C−C Bond Variation in the 1-Phenyl-*o*-carborane: Steric versus Electronic Effects

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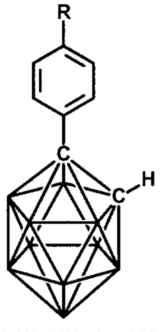
Using the "Atoms in molecules" topological theory the nature of the C_{carb}–C_{carb} bond variation in 1-phenyl-*o*-carborane upon rotation of the phenyl ring was investigated within B3LYP/6-31G** calculations. Despite the low barrier to the rotation of the phenyl ring, the bond paths linking hydrogen atoms of the phenyl ring and the ones of the carborane cage were found for all conformations. The length of the C_{carb}–C_{carb} bond increases by 0.031 Å without large energetic inputs due to back-donation of the π-density of the phenyl ring to the antibonding C_{carb}–C_{carb} orbital.

Introduction

The $C_{carb}-C_{carb}$ bond in icosahedral *o*-carboranes (i.e., that between two carbon atoms of the icosahedron) is characterized by several unusual features, among which its high "plasticity", which is reflected in significant variation of its length in organic and organometallic derivatives, can be especially emphasised.[1−3] In the case of metallacarboranes this can lead to the formation of pseudocloso structures[4] in which two carbon atoms of the cage are not chemically bonded. This is important not only from a theoretical point of view but also for understanding the isomerisation process that occurs between the *ortho*-, *meta*- and *para*-isomers of the carboranes. The plasticity of the $C_{carb}-C_{carb}$ bond is in line with its low force constant[5] as well as with the intermediate type of interatomic interaction [positive value of the Laplacian of the electron density in the critical point (3,−1)] found for the homopolar $C_{carb}-C_{carb}$ bond in the crystal of 8,9,10,12-tetrafluoro-*o*-carborane.[6]

Three factors are usually considered to be the main ones that influence the $C_{carb}-C_{carb}$ distance in the *o*-carborane derivatives: steric repulsion between one or two substituents, an electronic effect due to electronegativity differences between the hydrogen atom and the substituent group and, finally, stereoelectronic effects as a result of charge transfer from the electron lone-pair or occupied orbital of a substituent to the antibonding orbital of the $C_{carb}-C_{carb}$ bond.[3] The role of the latter can be dominant, as was demonstrated previously in the case of *o*-carborane dithia, diaryl- and dialkylphosphanyl derivatives.[3] In particular, in 1,2-$(SPh)_2$-*o*-carborane the charge transfer from the sulfur lone-pair to the antibonding orbital of the $C_{carb}-C_{carb}$ bond leads to a $C_{carb}-C_{carb}$ bond elongation of up to 1.798(3) Å.[3a] It should be noted that a similar $C_{carb}-C_{carb}$ bond elongation (1.720 Å and 1.733 Å) was found in 1,2-diphenyl-*o*-carborane,[7] in which the possibility of charge transfer from the phenyl group to the $C_{carb}-C_{carb}$ bond of the icosahedron is not so evident.

In order to study whether the bond elongation in diphenyl-*o*-carborane is the result of steric effects[1] or electronic ones, in this paper we have chosen 1-phenyl-*o*-carborane (**1**) as a model compound. Despite the fact that this compound is not sterically overcrowded with respect to the pure *o*-carborane we cannot exclude the influence of intramolecular H···H contacts on the molecular geometry. Such interactions are important in the formation of host-guest complexes of carboranes.[8] So, in addition to analysis of the phenyl interaction with the $C_{carb}-C_{carb}$ bond, we paid great attention to the nature of the $C_{ph}-H\cdots H-B$ and $C_{ph}-H\cdots H\text{-}C_{carb}$ contacts.



