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EFFECT OF SOLVENTS ON THE ELECTRONIC PROPERTIES OF 1-*o*-, 3-*o*- AND 1-*m*-CARBORANYL GROUPS

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SUMMARY

The dependence of the electronic properties of 1-*o*-, 3-*o*- and 1-*m*-carboranyl groups on the type of solvent has been studied using Taft's method. The electron-attraction effect of the 1-*o*- and 3-*o*-carboranyl groups changes with hydrogen bond formation between the acidic hydrogens of the *o*-carborane nucleus and the proton-attracting solvent. The electronic properties of the 1-*m*-carboranyl group are practically solvent-independent.

The electron-attraction abilities of the 1-*o*- and 3-*o*-carboranyl groups in various solvents are determined by changes in the inductive effect (σ_I), whereas the resonance effect (σ_R^0) remains practically constant.

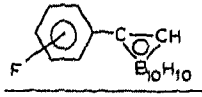
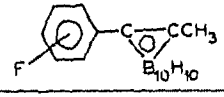
Substitution with methyl groups of the acidic hydrogens in the 1-*o*-, 3-*o*- and 1-*m*-carboranyl groups does not alter the dependence of the electronic properties on the solvents; this shows an absence of noticeable donor–acceptor interaction between the boron skeleton of carboranes and the proton-accepting and -donating solvents.

It has been stated that the carboranyl groups display rather small accepting conjugative effects ($\sigma_R^0 > 0$) while a negligible donating conjugative effect is observed ($\sigma_R^0 < 0$) for the *m*-carboranyl group.

Electronic effects of carboranyl groups ($B_{10}H_{11}C_2$) have been the subject of a number of papers. The first communications[1-3] showed that *o*- and *m*-carborane systems display a considerable electron-attracting effect. Later the Hammett constants were determined for 1-*o*-[4,5] 3-*o*-[5] and 1-*m*-carboranyl[5] groups. Their electron-attracting effects decrease in the sequence: 1-*o*- > 1-*m*- > 1-*p*- > 3-*o*-carboranyl groups[5,6]. Inductive (σ_I) and resonance (σ_R^0) constants[4] have been calculated by the method of Taft *et al.*[7]; their values were σ_I +0.375, σ_R^0 +0.003 for 1-*o*- and σ_I +0.194, σ_R^0 −0.039 for 1-*m*-carboranyl groups in a cyclohexane solution. Later, however, the electronic effects of carboranyl groups were found to depend on the solvent and the position of the substituent in the carborane nucleus. To explain solvent effects on the electronic properties of the carborane system[5] it was suggested that the carborane nucleus is able to coordinate with basic solvents. Such a coordination may be a result of either hydrogen bond formation by acidic hydrogens at the carbons, or the donor–acceptor interaction between the oxygens of the solvent and the borons of the carborane nucleus.

