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Pioneering the Power of Twin Bonds in a Revolutionary Double Bond Formation. Unveiling the True Identity of *o*-Carboryne as *o*-Carborene

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Dedicated to Professors Evamarie Hey-Hawkins, Rainer Streubel and Manfred Scheer on the occasion of their retirement, celebrating their exceptional contributions to p-block chemistry through groundbreaking research

The homolytic elimination of two H atoms from two adjacent carbons in benzene results in the aromatic product *o*-benzyne. In a similar way, the homolytic elimination of two H atoms from the two adjacent carbons in 1,2-$C_2B_{10}H_{12}$ results in the aromatic product *o*-carboryne. In this work, we provide experimental and computational evidences that despite the similarity of *o*-carboryne and *o*-benzyne, the nature of the C–C bond generated between two adjacent carbons that lose H atoms is different. While in *o*-benzyne the C–C bond behaves as a triple bond, in *o*-carboryne the C–C bond is a double bond. Therefore, we must stop naming 1,2-dehydro-*o*-carboryne as *o*-carboryne but instead call it *o*-carborene.

Introduction

The phenyl group is present in almost 45 % of small molecule-based therapeutic drugs on the market. It is the most abundant aromatic group followed at a distance by the pyridine heterocycle. The reasons for the ubiquity of the phenyl group are well defined,[1] but central to this work is that its substituents project outwards along a line passing through the centre of the aromatic cycle and the carbon atom of the ring, thus avoiding stereochemical problems. The *o*-carborane, which has three isomers, i.e., *ortho*- (*o*-), *meta*- (*m*-) and *para*- (*p*-) $C_2B_{10}H_{12}$, has some similarities with the phenyl group. For example, both are very stable as they are aromatic abiding Hückel's rule,[2] and both are also lipophilic, a property of relevance in drug design. As in benzene, the substituents also project radially out of the core by a line passing through the centre of the icosahedron and through a B or C atom at its vertices. Because the projection of the icosahedron on a surface is a hexagon and the benzene itself is a hexagon there is an unfounded assumption that the *o*-carborane occupies the same volume as the phenyl when this latter rotates around one of its axes. This is not the case, as the volume of rotating benzene (vdW) is 102 Å^3, while that of the *o*-carborane varies between 141 (*o*-) and 148 (*m*-) Å^3.[3] However, this conceptualization of the *o*-carborane/benzene is prevalent among researchers and many compounds have been synthesized in which a phenyl group is replaced by an *o*-carborane. A paradigmatic example is Asborin, which is the carborane analogue of Aspirin,[4] although they do not do the same task. While Aspirin relieves inflammation because it inhibits the enzymes in the body COX-2 and COX-1, Asborin does not inhibit any of the two COX variants but is a potent aldo/keto reductase 1 A1 (AKR1 A1) inhibitor.[5] Other examples of direct substitution of the phenyl group by an *o*-carborane can be found in the literature.[3]

The isosteres concept relates to one of two or more substances that exhibit similarity of some properties as a result of having the same number of total or valence electrons in the same arrangement and that consist of different atoms and not necessarily the same number of atoms. *o*-Carborane and benzene are not isosteres,[6] and in general are not bioisosteres. This does not exclude the possibility that they may give rise to other therapeutic drugs. Among other reasons, the different behavior of the *o*-carborane and the benzene is due to the non-equivalence of a carboranyl with a rotating phenyl. Both are aromatic, which is expressed in several ways, one of them

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preserving the original structure following an electrophilic aromatic substitution. But despite these similarities due to the aromaticity, it is neither conceptually simple to imagine nor experimentally easy to demonstrate that the *o*-carboranyl group is an isostere of the phenyl group. Figure 1 shows a benzene (C_6H_6) and two molecules with the same number of heavy atoms, biphenyl ($C_{12}H_{10}$) and *o*-carborane (1,2-$C_2B_{10}H_{12}$). It is clear that *o*-carborane is not isosteric to biphenyl and much less a mimic to benzene. The dimensions of the connectivities are important and we will see this clearly by discussing two very relevant reagents, *o*-benzyne and *o-carboryne.* The latter is indicated in italics in the following pages in order to maintain the nomenclature adopted so far with respect to *o*-benzyne, but we will finally prove that it is in fact a carborene. Earlier work has already shown that 3D aromaticity does not match 2D aromaticity.[2d,7] And, why is that?

