

STRUCTURE OF DECAHALO-*o*-CARBORANE ADDUCTS WITH Me₂SO AND Me₂NCHO. A NEW CLASS OF COMPOUNDS CAPABLE OF HYDROGEN BONDING

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SUMMARY

Decahalo-*o*-carboranes have been shown to form a hydrogen bond of type $o\text{-RCB}_{10}\text{Hal}_{10}\text{CH} \cdots \text{B}$, with a variety of basic compounds. The existence of the stable crystalline adducts (1 : 1) of decahalo-*o*-carboranes with dimethylsulfoxide and dimethylformamide is due to this bonding.

In a previous communication¹ decachloro-*o*-carborane ($o\text{-B}_{10}\text{Cl}_{10}\text{C}_2\text{H}_2$), dibromooctachloro-*o*-carborane, C-methyl- and C-ethyl-decachloro-*o*-carboranes have been shown to give 1 : 1 crystalline adducts with dimethylsulfoxide and dimethylformamide. Decahalo-*o*-carboranes are strong C-acids¹; on the other hand, the decahalo-*o*-carborane nucleus is highly electron deficient and the structure of above adducts was therefore questionable because the bonding in them could be result of salt formation or hydrogen bonding or some other interaction of donor-acceptor type. In this paper the nature of these adducts is investigated using infrared spectroscopy.

The recorded spectra of adducts and, for comparison, those of the starting

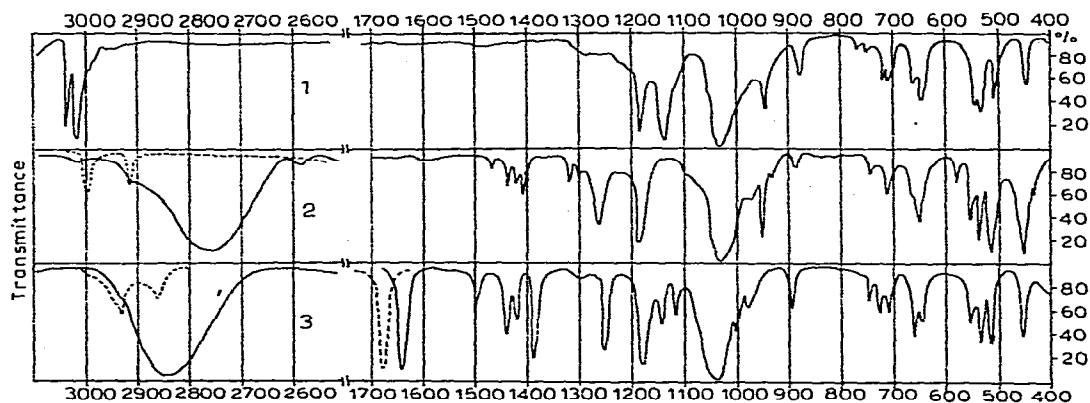


Fig. 1. IR-spectra of decachloro-*o*-carborane and its adducts with Me₂SO and Me₂NCHO (solids pelletized with KBr). 1. decachloro-*o*-carborane (I). 2. (—), adduct of I with Me₂SO; (---), Me₂SO (thin liquid film). 3. (—), adduct of I with Me₂NCHO; (---), Me₂NCHO (thin liquid film).

crystalline decahalocarboranes and of liquid Me_2SO and Me_2NCHO , are shown in Figs. 1–5. Although the spectra of the adducts contain some bands observed in the spectra of the starting compounds, they are not just the superpositions of these spectra, but principally provide new information.

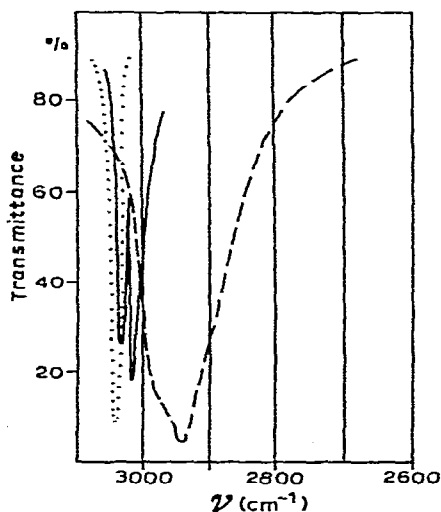


Fig. 2. IR-spectra of decachloro-*o*-carborane in the region of 2600–3100 cm^{-1} . (—), pelletized with KBr; (· · · · ·), CCl_4 soln.; (---), CH_3CN soln.