R = H (**1**), NH_2 (**2**), NO_2 (**3**)

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According to the theoretical and experimental studies, the replacement of CH by a CPh group in the *o*-carborane has a small electronic influence on the cage, but results in significant steric changes in the molecule due to H···H contacts.[1] It was found that in the isolated molecule **1**, there is an optimum value of the torsion angle θ [C(2)−C(1)−C(13)−C(14)], equal to 25°,[9] defining the conformation of the ring with respect to the carborane cage (see Figure 1). Although the H···H contacts in all conformations are substantially shorter than the sum of the van der Waals radii the barrier to rotation of the phenyl ring according to the HF/6−31G* calculations is very small (2.1 kJ·mol^{-1}). This low barrier was also found in the gas phase by electron diffraction and in the solid state.[9] Compound **1** has two polymorphs with two and one independent molecules in the unit cells, respectively[9,10] (α and β forms). The molecules in these forms differ in the orientation of the phenyl ring, with θ values equal to 22.2° and 18.3° in the α and β forms, respectively. It should be noted that in the α form one of the independent molecules is disordered due to the superposition of different conformations.[9]

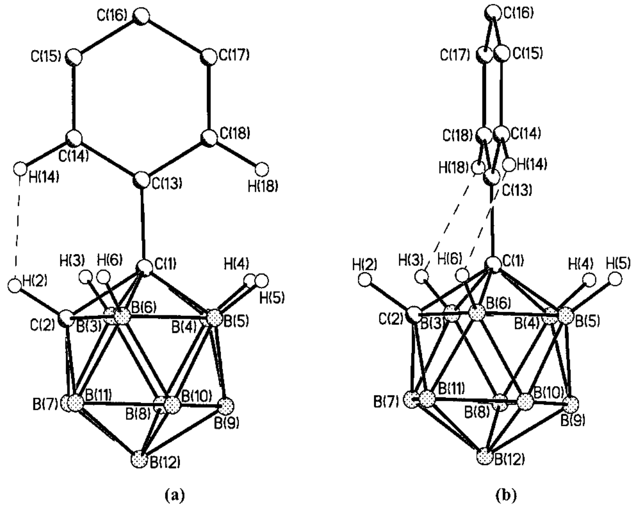

Figure 1. The general view and the numbering scheme of two limiting conformations of **1** with θ angles equal to 0° (a) and 90° (b); hydrogen atoms that do not participate in H···H contacts are omitted for clarity

Clearly, due to the low barrier of rotation, no significant back-donation from the phenyl group is expected, although we cannot exclude that this effect may be noticeable in the conformation with θ = 90° because, in this case, the π-density of the phenyl ring is positioned right above the $C_{carb}-C_{carb}$ bond, which makes charge transfer from the phenyl π-system to the antibonding orbital of the $C_{carb}-C_{carb}$ bond possible.

Results and Discussion

To investigate the nature of the $C_{carb}-C_{carb}$ bond elongation in mono- and diaryl-substituted *o*-carboranes we traced the changes in the icosahedron structure accompanying the phenyl ring rotation. We used a potential energy surface (PES) scan with the density functional B3LYP method at the 6−31G** level of theory along the coordinate corresponding to the above-mentioned torsion angle, changing from 0° to 90° in 10° steps with a full optimization of other geometric parameters at each step. The electron density distribution (EDD) properties and the most important bond lengths are summarized in Table 1.

The global minimum on the PES corresponds to the structure with θ = 30.2° which is close to the value obtained from the HF calculation (25°)[9] and is in good agreement with the experimental values (18° and 22°).[9,10] The geometry of the icosahedron obtained from the B3LYP calculation, in contrast to the HF one, is in excellent agreement with the X-ray diffraction data for the β form. In particular, the C(1)−C(2) bond length, according to HF and DFT calculations, and X-ray diffraction data, is equal to 1.626, 1.645 and 1.640 Å, respectively.

The estimated barrier to rotation of the phenyl ring is even lower (about 1.2 kJ·mol^{-1}) than reported earlier and the energy difference for the ideally eclipsed conformation (θ = 0°) and the conformation with θ = 90° becomes as low as 0.152 kJ·mol^{-1} (see Table 1).

To analyze the peculiarities and the nature of the intramolecular interactions in **1** we performed topological analysis of the EDD function $\rho(r)$ within Bader's "Atom in Molecules" theory (AIM).[11] Among the benefits of the AIM theory in analysis of the nature of the interactions is the availability of a clear definition of the chemical bonds and their properties in terms of the topological properties of the $\rho(r)$ function.