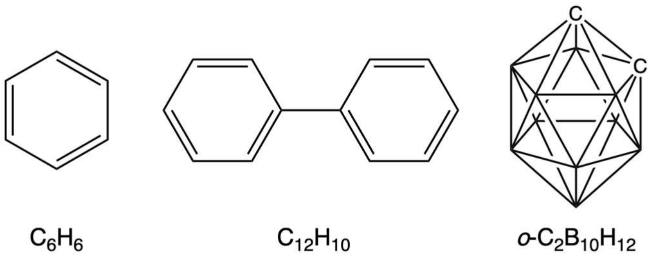


Figure 1. Structures of benzene, biphenyl and *ortho*-carborane.

If we take 1,2-$C_2B_{10}H_{12}$ as a 3D aromatic model, we see that the C–C bond distance is far from being the conventional one in organic common structures. The C–C distance in 1,2-$C_2B_{10}H_{12}$ is 1.64 Å, that corresponds to a bond order of 0.74 following the bond distance/bond order correlation established by Linus Pauling $n_x = n_o \exp((r_o - r_x)/c)$, where the bond order n_x of a bond of length r_x is a function of a reference bond of length r_o, whose bond order is defined as n_o. This matches precisely with the Jemmis computed 0.74 bond order.[8] The C–C 0.74 bond order in 1,2-$C_2B_{10}H_{12}$ is definitely much less than a single C–C bond. Conversely the pK_a of 1,2-$C_2B_{10}H_{12}$ is very similar to that of the acetylene ($pK_a \approx 24$). These data are at odds with each other, a triple bond against less than a single bond but similar pK_a is simply a realization that in this case what influences the pK_a is not the bond order between the two carbon atoms but the hybridisation on the carbon, which is sp both in the *o*-carborane and in the acetylene. This may have given rise to mistaken interpretations such as considering that two aromatic units that fuse together give rise to another aromatic unit, although this is valid for two units of the same 2D/2D or 3D/3D aromaticity, but not 2D/3D.[2d]

Results and Discussion

Preliminary discussion. Comparison of *o*-benzyne with *o*-carboryne

o-Benzyne was first introduced as a reactive intermediate in 1927.[9] Since then, many investigations on this reagent have followed. Figure 2 shows three possible models for *o*-benzyne. A nice and competent description is given as "The Benzyne Story".[10] In this work, we will limit ourselves to those aspects that will be relevant to our discussion of *o-carboryne.*[11] In a similar way as the homolytic elimination of two H atoms from two adjacent carbons in benzene generates *o*-benzyne, which is aromatic, the same applies when two H atoms are eliminated from the two adjacent carbons of 1,2-$C_2B_{10}H_{12}$ to make *o-carboryne*, which is also aromatic. Geometric constraints on the triple bond in *o*-benzyne result in diminished overlap of in-plane sp-orbitals, and thus a weak triple bond. Indeed, the vibrational frequency of the triple bond in *o*-benzyne was assigned to be 1846 cm^{-1}, confirming the weaker triple bond than in unstrained alkyne with vibrational frequency of approximately 2150 cm^{-1}. Nevertheless, *o*-benzyne is more like a strained alkyne than a diradical, as seen from the large singlet–triplet gap and alkyne-like reactivity. On the other hand, the 12-vertex *o*-carborane, 1,2-$C_2B_{10}H_{12}$[11–12] (Figure 3), is an outstandingly stable molecule whose strength derives both from its aromatic character and from the fact that it has a base structure, the icosahedron, which is one of the platonic solids.[2f] Although *o*-carborane has 3D-aromaticity,[13] its aromaticity can be related to 2D Hückel aromaticity as was recently demonstrated.[2b]