TABLE 1

^{19}F CHEMICAL SHIFTS AND CALCULATED σ-CONSTANTS FOR 1-*o*-CARBORANYL AND 1-(2-METHYL)-*o*-CARBORANYL GROUPS

Compound										
Solvent	δ_n^F	δ_M^F	σ_I	σ_R^0	σ_p^0	δ_n^F	δ_M^F	σ_I	σ_R^0	$\sigma_p^{0\,a}$
Chloroform	−2.51	−2.22	+0.40	+0.01	+0.41	−3.50	−2.18	+0.39	+0.04	+0.43
Carbon tetrachloride	−2.26	−2.10	+0.38	—	+0.38	−3.20	−2.11	+0.38	+0.04	+0.42
Cyclohexane	−2.18	−2.00	+0.36	+0.01	+0.37	−3.04	−2.14	+0.39	+0.03	+0.42
Phenylacetylene	—	−1.96	+0.36	—	—	—	—	—	—	—
Methylene chloride	−2.38	−1.93	+0.36	+0.01	+0.37	−3.28	−1.82	+0.34	+0.05	+0.39
Diethyl ether	−2.05	−1.86	+0.35	+0.01	+0.36	—	—	—	—	—
Carbon disulfide	—	−1.81	+0.34	—	—	—	—	—	—	—
Acetic acid	−2.00	−1.80	+0.34	+0.01	+0.35	—	—	—	—	—
Pyridine	−1.75	−1.75	+0.33	0	+0.33	−3.30	−2.20	+0.39	+0.04	+0.43
Methanol	−1.78	−1.74	+0.33	0	+0.33	−3.43	−2.18	+0.39	+0.04	+0.43
Acetonitrile	−2.10	−1.73	+0.33	+0.01	+0.34	−3.35	−1.92	+0.36	+0.05	+0.41
Aceton	−1.75	−1.60	+0.31	0	+0.31	—	—	—	—	—
Dimethoxyethane	−1.70	−1.56	+0.30	0	+0.30	—	—	—	—	—
Benzene	−1.85	−1.53	+0.30	+0.01	+0.31	—	—	—	—	—
THF	−1.68	−1.50	+0.30	+0.01	+0.31	+3.10	−1.96	+0.36	+0.04	+0.40
Dioxane	−1.54	−1.48	+0.29	0	+0.29	−2.93	−1.86	+0.35	+0.04	+0.39
DMSO	−1.71	−1.50	+0.30	+0.01	+0.31	−3.35	−2.05	+0.37	+0.04	+0.41
DMF	−1.70	−1.43	+0.29	+0.01	+0.30	−3.22	−2.05	+0.37	+0.04	+0.41
Hexametapol	−1.74	−1.24	+0.26	+0.02	+0.28	−3.16	−1.94	+0.36	+0.04	+0.40

[a] $\sigma_p^0 = \sigma_I + \sigma_R^0$

In the present work solvent effects on the electronic properties of carboranyl groups have been investigated by Taft's method[7]. For this purpose the fluorine chemical shifts in NMR spectra were obtained in different solvents for 1-(*p*- and *m*-fluorophenyl)-*o*-carboranes, 1-(*p*- and *m*-fluorophenyl)-2-methyl-*o*-carboranes, 3-(*p*- and *m*-fluorophenyl)-*o*-carboranes, 1,2-dimethyl-3-(*p*- and *m*-fluorophenyl)-*o*-carboranes, 1-(*p*- and *m*-fluorophenyl)-*m*-carboranes, and 1-(*p*- and *m*-fluorophenyl)-7-methyl-*m*-carboranes. The corresponding inductive and resonance constants of these carboranyl groups were estimated using Taft's equations. The results are presented in Tables 1 and 2.

RESULTS AND DISCUSSION

1-*o*-Carboranyl group

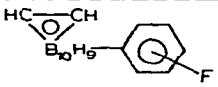
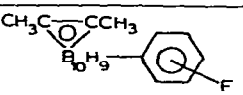
In the solvents investigated, the 1-*o*-carboranyl group behaves as an electron acceptor (positive σ_I and σ_R^0, their magnitudes varying with the solvent, Table 1). On the basis of the ability to change the electronic properties of this group, solvents may be divided into the following groups: (1) practically indifferent solvents (chloroform, carbon tetrachloride, cyclohexane, phenylacetylene, methylene chloride); (2) weakly interacting solvents (carbon disulfide, acetic acid, acetonitrile, pyridine, diethyl ether, methanol); (3) strongly interacting solvents (acetone, dimethoxyethane, benzene, dioxane, tetrahydrofuran, dimethyl sulfoxide, dimethyl formamide and hexametapol). Since aprotic solvents are π- and n-bases they usually cause a substantial upfield fluorine chemical shift in the NMR spectra of 1-(*p*- and *m*-fluorophenyl)-*o*-carboranes with respect to that observed in cyclohexane or carbon tetrachloride. On the other hand, protic solvents do not significant shift the fluorine signal with respect to that found in cyclohexane.

