The Molecular Structure of *C,C'*-Diiodine-*p*-carborane, 1,12-$C_2I_2B_{10}H_{10}$, Determined by Gas Phase Electron Diffraction

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The present work is a part of our systematic study of polyhedral carboranes and their derivatives. In the course of previous work we became interested in the stereochemistry of six-coordinate carbon and especially in its exopolyhedral distances. In order to measure them with sufficient accuracy it is expedient to avoid overlap with the many B – C and B – B distances in the icosahedral skeleton C_2B_{10}. Perhaps the most suitable bond distance for such a study is the C – I distance. In this connection *C,C'*-diiodine-*p*-carborane (DIPC), 1,12-$C_2I_2B_{10}H_{10}$, seems to be the simplest representative of the series of isomeric carboranes $C_2H_2B_{10}H_{10}$ with carbon atoms labelled by heavy substituents. The experimental part of this study has been carried out with the same sample in Oslo and in Moscow in order to achieve a reliable value of the C – I distance and to check experimental and computational procedures used in different laboratories, as advised by the Commission on Gas Electron Diffraction formed at the Ninth IUCr Congress.

Experimental and calculation procedure. DIPC was kindly supplied by A. F. Zhigach and V. N. Syryatskaya who prepared it in analogy to the synthesis of $C_2IHB_{10}H_{10}$;[1] its purity was checked by mass-spectrometry. The electron scattering patterns were recorded on the Oslo electron diffraction unit [2] and in Moscow on EG-100A, at nozzle-tip temperatures of approximately 230°. The data obtained cover the s-ranges from 1.5 to 30.25 Å^{-1} (Oslo) and from 3.0 to 29.0 Å^{-1} (Moscow). The different sets of experimental data were then analysed in Moscow according to the procedures normally used in our laboratories. The main difference between them lies in the type of modification of observed intensities. The Oslo-data were modified by the function $s/|f_I'|^2$, whereas s/BT was used for the Moscow data. The scattering factor, $f'(s)$, and the theoretical background, $BT(s)$, are defined in Ref. 3, which also contains other details of the structure analysis. Asymmetry constants,[3] $\varkappa_{ij} = au_{ij}^2/b$, were introduced for the bond distances using $a = 3$ Å^{-1} for r(B – H) and $a = 2$ Å^{-1} for the other bonded interactions. The structure refinements were carried out by the method of least squares based upon intensity data on the modified forms using a program written by H. M. Seip.[3]

Structure refinement. Molecular model of DIPC is shown in Fig. 1. It was assumed that the molecule has D_{5d} symmetry. Then its structure is determined by six parameters:

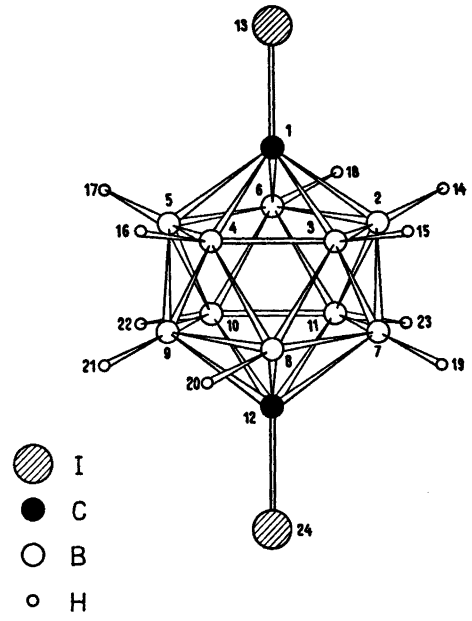

Fig. 1. Molecular model for 1,12-$C_2I_2B_{10}H_{10}$ molecule (DIPC).

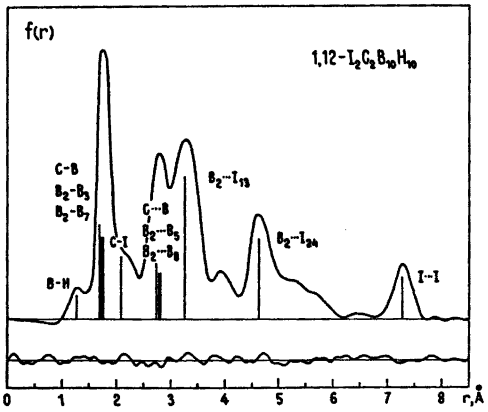

Fig. 2. Experimental radial distribution curve for DIPC molecule. The lower curve represents residual $\Delta f(r) = f(r)_{expl} - f(r)_{calc}$. Vertical bars correspond to principal internuclear distances. A damping factor, exp ($-0.002\ s^2$), was used.

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Table 1. Molecular parameters of 1,12-$C_2I_2B_{10}H_{10}$ obtained on the basis of experiments carried out in Moscow (A) and in Oslo (B) and their comparison with values (C) reported for 1,12-$C_2H_2B_{10}H_{10}$ (Ref. 4). Internuclear distances (r_a) and vibrational amplitudes (u) in Å and angles in degrees with estimated standard deviations (3σ) in parenthesis.