It is necessary to see whether, despite the similar reactivity between *o*-benzyne and *o-carboryne*, the compounds generated are comparable. In the two cases, the HOMO and the LUMO orbitals are mainly the bonding and antibonding orbitals of the bond formed after removal of two H atoms (Figure S7 in the Supporting Information). However, and taken as an example, the pK_a of the *o*-carborane is very similar to that of acetylene, but the products resulting from the reactivity of the C–H bond have very different properties. Or the reaction of *o*-benzyne (aromatic) with two alkynes [2+2+2] gives rise to naphthalene (global aromatic), while the same reaction but with *o-carboryne*

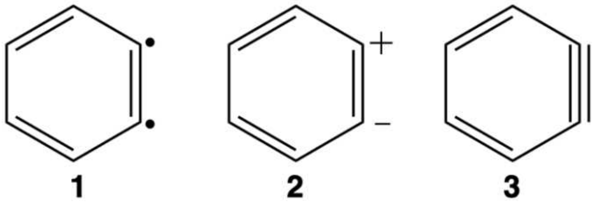


Figure 2. The different representations of *o*-benzyne.

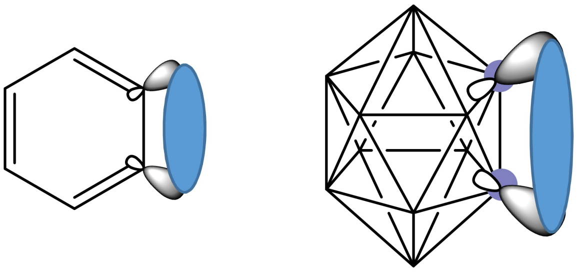


Figure 3. The molecular structures of *o*-benzyne (left) and *o-carboryne* (right), stressing that distance matters.

(aromatic) gives rise to benzeno-*o*-carborane, with local aromaticity on the carborane only.[14] This result highlights the relevance of the main scaffolding bonds in the outcome of the reaction despite having very similar reactivities.

In comparing the *o*-benzyne and the *o-carboryne*, it is seen that structurally the length of the *o*-benzyne's triple bond (1.24 Å) is closer to that of a typical triple bond (1.20 Å, acetylene) than to a double bond (1.34 Å, ethylene) and much less than the C–C in benzene (1.39 Å). If we contemplate again the Pauling's bond distance/bond order, the C≡C triple bond of *o*-benzyne has a 2.71 bond order, close to a triple bond. If we compare this value (2.71) with the C–C bond order of benzene (1.67), we see that they differ by 1.04 units. Almost a perfect bond order unit. If we make the same comparison between the *o-carboryne* and the *o*-carborane, we observe $1.84-0.74=1.10$. As the bond order should not exceed unity this would suggest that the formation of the sp-sp bond in the *o*-carborane to yield the *o-carboryne* exhalts the underlying bond order in the *o*-carborane from 0.74 to 0.84. This is consistent with a higher contribution of a 2c–2e in the CC, as shown in Figure 4 that bestows a marked C=C character, but definitely not C≡C. The formation of the additional sp-sp bond causes more electron density to build up in the CC connection, pinning a 2c–2e bond thus making it closer to a conventional double bond. It is therefore not surprising that this carboranyl-CC bond acts towards metals as a typical alkene-metal interaction,[15] being $(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)_2$ and $(\eta^2\text{-}C_2B_{10}H_{10})Cl_2Zr(THF)_3$ remarkable examples.[14a,16] However, upon the coordination of the C–C to metal the bond order in $(\eta^2\text{-}C_2B_{10}H_{10})Ni(PPh_3)_2$ drops to 1.06 from 1.84 in *o-carboryne* (Figure 4). This is practically a 0.8 loss of bond order. Excessive! Losses between 0.2 and 0.6 in bond order between an alkene and a coordinated alkene are not surprising, but the observed loss of 0.8 is so large that it must be accounted for by the loss of the 2c–2e from which had been pinned between the C–C of the *o-carboryne*. This suggests that it is the C–C sp-sp bond that interacts with the metal and ultimately the *o*-carborane returns to the comfort zone provided by its aromatic stabilization energy (ASE). The electron pinning is not only observed in *o-carboryne*, but also with *o*-benzyne although in this case it is observed in its complex with a metal, proven with a crystal structure. For *o*-benzyne in its coordination to Ta, the trapping has been so great that a loss of aromaticity has been observed with the failing to equalize distances, thus a propensity to cyclohexatriene has been observed. In 1979, Schrock and co-workers reported the synthesis and crystal structure of $Ta(\eta^5\text{-}C_5Me_5)(C_6H_4)Me_2$ in which the C–C distances alternate between 1.36 and 1.41 Å, C_1–C_2 1.364 (linked to Ta), C_2–C_3 1.410, C_3–C_4 1.362, C_4–C_5 1.403, C_5–C_6 1.375, and C_6–C_1 1.408 Å.[17] This definitely proves that although the third bond, the sp-sp, of the triple bond is orthogonal to these π orbitals bestowing aromaticity, its existence affects the aromaticity of the system.