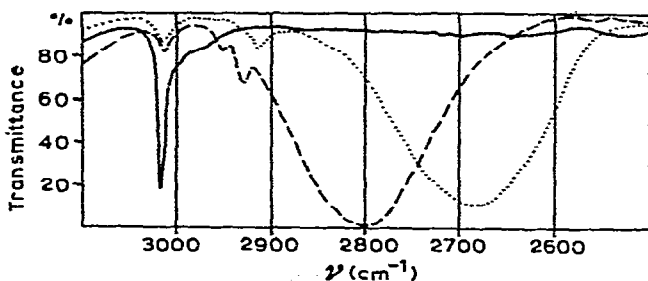


Fig. 3. IR-spectra of C-methyldecachlorocarborane (II) and its adducts (pelletized with KBr). (—), II; (---), adduct of II with Me_2NCHO ; (· · · · ·), adduct of II with Me_2SO .

Crystalline decachlorocarborane shows in the infrared spectrum a doublet in the C–H stretching region with components at 3020 and 3040 cm^{-1} . This splitting is associated with some crystalline lattice effects since in CCl_4 solution the doublet shows up as a very sharp strong band at 3042 cm^{-1} ² (*cf.* Fig. 2).

It can be seen from Figs. 1.3–5 that for the crystalline adducts of decachlorocarborane, its C-ethyl- and C-methyl derivatives, and dibromooctachlorocarborane with Me_2SO and Me_2NCHO , the narrow bands in the region 3020–3050 cm^{-1} nearly (or completely) disappear being replaced by a very wide strong absorption at 2700–2900 cm^{-1} . The C–H deformation frequencies exhibited by decachlorocarborane and its mono-C-derivatives at 1100–1200 cm^{-1} ² are shifted in the spectra of the adducts to the high frequency region. It is well known that such spectral properties, *i.e.*, the shift into low frequencies, broadening and intensification of the A–H stretching

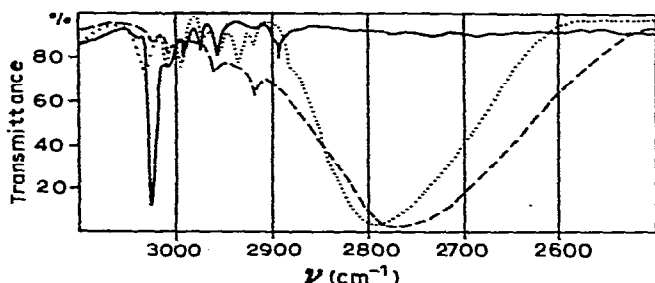


Fig. 4. IR-spectra of C-ethyldecachlorocarborane (III) and its adducts (pelletized with KBr). (—), III; (⋯), adduct of III with Me₂NCHO; (---), adduct of III with Me₂SO.

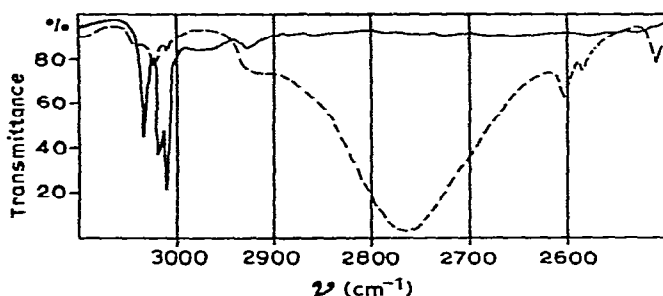
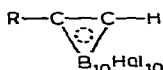


Fig. 5. IR-spectra of dibromooctachlorocarborane (—) and its adduct with Me₂SO (---) (pelletized with KBr).

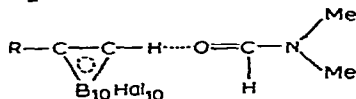
band, and increasing of A-H deformation frequency, are specific criteria for A-H ··· B hydrogen bond formation³.

Our results lead to the conclusion that the decahalocarboranes of the following general formula:



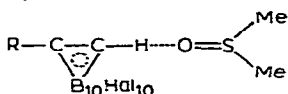
form a new class of compounds capable of very strong C-H ··· B hydrogen bonding. The existence of the stable crystalline adducts discussed here is due to this bond. We believe this to be the first reported evidence for the existence of an individual solid due to the C-H ··· B hydrogen bond, since the H-bonding of the type described for acetylenic hydrocarbons, highly halogenated paraffins and aromatic compounds³⁻⁵ have been elucidated only in their solutions.