The interaction of the *o*-carborane nucleus with solvents may be discussed in terms of two possible mechanisms: hydrogen bond formation between basic solvents and the acidic hydrogens of the *o*-carborane nucleus, and the mechanism involving the donor–acceptor interaction between solvents and boron. In the case of the latter mechanism, owing to the non-equivalent electron densities at different borons in the *o*-carborane nucleus, one may expect only two types of the donor–acceptor interaction. First, electrophilic boron atoms 3 and 6 may coordinate with basic solvents thus increasing the electronic density within the *o*-carborane nucleus and decreasing its electron-attraction ability. This in turn causes larger fluorine shielding in 1-(*p*- and *m*-fluorophenyl)-*o*-carboranes (upfield shift). On the other hand, nucleophilic borons 8, 9, 10 and 12 may interact with protic solvents, decreasing the electronic density within the *o*-carborane nucleus, *i.e.*, increasing its electron attraction effect. This results in lower fluorine shielding (downfield shift) in 1-(*p*- and *m*-fluorophenyl)-*o*-carboranes, but experiments show that, in the solvents investigated, the electron-attraction ability of the 1-*o*-carboranyl group does not increase with respect to that observed in non-interacting solvents. Thus, no experimental evidence was obtained for the assumed substantial interaction between borons 8, 9, 10 and 12 and the solvents investigated.

Fluorine chemical shifts measured in various solvents and estimated according to the equations of Taft *et al.* show that in 1-(*p*- and *m*-fluorophenyl)-2-methyl-*o*-carboranes the electron-attraction ability of the 1-methyl-*o*-carboranyl group is

TABLE 2

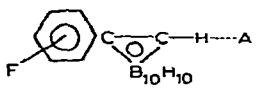
^{19}F FLUORINE CHEMICAL SHIFTS AND CALCULATED σ-CONSTANTS FOR 3-*o*-CARBONYL, 3-(1,2-DIMETHYL)-*o*-CARBORANYL, 1-*m*-CARBORANYL AND 1-(7-METHYL)-*m*-CARBORANYL GROUPS

Compound										
Solvent	δ_n^F	δ_M^F	σ_I	σ_R^0	σ_p^{0a}	δ_n^F	δ_M^F	σ_I	σ_R^0	σ_p^{0a}
Chloroform	−2.2	−0.35	+0.13	+0.06	+0.19	−1.80	−0.51	+0.16	+0.04	+0.20
Carbon tetrachloride	−2.16	−0.21	+0.11	+0.07	+0.18	−1.95	−0.70	+0.18	+0.04	+0.22
Methanol	−1.33	+0.22	+0.05	+0.05	+0.10	−1.90	−0.68	+0.18	+0.04	+0.22
THF	−1.31	+0.46	+0.02	+0.06	+0.08	−1.59	−0.50	−0.15	+0.04	+0.19
Dioxane	−1.38	+0.53	+0.01	+0.06	+0.07	−1.50	−0.42	+0.14	+0.04	+0.18
DMSO	−1.23	+0.60	0	+0.06	+0.06	−1.73	−0.58	+0.17	+0.04	+0.21
Hexametapol	−0.36	+1.04	−0.06	+0.05	−0.01	−1.67	−0.55	+0.16	+0.04	+0.20

[a] $\sigma_p^0 = \sigma_I + \sigma_R^0$.

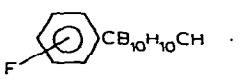
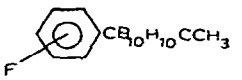
practically solvent-independent when it contains no acidic hydrogen. σ_I- and σ_R^0-constants change only within 0.04 internal. This shows that the donor–acceptor interaction of solvents does not take place with borons 8, 9, 10 and 12 or with those in positions 3 and 6 of the *o*-carboranyl nucleus.

Thus, it may be concluded that the electron attraction effect of the *o*-carboranyl group depends completely on hydrogen bond formation between basic solvents and the acidic hydrogen of the *o*-carborane nucleus:



The ability of *o*-carborane and its *C*-monosubstituted derivatives to form hydrogen bonds with basic solvents has been verified by IR spectral investigation of their dimethyl formamide and dimethyl sulfoxide solutions[9]. With respect to donor ability to hydrogen bond formation between solvents and the acidic hydrogen of *o*-carborane, such solvents as carbon disulfide, acetic acid, acetonitrile, pyridine, diethylether and methanol are within the same group, *i.e.*, oxygen, nitrogen and sulfur are capable of H-bond formation. Since the electron-attraction effect is also lower in benzene, the benzene-type bases are also capable of hydrogen bond formation with the acidic hydrogen of the *o*-carboranyl nucleus. Of n-type-donors, hexametapol forms the strongest hydrogen bond with *o*-carborane.