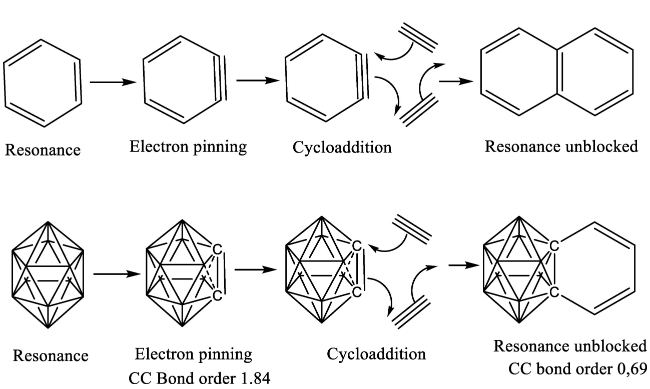


Figure 4. Comparison between *o*-benzyne and *o-carboryne*.

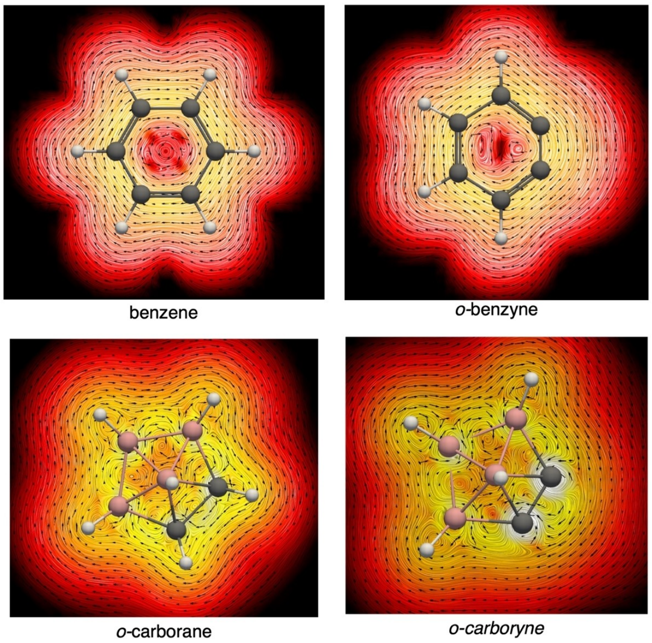
Thus, this process in which the double bond is highly localized before the reaction and reverts to delocalization after the reaction would agree with the statement above on the non-comparable results following reaction between *o*-benzyne and *o-carboryne*.[18] And next, what is the difference between *o-carboryne* and *o*-benzyne when involved in a cycloaddition reaction that could lead to the fusion of two aromatic halves? In the case of *o*-benzyne there is a strong scaffolding that does participate in the aromaticity, and two adjacent sp atomic orbitals each one holding a single electron that are orthogonal to the aromatic π-system. There may be pinning but at the moment that the cycloaddition is generated the initial aromatic system is unblocked generating two aromatic units, e.g., naphthalene (Figure 4). What happens to the *o-carboryne*? *o-carboryne* does not have a strong scaffolding, it has a system that when the sp-sp bond is formed determines a partial blockage of the aromatic system, favouring a C–C 2c–2e bond ready to participate in cycloaddition reactions.[12,19] Once this takes place, the scaffolding of the *o*-carborane is unblocked, eliminating the C=C and therefore generating a non-aromatic cyclic system and an aromatic cluster. Therefore, a full 3D/2D aromatic system can never occur, in contradiction to the recently reported experimental results of 3D/2D bonding.[7,19a] Thus we have studied again what could be the causes of the misinterpretation of the NICS and ASE in the *o*-carborane-fused carbo- and heterocycles.