The following structure should be assigned to the decahalocarborane adducts with Me₂NCHO:

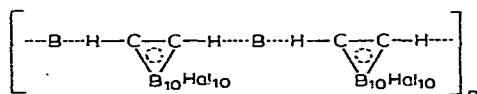


because the C=O stretching frequency in the spectra of the adducts decreases with respect to that of dimethylformamide by 20–30 cm⁻¹. The overlapping of the S=O stretching band with a very strong band assigned to B-Cl stretching makes it impossible to observe a shift in the S=O frequency in the spectra of Me₂SO adducts. However, in analogy with the DMFA adduct and based on reported data⁷ the

following structure is suggested for these adducts:



The behaviour of the C–H stretching vibration in the spectra of the adducts was unusual. C-alkyl decahalocarboranes have only one C–H bond, and after participation of this in adduct formation, a complete disappearance of the bands in the region of $\sim 3050\text{ cm}^{-1}$ (vibration of non-interacting C–H bond) is expected. But there are two C–H bonds in the unsubstituted decahalocarboranes and the formation of the adduct of 1:1 composition involves only one C–H bond. Hence, in this case we should observe in the spectrum a broad absorption due to the C–H \cdots B hydrogen bond formation near 2800 cm^{-1} , and the band at $\sim 3050\text{ cm}^{-1}$ corresponding to the non-interacting C–H bond. In fact, however, for unsubstituted (Figs. 1 and 5) and C-alkyl substituted (Figs. 3 and 4) decahalocarborane adducts, the spectra show only broad bands due to the C–H bond participating in the H-bonding. This fact may be explained by the formation in the solid state of conglomerates or chains of the following type:



The poor solubility of decahalocarborane adducts in comparison with that of C-alkyldecahalocarboranes (which cannot form such chains) may to some extent support this suggestion.

However, this phenomenon may be regarded from another point of view. In the previous paper² it was shown that introduction of an electropositive substituent, X, to one of the carbon atoms of the carborane nucleus results in a decrease in integral intensity of the C–H stretching band. Since the formation of an adduct due to H-bonding is equivalent to such a substitution, the intensity of the band corresponding to the vibration of non-interacting C–H bond may be essentially lowered.

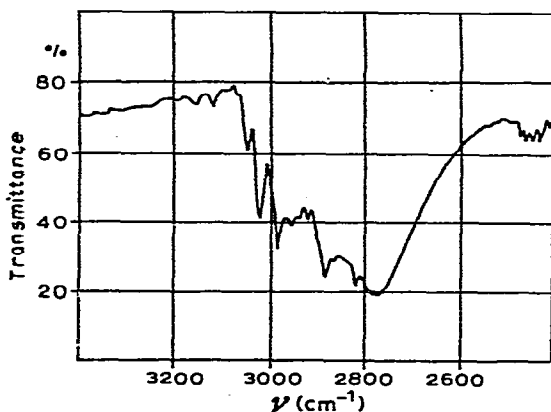


Fig. 6. IR-spectrum of decachlorocarborane adduct with THF (pelletized with KBr).



It was of interest to investigate the behaviour of decahalocarboranes towards other basic compounds. Tetrahydrofuran and dioxane have also been shown to form the crystalline adducts of the same type with decachlorocarborane (Figs. 6–7).

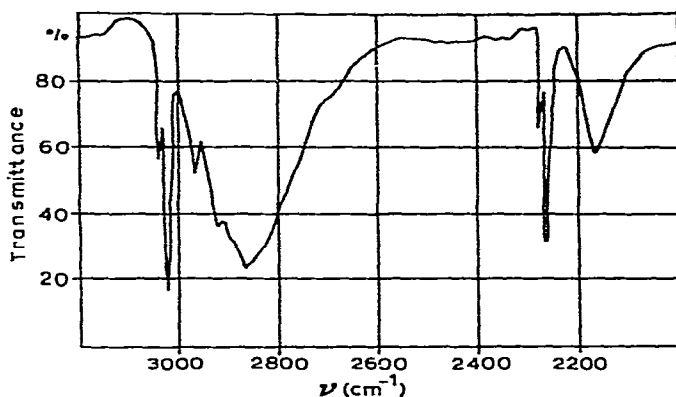


Fig. 7. IR-spectrum of decachlorocarborane and deuterodecachlorocarborane adducts with dioxane (pelletized with KBr).