The characteristic set of critical points (CPs) contains CPs (3,−1) in the interatomic area of all expected chemical bonds, namely B−B, $C_{carb}-B$, $C_{carb}-C_{carb}$, $C_{ph}-C_{carb}$, $C_{ph}-H$, $C_{carb}-H$ and B−H. In addition, in line with the Poincaré−Hopf relationship[11] CPs (3,+1) were found for all triangular faces of the carborane icosahedron and in the center of the phenyl ring and, finally, CP (3,+3) was found in the center of the cage. Taking into account that in all bonds (with the exception of the $C_{carb}-B$ bonds, where the boron atom is bonded to one carbon atom), the Laplacian of the electron density $\nabla^2\rho(r)$ in CPs (3,−1) is negative, we may conclude that these bonds correspond to "shared-type" interatomic interactions. The other $C_{carb}-B$ bonds are characterized by the positive values of the $\nabla^2\rho(r)$ (0.1161−0.1511 a.u.)[12] in the CPs (3,−1). Taking into account the negative values of the electron energy density $h_e(r)$ [13] (−0.1022 to −0.1017a.u.) for these bonds, they may be considered as corresponding to the "intermediate type" of interatomic interactions.[11a] It should be noted that the values of the electron density in CPs (3,−1) for the $C_{carb}-B$ (0.1170−0.1214 a.u.) and B−B (0.1156−0.1235 a.u.) bonds are close to the corresponding values in CP (3,+1) (0.1099−0.1160 a.u.) for the triangular edges. For the $C_{carb}-C_{carb}$ bond the electron density is noticeably higher (0.1799 a.u.), as was found earlier for both small carboranes and icosahedral ones.[6,14,15] For comparison, the values of

Table 1. The relative energies and important geometrical and topological parameters of **1** in CPs (3,−1) at different θ angles

θ	ΔE (kJ·mol^{-1})	C(1)−C(2) (Å)	C(1)−Ph (Å)	C(2)···B(3) (Å)	C(2)···B(6) (Å)	$\rho(r)$ [C(1)···C(2)] (a.u.)	$\nabla^2\rho(r)$ [C(1)···C(2)] (a.u.)
0	1.006	1.641	1.510	1.714	1.715	0.1816	−0.1819
10	0.620	1.642	1.511	1.713	1.716	0.1813	−0.1808
20	0.584	1.642	1.511	1.713	1.716	0.1812	−0.1801
30.2	0.000	1.645	1.512	1.712	1.717	0.1799	−0.1754
40	0.318	1.648	1.513	1.711	1.717	0.1789	−0.1710
50	0.860	1.652	1.514	1.711	1.717	0.1773	−0.1648
60	0.866	1.657	1.514	1.710	1.713	0.1754	−0.1568
70	1.162	1.663	1.514	1.708	1.711	0.1735	−0.1494
80	1.123	1.669	1.513	1.706	1.708	0.1713	−0.1408
90	1.158	1.672	1.513	1.705	1.706	0.1703	−0.1369

$\rho(r)$ (0.3082−0.3136 a.u.) in CPs (3,−1) for $C_{ph}-C_{ph}$ bonds are significantly higher than the corresponding values in CP (3,+1) (0.0202 a.u.) in the center of the phenyl ring.

At the same time, as a result of the forced H···H interactions between the hydrogen atoms of the phenyl ring and the carborane cage, some additional critical points appear. Starting from θ = 0° we found CP (3,−1) between the H(2) and H(14) atoms. Also, one CP (3,+1) appears as the result of the six-membered-ring formation. The distance between the hydrogen atoms is 2.007 Å. Although other H···H contacts H(4)···H(18) and H(5)···H(18) are about 0.4 Å longer (2.424 Å each) they do not correspond to attractive interactions. Rather small values of $\rho(r)$, positive values of $\nabla^2\rho(r)$ and positive values of $h_e(r)$ point to a "closed-shell" type of interaction for these two contacts.