Comparison of o-benzyne to *o*-carboryne

The above results support the particularity of the sp-sp generated double bond in *o-carboryne*, which is not the typical σ or π bond, and it should be of a strength comparable to the third bond in *o*-benzyne. Therefore, the new bonds in *o*-benzyne and *o-carboryne* are not conventional, and not precisely equal. However, the new sp-sp bond either in *o*-benzyne or *o-carboryne* does not prevent the aromaticity of $C_2B_{10}H_{12}$ or benzene; and in this way the Wade-Mingos rule[20] continues being fulfilled as the number of electrons of the cage is not affected. Importantly, this aromaticity appears to be strengthened from benzene to *o*-benzyne according to both electronic-based aromaticity MCI (from 0.072 to 0.077 a.u.), as well as by magnetic-based NICS(0) (from −8.1 to −18.1 ppm, see Table 1). And the same trend is observed from *o*-carborane to *o-carboryne*, with an apparent strengthening of aromaticity (Table 1). At this point, it must be pointed out the ring-size dependency of NICS.[21] The NICS values are higher for smaller

Table 1. NICS (in ppm) and MCI (in au) of benzene and *o*-benzyne, together with NICS of *o*-carborane and *o-carboryne*.

	NICS(0)	$\text{NICS}(0)_{zz}$	NICS(1)	$\text{NICS}(1)_{zz}$	MCI
benzene	−8.1	−14.6	−10.2	−29.2	0.072
o-benzyne	−18.1	−31.2	−12.8	−33.0	0.077
	$\text{NICS}(B_4C)$	NICS(center)			
o-carborane	−33.3	−27.3			
o-carboryne	−40.5	−35.4			


benzene

o-benzyne

o-carborane

o-carboryne

Figure 5. Top: current-density vector field of benzene and *o*-benzyne, with currents at 1 Å above the molecular plane, perpendicular to the magnetic field vector ($\vec{B}$). Bottom: current-density vector field of *o*-carborane and *o-carboryne*, with currents at the central molecular plane (see additional plots in Figures S1–S4 in the Supporting Information), perpendicular to the magnetic field vector ($\vec{B}$). Colour code: dark red – zero intensity; red – low intensity; yellow – high intensity.

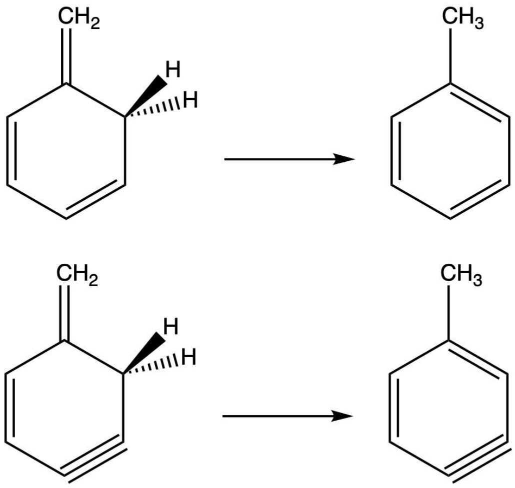


Figure 6. Isomerization stabilization energies of toluene (top) and 4-methyl-benzyne (bottom) are −33.9 and −26.6 kcal mol^{-1}, respectively.