But in this case the THF or dioxane to decachlorocarborane ratio varies and depends on experimental conditions. An attempt was made to deuterate the decachlorocarborane with D₂O in dioxane solution. The solvent was evaporated and the residue dried to give a solid which was shown to be a mixture of indefinite composition containing the dioxane adducts with decachlorocarborane and deuterodecachlorocarborane. The IR-spectrum of this solid (Fig. 7) exhibits in the C–H stretching region a doublet at 3020 and 3040 cm⁻¹ corresponding to decachlorocarborane, and a wide band assigned to the C–H ··· O system of the decachlorocarborane–dioxane adduct. This wide band has a shoulder caused by C–H vibrations of dioxane itself. In the C–D

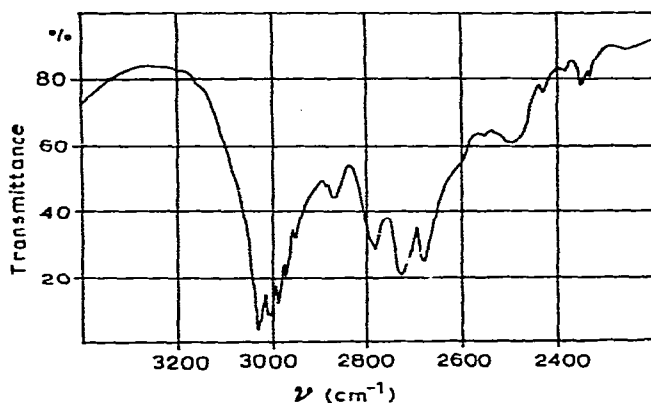


Fig. 8. IR-spectrum of decachlorocarborane adduct with trimethylamine (pelletized with KBr).

stretching region we have found a double of C–D vibrations of deuterodecachlorocarborane and a broad band assigned to the C–D ··· O bonding in the deuterodecachlorocarborane–dioxane adduct. Decachlorocarborane gives no solid adduct with acetonitrile, but the infrared spectrum of their solution shows an intensive absorption near 2950 cm^{-1} indicating C–H ··· N bond formation (Fig. 2).

All the solid adducts in question are sparingly soluble in CCl_4 . In the spectra of these solutions, the strong absorption near 2800 cm^{-1} due to the hydrogen bond, disappears, being replaced by sharp bands in the region of $3020\text{--}3050\text{ cm}^{-1}$. These adducts evidently completely dissociate at such low concentrations (about 0.005 M).

We have also obtained the IR-spectra of the crystalline adducts of decachlorocarborane and its C-alkyl derivatives with trialkylamines (see, for example, Fig. 8). These spectra show that the nature of the amine adducts is different from that of the adducts described above. The extremely wide absorption with fine structure found in these spectra in the region of $2000\text{--}3000\text{ cm}^{-1}$ are reminiscent to some extent of the spectra of ammonium salts³.

EXPERIMENTAL

The IR-spectra were recorded by a double-beam UR-10 Model spectrophotometer between 3700 and 400 cm^{-1} . The crystalline solids were pelletized with KBr. The spectra of liquid Me_2SO and Me_2NCHO were registered on thin films.

The solvents and starting compounds were dried and purified by standard methods.

The melting points are uncorrected and were taken in sealed capillaries.

Decachlorocarborane-dioxane adduct

Slow evaporation of the decachlorocarborane–dioxane solution gave a white crystalline precipitate which was filtered off and dried in a vacuum desiccator; m.p. $190\text{--}205^\circ$. (Found: C, 17.29; B, 16.29; Cl, 57.93; H, 2.69. $\text{B}_{10}\text{Cl}_{10}\text{C}_2\text{H}_2(\text{CH}_2)_4\text{O}_2 = \text{B}_{10}\text{Cl}_{10}\text{C}_6\text{H}_{10}\text{O}_2$ calcd.: C, 12.49; H, 1.75; B, 18.75; Cl, 61.46%; $\text{B}_{10}\text{Cl}_{10}\text{C}_2\text{H}_2\text{--}[(\text{CH}_2)_4\text{O}_2]_2 = \text{B}_{10}\text{Cl}_{10}\text{C}_{10}\text{H}_{18}\text{O}_4$ calcd.: C, 18.06; H, 2.73; B, 16.27; Cl, 59.32%.)

Preparation of deuterodecachlorocarborane

1 ml of D_2O was added to 0.5 g of decachlorocarborane in 10 ml of anhydrous dioxane and the mixture allowed to stand for 1 day. Dioxane, water and D_2O were evaporated without heating (3 mm Hg). The solid obtained was recrystallised from CCl_4 .

Decachlorocarborane–tetrahydrofuran adduct

This compound, of indefinite composition, was prepared by an analogous method to that of the dioxane adduct.

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