Distance type	A r_a	u	B [a] r_a	u	C [a] r_a	u
C1 – B2	1.708(8)		1.703(10)		1.710(11)	
B2 – B3	1.777(8)	0.057(6)	1.780(8)	0.058(8)	1.792(7)	0.063(5)
B2 – B7	1.775(11)		1.780(13)		1.772(13)	
C1 – I13	2.082(14)	0.044(29)	2.107(18)	0.071(39)	–	–
B2 – H14	1.205(21)	0.091(41)	1.215(23)	0.071(40)	1.216(21)	0.093(17)
C1· ·B7	2.757(9)					
B2· ·B5	2.875(8)	0.080(9)		0.070(11)		0.075(5)
B2· ·B8	2.874(6)					
C1· ·C12	3.101(25)	0.060(28)		0.072(33)		0.071(14)
B2· ·B9	3.379(7)					
C1· ·H14	2.557(15)					
B2· ·H15	2.603(14)	0.121(16)		0.124(18)		0.127(33)
B2· ·H19	2.654(18)					
C1· ·H19	3.873(21)					
B2· ·H16	3.924(18)	0.105(20)		0.106(23)		0.129(24)
B2· ·H20	3.957(12)					
B2· ·H21	4.581(14)	0.075(53)		0.078(58)		0.098(61)
B2· ·I13	3.251(7)	0.108(10)		0.088(8)		–
B2· ·I24	4.640(6)	0.087(9)		0.085(10)		–
I13· ·I24	7.266(8)	0.115(9)		0.098(9)		–
I13· ·H14	3.412(28)	0.138(25)		0.086(22)		–
C1· ·I24	5.184(13)	0.118		0.065		–
I24· ·H14	5.611(20)	0.148		0.096		–
∠B7B2H14	124.8(3.6)	–	125.3(2.4)	–	130.0(1.8)	–
R-factor	0.087		0.101		0.077	

[a] Dependent internuclear distances in A and B are practically the same; they are not reported for C (Ref. 4).

Table 2. The C – I distances (Å) in different molecules.

Type of distance	Coordination number of carbon	Molecule	C – I	Ref.
Exopolyhedral	6	DIPC	2.09	This work
Aliphatic	4	CH_3I	2.139	7
Ethylenic	3	$I_2C=CI_2$	2.106	8
Acetylenic	2	I – C≡N	1.995	9
		I – C≡C – Br	1.985	10

bond distances C – I, C – B, B – B(basal), B – B(belt), B – H and bond angle C – B – H. These were refined with the most important vibrational amplitudes shown in Table 1. The observed radial distribution curve is shown in Fig. 2. One notes, in particular, a pronounced peak at ≃7.3 Å, which is due to the longest distance I···I in this molecule.

Discussion. 1. *C_2B_{10} cage.* There is satisfactory agreement between different sets of data concerning dimensions of C_2B_{10} cage as can be seen from Table 1. These geometrical parameters are also close to the values reported for 1,12-$C_2H_2B_{10}H_{10}$,[4] indicating that the substitution has negligible effect, if any.

2. *The C–I bond.* The parameter of greatest interest is obviously the C–I distance. Unfortunately, different values were obtained in two sets, although statistically the difference cannot be regarded significant. One of the possible reasons is the different atomic scattering factors used which may be important especially for heavy atoms. The Norwegian school computes atomic factors by the partial wave method (details see in Ref. 3), while in Moscow they are taken from the tables of Cox and Bonham.[5] Indeed, when the "hybrid" attempt was made to refine the Norwegian intensity data according to the procedure adopted in Moscow, the result was $C-I=2.09\pm0.01$ Å. Because this corresponds to the arithmetic mean of values cited in Table 1, we regard it as our final result. An associated amplitude of vibration measured in Moscow is lower than might be expected. A similar phenomenon has been observed by Beagley and McAloon [6] in studies of a number of tin compounds. The authors attributed it to overdamping of calculated intensities by the Cox and Bonham scattering factors.

The C–I distance obtained for DIPC is compared to C–I distances measured in different molecules in Table 2. One might anticipate the C–I distance in DIPC to be *larger* than aliphatic types due to a higher coordination number for the exopolyhedral carbon. This is, however, not the case and in fact, the C–I bond distance in question is practically equal to the ethylenic type. The chemical behaviour of carboranes as strong electron acceptors toward substituents on carbon atoms [11] provides a reasonable explanation of this remarkable feature, as pointed out earlier.[12] There is also additional evidence for "short" exopolyhedral bonds formed by six-coordinate carbon:

(1) The C–H stretch frequency in carboranes $C_2H_2B_{10}H_{10}$ falls into the region which is characteristic for the ethylenic bond.[13]

(2) The frequency of Cl in nuclear quadrupole resonance spectra for Cl-substituted carboranes is quite similar to those compounds where chlorine is bonded to the group with strong acceptor properties as in $ClCH(NO_2)_2$.[14]

It should be noted that in contrast exopolyhedral distances in carboranes formed by boron are *longer* than in corresponding reference compounds.[15]

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The Crystal Structure of Ethylenediammonium Bromide

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Infrared and far infrared spectra of normal and *C*-deuterated 1,2-ethylenediammonium difluorides, dichlorides, and dibromides have been measured.[1] A number of bands found for the fluorides and the chlorides have no analogues in the spectra of the bromides. Some of these bands may be due to the hydrogen-bonding in the crystals. However, only the crystal structure of the chloride has been reported.[2,3] The present X-ray investigation was carried out in order to find the hydrogen-bonding system of the bromide.