rings, so the more negative NICS of *o*-benzyne and *o-carboryne* could be in part attributed to the ring size shrink. Moreover, the increase in the aromaticity when going from benzene to *o*-benzyne and from *o*-carborane to *o-carboryne* is not observed by means of the computed magnetic induced current densities (Figure 5). It can be observed how the intensity of the currents is similar or somehow reduced when going from benzene to *o*-benzyne, with the main change next to the two carbon atoms from which the H atoms have been removed to form the triple bond. And the same is found when comparing the ring currents of *o*-carborane and *o-carboryne.* Furthermore, isomerization stabilization energies (ISEs) of toluene show a reduction of the aromaticity of the benzene ring when going from toluene to 4-methyl-benzyne (Figure 6). As a whole, various indicators of aromaticity provide different trends, but, in general, it can be concluded that the aromaticity of the ring in benzene and the cage in carborane slightly changes when *o*-benzyne and *o-carboryne* are formed.

Back to the bonds, despite the C–C bond length shortening from *o*-carborane to *o-carboryne* (16.5 %) is larger than from benzene to *o*-benzyne (10.8 %), which might mean a stronger interaction (Table 2 and Figure 7) and is in support of the pinning in electron density in the C–C bond in *o-carboryne*, the delocalization indices[22] support the double bond character of *o-carboryne* (DI = 1.883) versus the triple bond character of *o*-benzyne (DI = 2.249). For completeness, we calculated WBI[23] and MBO[24] bond orders that give the same trends as DI (Table 2). Noticeably, this is further confirmed by computed ^{13}C NMR chemical shifts, with that of *o-carboryne* close to benzene (128.8 and 125.9 ppm, respectively), whereas the chemical shift of *o*-benzyne is much more deshielded (188.4 ppm). In addition, through a fragment analysis (Figure 8), we have computed the overlap between the sp-sp molecular orbitals of *o-carboryne* and compared to the sp-sp of *o*-benzyne to form the corresponding HOMO orbitals. These overlaps further support the stronger interaction present in *o*-benzyne (0.218) than in *o-carboryne* (0.130), despite the bond length shortening in the latter is larger. The reason is the fact that the C–C distance in benzene is already shorter, and thus it is more difficult to shorten it further when generating *o*-benzyne.

Table 2. C–C bond length (in Å) and C–C delocalization index (in au), together with percentage in which C–C bond length is decreased from *o*-carborane to *o-carboryne*, and from benzene to *o*-benzyne. Wiberg Bond Index[23] and Mayer Bond Order[24] have been included for comparison. Computed ^{13}C NMR chemical shifts (in ppm) are also included. Computed at B3LYP/6-311++G(d,p) level (see Figure S5 in the Supporting Information).

	dist(C=C)	%dist	DI(C=C)	WBI	MBO	^{13}C δ
$C_2B_{10}H_{12}$	1.623		0.983	0.735	0.874	58.7[a]
o-carboryne	1.356	16.5	1.813	1.645	2.134	128.8
benzene	1.394		1.389	1.442	1.704	125.9[b]
o-benzyne	1.244	10.8	2.249	2.360	2.447	188.4[c]

[a] Exp. value is 55.5 ppm.[25] [b] Exp. Value in $CHCl_3$ solution is 128.5 ppm.[26] [c] Exp. value of benzyne incarcerated in a molecular container is 181.33 ppm.[27]