Calculation of inductive and resonance constants for the 1-*o*-carboranyl group using the equations of Taft *et al.* shows that its electron attraction effect in different solvents is determined almost exclusively by an inductive component (σ_I). Negligible resonance contribution into σ_R^0 in different solvents remains almost unaltered. In passing from 1-*o*- to 1-(2-methyl)-*o*-carboranyl groups, the latter has been shown to exhibit the electron-attraction effect with its inductive component predominating although its positive resonance constituent is larger than in the unsubstituted 1-*o*-carboranyl group. The resonance component, as with an inductive component, remains practically constant in different solvents. Comparison of σ_I- and σ_R^0-constants

δ_n^F	δ_M^F	σ_I	σ_R^0	$\sigma_p^{0\,a}$	δ_n^F	δ_M^F	σ_I	σ_R^0	$\sigma_p^{0\,a}$
+0.14	−0.82	+0.20	−0.03	+0.17	+0.28	−0.77	+0.19	−0.04	+0.15
−0.20	−0.87	+0.21	+0.05	+0.25	+0.38	−0.73	+0.19	−0.04	+0.15
−0.18	−1.04	+0.23	−0.04	+0.19	−0.03	−1.11	+0.24	−0.04	+0.20
+0.10	−0.85	+0.20	−0.03	+0.17	+0.21	+0.92	+0.21	−0.04	+0.17
+0.40	−0.82	+0.20	−0.04	+0.16	+0.47	−0.85	+0.20	−0.04	+0.16
−0.12	−1.15	+0.24	−0.04	+0.20	−0.16	−1.12	+0.24	−0.03	+0.21
0.00	−0.91	+0.21	−0.03	−0.18	−0.15	−0.93	+0.21	−0.02	+0.19

of 1-(2-methyl)-*o*- and 1-*o*-carboranyl groups indicates that the introduction of a methyl group in place of hydrogen increases the electron-attraction effect. This disagrees to some extent with previous data[9,10] where the methyl group was shown to behave as a donor during transmission along the C–C bond of the *o*-carborane nucleus. The nature of this inconsistency remains unresolved.

3-o-Carboranyl group

On the basis of the method employed in this work the 3-*o*- has less electron-attraction power than the 1-*o*-carboranyl group (Table 2), *i.e.*, as shown in our previous paper[5] it is the position of the substituent in the carborane nucleus that determines its electronic effects and σ_I- and σ_R^0-components. For the 3-*o*-carboranyl group, where the aryl fragment is combined with the carborane boron (but not with carbon), it should be noted that its resonance component (σ_R^0) is larger although the inductive part (σ_I) is smaller than the σ_I of the 1-*o*-carboranyl group. The inductive electron-attraction effect of the 3-*o*-carboranyl group is solvent-dependent and decreases in the following series: chloroform > carbon tetrachloride > methanol > tetrahydrofuran > dioxane, while its resonance part, σ_R^0, is almost unchanged. In dimethyl sulfoxide, the resonance component completely determines the electron-attraction effect and σ_I is negligible. In hexametapol, σ_I is negative and the total effect, $(\sigma_I+\sigma_R^0)$, of the 3-*o*-carboranyl group is that of a weak electron-donor *i.e.*, hydrogen bond formation by the acidic hydrogen determines the electronic properties of the 3-*o*-carboranyl group. It should be noted that the constancy of the resonance component (σ_R^0) in various solvents is evidence that during hydrogen bond formation, transmission along the B–C bond involves an inductive mechanism.

The electron-attraction effect of the 3-(1,2-dimethyl)-*o*-carboranyl group containing no acidic hydrogens changes only negligibly in the solvents investigated. Its value, however, exceeds that for the 3-*o*-carboranyl group, although the introduction of two methyls somewhat decreases the σ_R^0 of 3-(1,2-dimethyl)-*o*- with respect to that of the 3-*o*-carboranyl group. The solvents investigated have a greater effect on the electronic properties of the latter group than on those of the 1-*o*-carboranyl group which may be due to the two acidic hydrogens in the 3-*o*-carboranyl group, or the

better conductivity of the B–C (compared with the C–C) bond or a result of both factors.