The value of $\rho(r)$ in the CP (3,−1) for the H(2)···H(14) contact, equal to 0.0117 a.u., and other topological EDD parameters are close to those obtained for similar H···H interactions found in the biphenyl molecule [the $\rho(r)$ value is equal to 0.0136 a.u.][16a] and different polybenzoid compounds.[17] In spite of the fact that the validity of the analysis of $\rho(r)$ within AIM theory for weak interactions was at one point debatable,[16] later comparison of the $\rho(r)$ topology and potential energy density distribution function resolved this controversy:[11b] it was demonstrated by Bader that each bond path in the electron density is mirrored by the virial path, a line of maximum potential energy density, which, in turn, indicates that the presence of the bond path or critical point (3,−1) between the pair of atoms in question is the "universal indicator of bonding between atoms".[11b] Thus, H···H interactions observed both for the $\rho(r)$ and potential energy density functions lead to additional stabilization of the molecules (up to 46.9 kJ·mol^{-1} in chrysene).[17] The barrier to rotation of the ring in biphenyl is about 6.7 kJ·mol^{-1},[16a] which is only slightly higher than in **1**.

In this paper we have traced in detail the changes in the intramolecular contact network as a result of the phenyl ring rotation. For all conformations investigated intramolecular H···H distances that are significantly shorter than the sum of the van der Waals radii[18] were found. Surprisingly, the shortest H···H contact (2.007 Å) was observed for the $C_{carb}-H\cdots H-C_{ph}$ interaction at θ = 0°, while the minimum value for the H···H distance among all $C_{ph}-H\cdots H-B$ contacts is 2.023 Å at θ = 70° (see Table 2). At θ = 30° the $C_{carb}-H\cdots H-C_{ph}$ contact disappears and only $B-H\cdots H-C_{ph}$ contacts are present. The possibility of $B-H\cdots H-C_{ph}$ contact formation is more evident because the difference in the atomic charges of the hydrogen atoms in this case is higher than that for the $C_{carb}-H\cdots H-C_{ph}$ contact.

We also determined the contact interatomic separation (CIS) — the distance between two nuclei at which a "fold catastrophe" occurs.[16a] At the CIS distance the values of the electron density and its Laplacian become equal in the CPs (3,−1) and (3,+1), leading to loss of the interatomic

Table 2. Important geometrical and topological parameters in CPs (3,−1) of the intramolecular $C_{ph}-H\cdots H-C$ and $C_{ph}-H\cdots H-B$ contacts

θ	H(14)···H(X) (Å)	X[a]	$\rho(r)$ (a.u.)	$\nabla^2\rho(r)$ (a.u.)	H(18)···H(Y) (Å)	Y[a]	$\rho(r)$ (a.u.)	$\nabla^2\rho(r)$ (a.u.)
0	2.007	2	0.0117	0.0467				
10	2.030	2	0.0113	0.0460	2.264	4	0.0093	0.0363
20	2.086	2	0.0107	0.0452	2.166	4	0.0104	0.0389
30.2					2.106	4	0.0113	0.0412
40	2.232	6	0.0100	0.0391	2.092	4	0.0115	0.0419
50	2.110	6	0.0117	0.0440	2.122	4	0.0111	0.0412
60	2.041	6	0.0128	0.0466	2.206	4	0.0101	0.0386
70	2.023	6	0.0139	0.0472				
80	2.043	6	0.0127	0.0468	2.266	3	0.0100	0.0407
90	2.105	6	0.0119	0.0452	2.134	3	0.0115	0.0442

[a] X and Y are the number of hydorgen atoms, according to Figure 1.

interaction line. Because of the large value of the increment used during the PES scan we could not determine precisely the CIS value for the B−H···H−C_{ph} interaction. Nevertheless, according to our estimations its value is about 2.27 Å, which is higher than the corresponding value obtained for the corresponding contact in biphenyl (2.179 Å).[16a,17] This can be explained by an increase of the electron density near the H atom of the B−H group in comparison to the C_{carb}−H one. This result confirms the supposition of other authors about the nontransferability of these values between different systems.[16a]