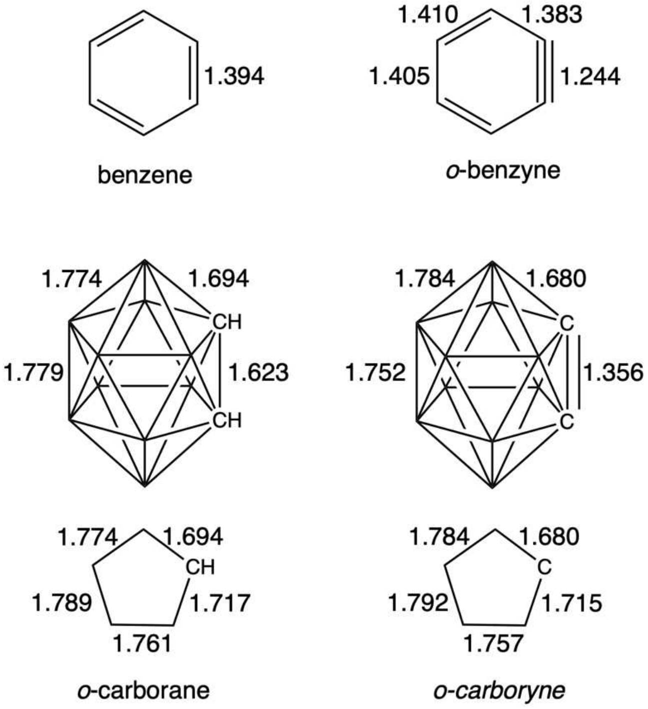


Figure 7. Bond lengths (in Å) for *o*-carborane, *o-carboryne*, benzene, and *o*-benzyne. Computed at B3LYP/6-311++G(d,p) level.

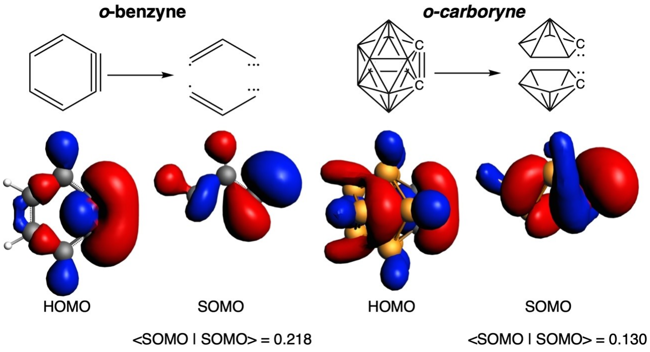


Figure 8. Overlap between single occupied molecular orbitals (SOMOs) of *o*-benzyne (left) and *o-carboryne* (right). Localized MOs are enclosed in Figure S6 in the Supporting Information.

Trimerization of *o*-benzyne and *o*-carboryne

Related to the double vs. triple bond character discussed above, could *o-carboryne* undergo cyclotrimerization as both *o*-benzyne and 9,10-phenanthryne? (Figure 9). First, the cyclotrimerization is calculated to be thermodynamically favorable for all three systems (−283, −249, and −234 kcal mol^{-1} for *o*-benzyne, 9,10-phenanthryne, and *o-carboryne*, respectively). With respect to aromaticity, both *o*-benzyne and the terminal rings of phenanthryne, as well as *o-carboryne*, keep their aromaticity or it is slightly reduced upon cyclotrimerization (Table 3). But, more importantly, the central ring is non-aromatic for triphenylene and for tri-*o-carboryne*, and just a little bit aromatic for triphenanthryne. The two hydrocarbons not only present smaller bond length alternation in their central ring as compared to *o-carboryne* (0.046 and 0.029 vs. 0.150 Å for *o*-benzyne, 9,10-phenanthryne, and *o-carboryne*, respectively), but the bond lengths are in the order of aromatic bonds. However, that for triphenylene is non-aromatic due to the localization of Clar π-sextets in the three terminal rings and none in the center (Figure 9). Meanwhile, that of triphenanthryne is slightly aromatic as expected from Clar's π-sextet theory, that locates a π-sextet in the central ring together with a π-sextet on each terminal ring, and despite the non-planarity of this central ring. And finally, the central ring of tri-*o-carboryne* has bond lengths with single-bond character, in agreement with above, and thus it can be considered a cyclohexane. However, it remains planar to reduce the steric repulsion between the three connected *o*-carborane clusters.

