10^4) for non-hydrogen atoms and equivalent temperature coefficients (Å^2) with e.s.d.s in parentheses for $B_9C_{14}H_{38}NO_3S_2$

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
S1	3873(1)	2226(2)	2577(1)	3.64
S2	1790(1)	461(3)	2348(1)	3.75
B1	3553(6)	−1281(12)	4006(4)	4.03
B2	4199(5)	451(11)	3755(4)	3.53
B3	3433(5)	−822(10)	3246(3)	3.14
B4	2407(6)	−1407(12)	3558(3)	3.68
B5	2526(6)	−389(13)	4251(4)	4.10
B6	3665(6)	814(13)	4371(3)	4.30
C7	3380(4)	1456(9)	3204(3)	2.87
C8	2380(4)	448(9)	3107(3)	2.93
B9	1794(5)	650(12)	3650(3)	3.44
B10	2554(6)	1978(14)	4192(4)	4.81
B11	3555(6)	2492(12)	3837(4)	4.09
C12	3544(5)	4554(10)	2522(3)	4.56
C13	2517(5)	4974(9)	2264(3)	4.49
O14	2313(3)	4469(7)	1660(2)	4.45
C15	1348(6)	4938(10)	1422(3)	4.66
C16	1112(6)	4314(12)	786(3)	5.37
O17	869(4)	2485(7)	731(2)	5.07
C18	−104(5)	2098(12)	787(4)	5.60
C19	−215(6)	112(12)	828(3)	5.62
O20	354(3)	−639(7)	1339(2)	4.43
C21	−45(5)	−340(11)	1868(3)	4.48
C22	713(5)	−834(11)	2383(3)	4.32
N1′	6627(4)	366(8)	9144(2)	3.77
C2′	6305(6)	1381(11)	8597(3)	5.85
C3′	7679(5)	626(14)	9328(4)	7.37
C4′	6147(6)	1003(12)	9631(3)	6.22
C5′	6451(7)	−1522(11)	9053(5)	7.97

TABLE 3. Bond lengths (Å) with e.s.d.s in parentheses for $B_9C_{14}H_{38}NO_3S_2$

C7–S1	1.795(06)	B10–B6	1.780(12)
C12–S1	1.813(08)	B11–B6	1.751(13)
C8–S2	1.805(06)	C8–C7	1.581(08)
C22–S2	1.815(07)	B11–C7	1.634(10)
B2–B1	1.741(12)	B9–C8	1.610(09)
B3–B1	1.760(11)	B10–B9	1.806(11)
B4–B1	1.766(11)	B11–B10	1.780(13)
B5–B1	1.766(11)	C13–C12	1.502(08)
B6–B1	1.784(13)	O14–C13	1.421(08)
B3–B2	1.742(11)	C15–O14	1.423(08)
B6–B2	1.730(11)	C16–C15	1.519(09)
C7–B2	1.740(10)	O17–C16	1.420(09)
B11–B2	1.811(12)	C18–O17	1.425(09)
B4–B3	1.767(11)	C19–C18	1.509(10)
C7–B3	1.721(10)	O20–C19	1.424(08)
C8–B3	1.748(10)	C21–O20	1.437(08)
B5–B4	1.750(11)	C22–C21	1.504(08)
C8–B4	1.737(10)	C2′–N1′	1.477(07)
B9–B4	1.802(12)	C3′–N1′	1.483(07)
B6–B5	1.821(12)	C4′–N1′	1.478(07)
B9–B5	1.765(11)	C5′–N1′	1.454(07)
B10–B5	1.790(14)		

TABLE 4. Selected bond angles with e.s.d.s in parentheses for $B_9C_{14}H_{38}NO_3S_2$

