DIPOLE MOMENTS OF ISOMERIC MONOSUBSTITUTED *o*-CARBORANES*

V. GREGOR[a], V. JEHLIČKA[b] and J. STUCHLÍK[a]

[a] *Institute of Inorganic Syntheses,*
Czechoslovak Academy of Sciences, Prague-Řež,
[b] *Department of Physical Chemistry,*
Institute of Chemical Technology, Prague 6

Received November 4th, 1971

Dipole moments of isomeric icosahedric monobromo-*o*-carboranes have been measured. The isomer with bromine bound to the carbon atom has the lowest value of the dipole moment. Dipole moments of other isomers increase with the increasing distance between the substituted boron atom and the carbon atom.

From the calculations of the charge distribution for the presumed carborane molecules with the icosahedric structure it follows that the highest electron density is opposite the carbon atoms that carry the positive charge[1]. The conclusion on the preferent electrophilic substitution of *o*-carboranes in positions 9 and 12 (*i.e.* in sites of the highest electron density) is established by the results of X-ray diffraction measurements[2,3]. The assumption on the high dipole moment of this molecule[4-7] has also been confirmed. The dipole moments of monobromocarboranes have been estimated from the experimental values of dipole moments of carboranes and dibromocarboranes using the reciprocal relation between the dipole moments and chromatographic R_M values of these compounds[8]. The main purpose of this study was to determine the dipole moments of all monobromo-*o*-carboranes, *i.e.* 1 (2), 3 (6), 4 (5, 7, 11), 8 (10), 9 (12). From this series of isomers only 1 (2) bromo- and 9 (12) bromo-*o*-carborane have been measured and reported previously[6,7].

The dipole moments have been calculated from the permittivities (dielectric constants) of a series of diluted benzene solutions (weight fraction max. 0·01) at 25°C. The permittivities were measured by the beat method at the frequence of 1·2 MHz with a precision better than 0·01%, their densities were measured in adapted Oswald–Sprengel pycnometers with a similar precision. The method of Halverstadt and Kumler[9] was used, for the calculation of the dipole moments. The electron polarizations used are those published in the paper[7]. The atomic polarizations have been corrected by a value equal to 5% of the molar refraction R_D.

From the obtained values (Table I), corresponding to the values estimated from the chromatographic data, it follows that the substitution by bromine in the equatorial

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[*] The term *o*-carborane is used to designate 1,2-dicarba-closo-dodecaborane (12).

TABLE I

Melting Points of Isomeric Bromo-*o*-carboranes, Their Polarizations and Dipole Moments in Benzene at 25°C

o-Carborane	M.p., °C	P_2^0, cm^3	μ, D
1-Br	180	288·1	3·34
3-Br	122—123	337·9	3·69
4-Br	142	469·4	4·47
8-Br	185·5—186	674·6	5·48
9-Br	191·5	732·7	5·98

plane of the icosahedric skeleton has but a negligible effect on the dipole moment of the unsubstituted *o*-carborane. On the other hand, if the skeleton is substituted in other position, the dipole moment decreases towards the C atom and increases in the opposite direction, having the lowest value for the 1-Br-derivative and the highest value for the 9-Br-derivative.

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Translated by Z. Prášil.