As concerns the X−H···H and H···H−C_{ph} bond angles of the X−H···H−C_{ph} (X = B or C_{carb}) interactions, they vary in the range 111.7−129.0° for the H···H−C angle and 99.8−118.8° for the X−H···H one. These values may be compared to those obtained for the intermolecular contacts of the B−H···H−N type for which the B−H···H angles are 95−115° and the N−H···H angles are equal to 150−170°.[19]

Despite almost unrestricted rotation of the phenyl ring and variation of the strength and number of the H···H contacts, we noticed some other changes in the carborane-cage geometry, accompanying the rotation of the phenyl group. The most dramatic change is the increase of the C(1)−C(2) bond length from 1.641 Å at $\theta = 0°$ to 1.672 Å at $\theta = 90°$; the C(2)−B(3) and C(2)−B(6) distances decrease by only 0.009 Å each. Other bonds, including the C(1)−C(13) one, do not vary so significantly (only within 0.004 Å) and the C(14)−C(13)−C(18) *ipso* angle increases by 0.2°. Despite these geometric changes, the character of the chemical bonding for the C_{carb}−C_{carb} bond remains invariable [the value of $\nabla^2\rho(r)$ varies from 0.1816 to 0.1703 a.u.].

In contrast to these data, the C(2)−B(3) and C(2)−B(6) bonds are more sensitive to changes in the icosahedron. At a θ value close to 90°, the $\nabla^2\rho(r)$ values in CPs (3,−1) are close to zero (0.0016 and 0.0023 a.u.). This result suggests a change of the bonding nature from the shared type to an intermediate one, thus indicating that small variations of the C_{carb}−C_{carb} bond strength are sufficient for the change of the B−C_{carb} bonding type.

At the same time the C_{carb}−C_{carb} bond elongation causes not only an expected decrease of the $\rho(r)$ and the absolute $\nabla^2\rho(r)$ values but also a substantial increase of its ellipticity from 0.79 at $\theta = 0°$ to 0.96 at $\theta = 90°$. The difference between the C_{carb}−C_{carb} bond path length and the corresponding interatomic distance is less than 0.001 Å at $\theta = 0°$ and does not increase at $\theta = 90°$. The same difference for the C_{carb}−B_{carb} bonds is substantially bigger and, for instance, at $\theta = 90°$ it is equal to 0.114 Å. Thus, the C_{carb}−C_{carb} bond lengthening does not lead to a shift of the CP from the interatomic line; the high ellipticity value indicates either "banana bonding" or a substantial contribution of the π component.[20]

The minimum on the PES corresponding to the structure with $\theta = 30.2°$ is characterized by only one intramolecular B(4)−H(4)···H(18)−C(18) closed-shell interaction, with an interatomic separation equal to 2.106 Å. The phenyl ring is slightly inclined away from the contacting hydrogen atoms, with the B(4)−C(1)−C(13) angle equal to 118.2° The value of $\rho(r)$ at the CP (3,−1), equal to 0.0115 a.u., is slightly less than that in the biphenyl (0.0136 a.u.). At $\theta = 70°$ the corresponding interaction is even stronger, as is clear from the shorter distance between the hydrogen atoms (2.023 Å) and the maximum value of $\rho(r)$ (0.0139 a.u.). This conformation, however, does not correspond to the local minimum on the PES. Evidently, the total energy decrease related to this interaction is neutralized by energy inputs related to the lengthening of the C_{carb}−C_{carb} bond.

What is the reason for this C_{carb}−C_{carb} elongation? Starting with a θ value equal to 40°, at which the substantial growth of the C_{carb}−C_{carb} bond occurs (see Figure 2), the back-donation of the π-electron density of the phenyl ring to the anti-bonding C_{carb}−C_{carb} orbital becomes geometrically possible. It should be noted that the lengthening of the C_{carb}−C_{carb} bond is accompanied by an increase of its ellipticity, which can be explained by an increase of the π-bond contribution. At the same time the C_{carb}−C_{ph} distance and the *ipso* angle do not change, which allows us to conclude that the extent of such an interaction is rather small.