C12–S1–C7	103.9(3)	O17–C16–C15	113.4(7)
C22–S2–C8	102.1(3)	C18–O17–C16	114.3(6)
B2–C7–S1	115.3(4)	C19–C18–O17	108.6(6)
B3–C7–S1	110.4(4)	O20–C19–C18	113.3(7)
C8–C7–S1	119.5(4)	C21–O20–C19	113.0(6)
B11–C7–S1	122.6(5)	C22–C21–O20	107.6(6)
B3–C8–S2	114.9(4)	C21–C22–S2	108.7(5)
B4–C8–S2	122.9(4)	C3′–N1′–C2′	109.1(6)
C7–C8–S2	113.0(4)	C4′–N1′–C2′	111.2(6)
B9–C8–S2	122.4(4)	C4′–N1′–C3′	107.3(6)
C13–C12–S1	116.7(5)	C5′–N1′–C2′	111.3(7)
O14–C13–C12	110.9(6)	C5′–N1′–C3′	108.0(7)
C15–O14–C13	109.7(5)	C5′–N1′–C4′	109.8(7)
C16–C15–O14	109.8(6)		

Å). Only a longer C–C distance has been observed (2.00 Å) in the anion 1-oxo-2-phenyl-1,2-dicarbadodecaborate, although the delocalization of anionic charge into the carborane cage allows such an anion to be regarded as a *nido* shaped residue [$RCB_{10}H_{10}^-$] [16]. On the other hand the C–S distance remains practically invariable from one to the other type of compounds (1.75 Å in non-degraded, 1.78 Å in partially degraded).

The relative C–C shortening from the non-degraded to the partially degraded species is expected since a filled orbital derived from 6a$_1$ $[B_{11}H_{11}]^{4-}$ (orbital labelled as by Mingos [17]) is formed upon partial degradation.

In previous papers [1], we suggested that the overlap of the S(sp$_3$) with the aforementioned 6a$_1$ derived orbital, was the driving force that permits the unexpected partial degradation of the carborane cage. This reaction is indicated in our first reaction scheme and illustrates the formation of partially degraded and non-degraded species.

At first, there seems to be a contradiction between the above-mentioned driving force and the observed C–S distances. However, it can be well understood by considering the mechanism indicated in Fig. 2.

The formation of partially degraded and non-degraded species is thought to proceed through *nido* intermediates such as **XIV**. The key point in this mechanism is the existence of a dianion generated by deprotonation of 1,2-dithiol-*o*-carborane. Delocalization of the two anionic charges into the cage is formally equivalent to chemically reducing a *closo* cage, hence getting a *nido* species (**XIV**) [18]. The process is similar to the *closo*–*nido* conversion of 2,3-Me_2-1-Sn-2,3-$C_2B_9H_9$ [19] upon addition of thf or PPh_3, which bonds the Sn atom. In 2,3-Me_2-1-Sn-2,3-$C_2B_9H_9$, the Sn atom participates with two

TABLE 5. C–C and C–S distances in non-degraded and partially degraded compounds: 1, 3 C–C distances; 2,4 C–S distances

	Molecule				Reference
	1	2	3	4	
1	1.858	1.747			4
2			1.596	1.781	4
3	1.816	1.764			5
4			1.75		13
5			1.581	1.79	3
6			1.594	1.774	3, 2
7	1.6877				14
8			1.581	1.800	
9	1.64				15

1 = 1,2-μ-S($CH_2CH_2O)_2CH_2CH_2$S-1,2-$C_2H_{10}B_{10}$;
2 = Na[{7,8-μ-S($CH_2(CH_2OCH_2)_3CH_2$)S-7,8-$C_2B_9H_{10}$}];
3 = 1,2-μ-$SCH_2CH_2OCH_2CH_2S$-1,2-$C_2H_{10}B_{10}$;
4 = Cs[9,10,11-$(CH_3)_3$-7,8-$C_2H_9B_9$],
5 = [$C_3H_{10}N$][7,8-$(SH)_2$-7,8-$C_2H_{10}B_9$],
6 = [$C_3H_{10}N]_2$[7,7′,8,8′-S_4-(7,8-$C_2H_{10}B_9)_2$];
7 = 1,1′,2,2′-$(Si(CH_3)_2)_2$-(1,2-$C_2H_{10}B_{10})_2$;
8 = [$N(CH_3)_4$][{7,8-μ-S($CH_2(CH_2OCH_2)_3CH_2$)S-$C_2B_9H_{10}$}];
9 = 1,2-$C_2H_{12}B_{10}$.

electrons within the cluster, while the fragment thf–Sn participates with four electrons.