1-m-Carboranyl groups

Although *m*-carborane is capable of hydrogen bond formation[8], its carbon atoms are, however, separated by borons and the transmittance of the electronic effect of the substituent from one to another carbon is rather poor[9,10]. This also follows from the present results. While in the fluorine spectra of *o*-carborane the presence of the hydrogen bond is clearly evident, the electron-attraction effect of the 1-*m*-carboranyl group in all solvents investigated is almost unchanged (even in a strong aprotic solvent such as hexametapol). In methanol and dimethyl sulfoxide, the inductive components are somewhat higher than those in indifferent solvents. For the 1-*m*-carboranyl group, the resonance components are practically constant. An analogous picture was observed for the 1-(7-methyl)-*m*-carboranyl group where hydrogen bond formation is excluded. The inductive component determines the electron-attraction effect for both 1-*m*- and 1-(7-methyl)-*m*-carboranyl groups. Unlike the positive resonance components of the 1-*o*- and 3-*o*-carboranyl groups, σ_R^0 of the 1-*m*-carboranyl group, being rather small, is negative, *i.e.*, the 1-*m*-carboranyl group exhibits a negligible electron-releasing conjugative effect. The introduction of a methyl group has little effect on either the inductive or resonance constants. This shows that in the *m*-carborane nucleus, the boron system is sufficiently indifferent towards various solvents.

EXPERIMENTAL

m-Fluorophenylacetylene

m-Fluoroacetophenone (165 g) was added slowly with stirring to 257 g of finely powdered PCl_5. The reaction mixture was heated for 1.5 h on a water bath. Reaction completion was controlled by thin-layer chromatography on alumina and GLC analysis. Phosphoryl chloride was evaporated at lower pressure (100 mm Hg), and the residue distilled *in vacuo*; 176 g of the chloride mixture was obtained, b.p. 75–90°/15 mm. This chloride mixture was added at room temperature to a solution of 200 g of KOH in 400 ml of absolute ethanol. The mixture was heated to its boiling point and refluxed until the appearance of *m*-fluorophenylvinylethyl ether. The cooled mixture was poured into water and extracted with ether. The ethereal solutions were washed with water and dried over calcium chloride. The ether was evaporated, and *m*-fluorophenylacetylene was distilled *in vacuo*; 43 g of *m*-fluorophenylacetylene was obtained. The residue of the distillation containing chlorides and a small quantity of *m*-fluorophenylvinylethyl ether was returned for repeated dehydrodichlorination and an additional 13 g of *m*-fluorophenyl was obtained. The overall yield was 56 g (51%), b.p. 70–71°/70 mm, n_D^{20} 1.5140.

p-Fluorophenylacetylene

This was prepared as above, m.p. 27–28° (lit. m.p. 26–27°).

1-(p-Fluorophenyl)-o-carborane

N-Dimethylaniline (62 g) and *p*-fluorophenylacetylene (37 g) were added to

a solution of 34 g of decaborane in 300 ml of toluene. The reaction mixture was stirred at room temperature for 3 h, heated to boiling and refluxed until completion of hydrogen evolution. The solution was filtered and washed several times with dilute hydrochloric acid and water and dried over calcium chloride. After the evaporation of toluene, the residue was heated with methanol. The latter was evaporated, the residue dissolved in heptane and passed through an alumina column; 52 g (83%) of 1-(*p*-fluorophenyl)-*o*-carborane was obtained, m.p. 140–141° (lit.[4] m.p. 138–139°).

1-(*m-Fluorophenyl*)-*o-carborane*

This was prepared in the same way as the *p*-compound, yield 64%, m.p. 67–68° (lit.[4] m.p. 68–68.5°).

1-(*p- and m-Fluorophenyl*)-*m-carboranes*

These were obtained by thermal isomerization of the relevant 1-(*p*- and *m*-fluorophenyl)-*o*-carboranes under the conditions reported[4]. 1-(*p*-Fluorophenyl)-*m*-carborane: m.p. 62–63° (lit.[4] m.p. 61–62°). 1-(*m*-Fluorophenyl)-*m*-carborane: m.p. 46–47°. (lit.[4] m.p. 45–46°).

p- and m-Fluorophenylboron dichlorides

These were prepared by the same procedure from the dibutyl esters of *p*- and *m*-fluorophenylboric acids by reaction with PCl_5.