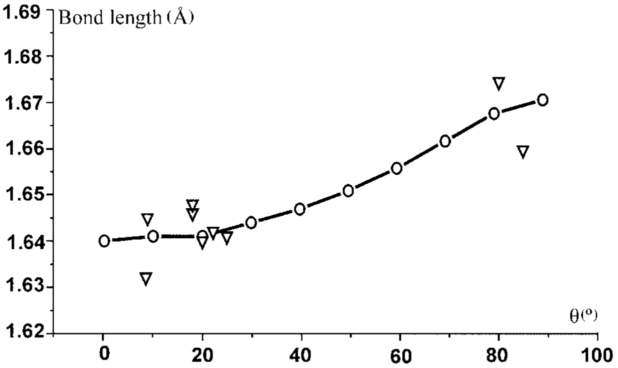

Figure 2. A plot of C_{carb}−C_{carb} bond length values vs. θ angles: the theoretical curve (circles) and the experimental data for phenyl-substituted *o*-carboranes (triangles)

To estimate if it is really observable we performed additional calculations on two derivatives of **1** with substituents in the phenyl ring in the *para* position with respect to the carborane cage. Two compounds were studied: with positive [NH_2 (**2**)] and negative [NO_2 (**3**)] mesomeric effects, their optimization was performed at the same level of theory using the same basis set for the conformation with a θ angle equal to 90°. The obtained data confirm the presence of the charge transfer from the phenyl ring to the antibonding orbital of the C−C bond. Thus, according to our calculations, at $\theta = 90°$ the C_{carb}−C_{carb} bond length in **2** is higher (1.680 Å), and in **3** is lower (1.669 Å) than in **1** (1.672 Å). It should be noted that the bond ellipticities for these derivatives also differ and are equal to 1.01 and 0.93 for **2** and **3**, respectively (in **1** at $\theta = 90°$ it is equal to 0.96). It should be noted that this effect cannot be explained by the alternation of the inductive effect of the substituted phenyl group that was checked for compounds **2** and **3** in the conformation with θ = 0°. In this case, the value of the $C_{carb}-C_{carb}$ bond length coincides with that in **1**.

Using ellipticity values for the $C_{carb}-C_{carb}$ bond in **1** at different values of the θ angle and the same values in **2** and **3** at θ = 90° we found a linear correlation between the bond length and its ellipticity (see Figure 3). Such a correlation is characteristic of multiple bonds but not banana bonds, as in cyclopropane for example.[20] The observed ellipticity increase with the increase of the $C_{carb}-C_{carb}$ bond length is quite surprising and points to the unusual character of the bonding in *o*-carboranes.

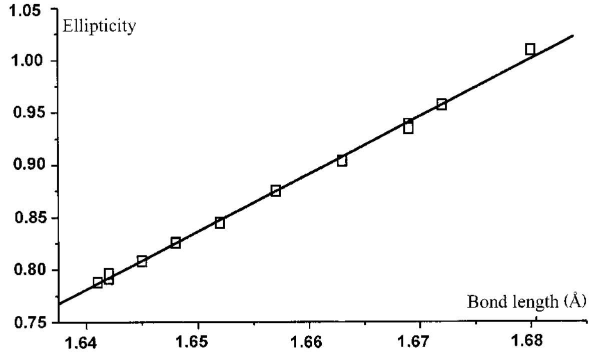

Figure 3. A plot of $C_{carb}-C_{carb}$ bond ellipticity vs. length; the dependence can be approximated by the linear function $y = 5.49105x - 8.22407$; the extrapolation to zero ellipticity gives a value of 1.50 Å for the bond length

Taking into account the low barrier to the rotation of the phenyl ring in **1** it is possible to suggest that the observed $C_{carb}-C_{carb}$ bond alternation accompanying rotation of the phenyl ring should also be observed in the crystal structures of different derivatives containing such a fragment.