Once **XIV** is formed, two competitive processes are possible: the attack either of a nucleophile (e.g. ROH) activated by X^- or of an electrophile (e.g. X---X). Depending on which takes place first, intermediates **XV** or **XVI** will be formed. If **XV** is formed, further reaction with the electrophile yields the partially degraded species **XVII**. On the contrary, if the electrophile reacts faster, **XVI** will be formed. It is important to notice the loss of the dianionic charge in this step. Consequently and 'oxidative like' process takes place concomitant with the electrophilic attack yielding the non-degraded species **XVII**. A variety of A/B ratios have been obtained depending on the electrophilic reagent.

We do not have enough data to hypothesize about the factors that influence the partially degraded/non-degraded ratio, but steric factors and the relative softness/hardness of the electrophile(s) are foreseen as determining factors.

At this stage, one may wonder why the C–S distance remains approximately constant in the partially-degraded and non-degraded species. In the dianionic species, **XIV**, there is no restriction to getting S(sp^3)–B(sp^3) overlap. Molecular orbitals of b_1 symmetry can be predicted (Fig. 3(a)). A hypothetical $C2_v$ fragment has been assumed to get this orbital.

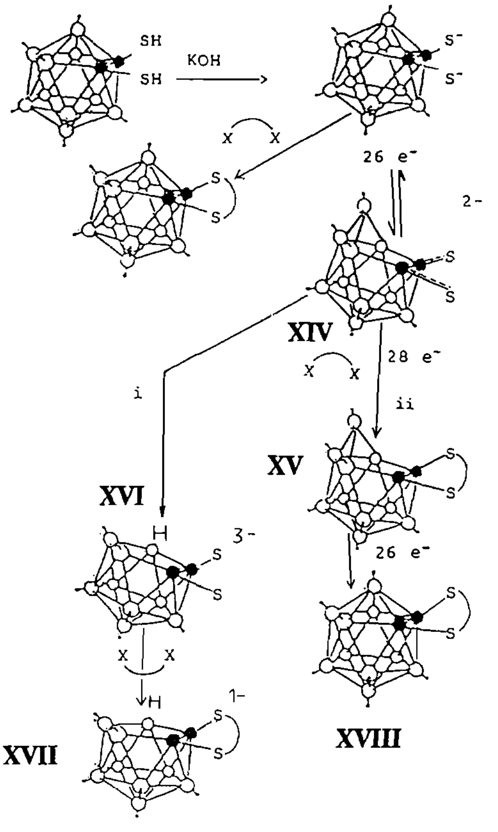
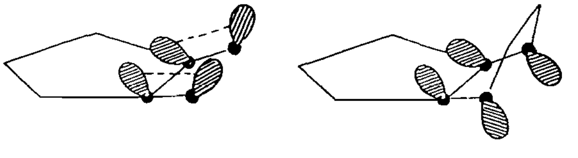


Fig. 2. Proposed mechanism for the partial degradation of 1,2-dithio-*o*-carborane derivatives during the S-alkylation reaction: (i) nucleophilic attack, (ii) electrophilic attack.



(a) (b)

Fig. 3. Diagrammatic representation of (a) the S(sp^3)–B(sp^3) overlap in XIV and (b) its impossibility once the *exo*-ring is formed.

Once the *exo*-ring is formed (Fig. 3(b)), severe sterical constraints appear which do not permit effective S(sp^3)–B(sp^3) overlap. As a consequence, similar C–S distances are expected in both partially degraded and non-degraded species.

This proposed partial degradation mechanism would also be compatible with the monothiolato derivatives. However the formation of a *nido* species similar to **XIV** is much less probable in this case, consequently lowering the formation of partially degraded molecules.

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