PCl_5 (1.7 g) was added at room temperature to a Claisen flask containing 13.5 g of *m*-fluorophenyldibutyl borate. The temperature rose to 55–60° and the PCl_5 partially dissolved. The mixture was heated to 100–110° when the PCl_5 dissolved completely. Phosphoryl and butyl chlorides were evaporated and an additional 11.7 g of PCl_5 was added to the mixture. After evaporation of phosphoryl and butyl chlorides, the residue was distilled *in vacuo*; 5.04 g (51%) of *m*-fluorophenylboron dichloride was obtained, m.p. 75–82°/28 mm.

3-(*m-Fluorophenyl*)-*o-carborane*

The trimethylammonium salt of dicarbaundecaborane (5.25 g)[13] was added to 2.70 g of sodium hydride in 35 ml of THF and refluxed until completion of hydrogen evolution. The solution was filtered from the excess sodium hydride and 5.04 g of *m*-fluorophenylboron dichloride in 15 ml of heptane was slowly added, with stirring, to the mixture at −65°. The temperature was allowed to increase to 20° and the reaction mixture was decomposed with dilute KOH solution. The organic layer was washed with water and dried over calcium chloride. After evaporation of the solvent, the residue was dissolved in heptane and passed through an alumina column; 4.76 g (69%) of 3-(*m*-fluorophenyl)-*o*-carborane was obtained, m.p. 64.0–64.5° (hexane). (Found: C, 40.55; H, 6.40. $C_8H_{15}B_{10}F$ calcd.: C, 40.40; H, 6.32%.)

General procedure for alkylation of p- and m-fluorophenylcarboranes

A solution of 0.012 mole of butyllithium (0.024 mole for dialkyl derivatives) in benzene was added to a solution of 0.01 mole of the appropriate carborane in 15 ml of absolute ether at −5 to 0° and stirred at 0° for 30 min. A 1.5-fold excess (with respect to the stoichiometric amount) of methyl iodide was added and the mixture was stirred for 30 min at room temperature. Reaction completion was controlled by

thin-layer chromatography on alumina. The reaction mixture was decomposed with dilute hydrochloric acid, and the organic layer washed with water and dried over calcium chloride. After evaporation of the solvent, the residue was crystallized from hexane, pentane or distilled *in vacuo*.

The following carboranes were obtained:

1-(*p*-fluorophenyl)-2-methyl-*o*-carborane, m.p. 84–85° (hexane). (Found: C, 42.50; H, 6.68. $C_9H_{17}B_{10}F$ calcd.: C, 42.80; H, 6.79%.)

1-(*m*-fluorophenyl)-2-methyl-*o*-carborane, m.p. 70–70.5° (hexane). (Found: B, 42.75. $C_9H_{17}B_{10}F$ calcd.: B, 42.90%.)

1-(*p*-fluorophenyl)-7-methyl-*m*-carborane, m.p. 44° (pentane). (Found: C, 43.12; H, 6.77. $C_9H_{17}B_{10}F$ calcd.: C, 42.80; H, 6.79%.)

1-(*m*-fluorophenyl)-7-methyl-*m*-carborane, b.p. 147–149°/5 mm. (Found: C, 43.75; H, 7.19. $C_9H_{17}B_{10}F$ calcd.: C, 42.80; H, 6.79%.)

1,2-dimethyl-3-(*p*-fluorophenyl)-*o*-carborane, m.p. 155–156° (hexane). (Found: C, 45.95; H, 7.48. $C_{10}H_{19}B_{10}F$ calcd.: C, 45.50; H, 7.18%.)

1,2-dimethyl-3-(*m*-fluorophenyl)-*o*-carborane, m.p. 108–109° (hexane). (Found: C, 45.79; H, 7.19. $C_{10}H_{19}H_{10}F$ calcd.: C, 45.50; H, 7.18%.)

The fluorine NMR spectra were obtained with the 56.4 Mcs H-60 Hitachi spectrometer at 34°. Chemical shifts were measured using fluorobenzene as internal reference. Distances were taken between centers of the corresponding multiplets.

All the measurements were carried out with dilute solutions (below 0.2 *M*). The accuracy of the chemical shift measurements was about ±0.1 ppm.

Solvents were purified by standard procedures.

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