To check our supposition we performed a search in the Cambridge Crystallographic Data Base[21] for ordered structures containing Ph-*o*-carborane fragment without other substituents in the carborane icosahedron, and with an *R* factor lower than 10% (five structures were found with REFCODEs FOSSIP,[22] NURLER,[23] TAVNAF,[24] ZUHTOL[10] and ZUHTOL1;[9] eight values were used). All analyzed values (bond lengths vs. θ angles) were found to be in good agreement with the theoretical curve, except for one value (not shown) in the crystal structure of FOSSIP, where the abnormally short $C_{carb}-C_{ph}$ bond length points to possible unresolved disorder of the phenyl ring. In Figure 2 the experimental and theoretical values are plotted against θ. It can be seen that a direct correlation exists between these values that allows one to predict the bond length value if the torsion angle, θ, is known.

Thus, both the theoretical and experimental data point to the fact that the dependence of the $C_{carb}-C_{carb}$ bond length on the torsion angle is caused by charge transfer from the phenyl ring to the antibonding orbital of this bond. A further question then arises: what can these results contribute to an explanation of the $C_{carb}-C_{carb}$ bong length elongation in 1,2-diphenyl-*o*-carborane (**4**)? Taking into account that the phenyl rings in **4** are almost perpendicular to the $C_{carb}-C_{carb}$ bond (θ values are equal to 81.5°/84° and 84°/89° for two independent molecules), and assuming that electron transfer has an additive effect, we obtain a value of 0.06 Å for the lengthening of this bond. Assuming also the inductive effect of the substituent replacement of the CH by the CPh group in the *o*-carborane according to B3LYP calculation,[25] which leads to an increase of the $C_{carb}-C_{carb}$ bond by approximately 0.02 Å at θ = 0°, we obtain a total value of 0.1 Å as the bond length difference between these compounds. Adding this value to the one for the $C_{carb}-C_{carb}$ distance in *o*-carborane (1.619 Å) leads to the bond length 1.720 Å, which is close to the experimental values for **4**.[7] At the same time, the difference in the $C_{carb}-C_{carb}$ bond in **4** [1.720(3) and 1.733(3) Å] can also be explained by the difference in the torsion angles: the shorter value is observed for the molecule with θ values deviating more from 90°.

Thus, the present study with the use of computational methods clearly shows that charge transfer from the phenyl ring to the carborane icosahedron exists and allows us to conclude that the $C_{carb}-C_{carb}$ bond in the *o*-carborane is characterized by a rather high π-component and that the bond length variation is caused not only by steric reasons but also electronic ones.

The presence of such an interaction is of interest from both theoretical and practical points of view. In particular, taking into account the high thermal stability of the carboranes, similar systems are of great interest for creation of new NLO materials.[26] Preliminary estimations show that the values of the first molecular hyperpolarizability for **2** is only slightly smaller than that in *p*-nitroaniline.[27] The study of 1,2-diaryl-*o*-carborane derivatives, like triazinyl-*o*-carboranes [the $C_{carb}-C_{carb}$ bond length is 1.712(3) Å],[28] in which the position of the aryl groups is constrained due to steric effects, might be promising for the design of NLO materials, and this will be the subject of our further investigations.

Computational Details

Ab initio calculations of **1−3** were performed with the Gaussian 98 program package[29] at the B3LYP level of theory. A potential-energy scan with C_1 symmetry of the molecules was carried out constraining one torsion angle and with full optimization of the other geometric parameters, with the 6−31G(d,p) basis set starting from the X-ray diffraction geometry. The torsion angle was changed in 10° steps starting from 0° up to 90°, except for 30°, because the value of 30.2° corresponds to the global minimum. As convergence criteria the normal threshold limits of 4.5×10^{-4} and 1.8×10^{-3} a.u. were applied for the maximum force and displacement, respectively. To enhance the B3LYP calculation accuracy the pruned (99,590) grid (keyword Grid=Ultrafine) was used. Topological analysis of the $\rho(r)$ function was performed using the MORPHY 98 program[30] based on the wavefunctions obtained from the B3LYP calculations.

Acknowledgments

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