Conclusions

This work was motivated by the interest observed in the development of new drugs in substituting the phenyl for the carboranyl group in a lead drug with a view to improving pharmacokinetic or pharmacodynamic properties. It is considered that the phenyl group, which is an aromatic group, could be replaced by a carboranyl group because the latter, by is also aromatic, has a strong resemblance to a phenyl in rotation, the substituents beam out from the center and both are hydrophobic. Opposite to previous assumption, to us they seem to be far away from the isosteres concept but this is not simple to be demonstrated. In this work, we wanted to refer to the

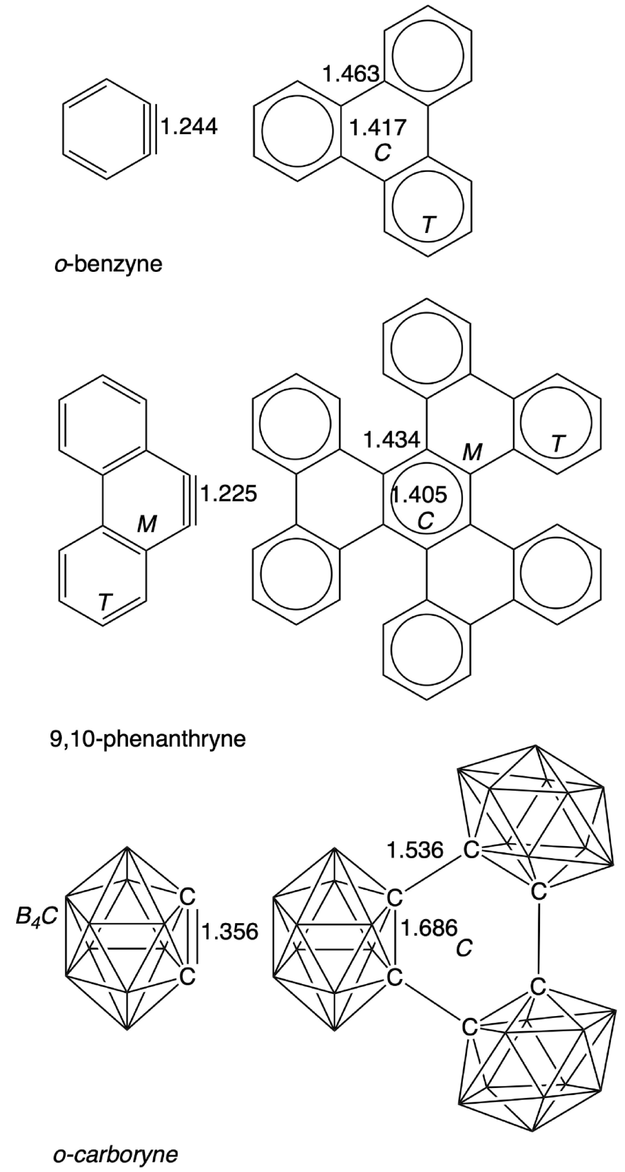


Figure 9. Cyclotrimerization products of *o*-benzyne, 9,10-phenanthryne, and *o-carboryne*. Bond lengths (in Å) of the central rings are included, together with localization of π-sextets. Naming of rings (in italics) are also included.

concept of a similar number of valence electrons in a similar environment. And the concept of similarity in the number of electrons could be very well related to the concept of aromaticity since both are aromatic and follow either Hückel's or Wade–Mingos rules. And also because of the type of reactivity they offered and the similar environment that could be related to the dimensions, in particular the C–C distance. For this reason, we decided to explore the similarities and differences between one derivative of each the benzene and the *o*-carborane, to say the *o*-benzyne and the *o-carboryne* that are really reactive and produce similar reactions, e.g. the [2+2+2] cycloaddition. From this, we reached the conclusion that the outcome of each reaction is apparently similar, electronically very different, and similar in terms of their initial stability. The dimensions of the C–C bond and the dimensions of the "isosteric" parts, C_6H_6 and $C_2B_{10}H_{12}$, define the electronic and steric differences between the two compounds. Both are aromatic but the C–C distance is very decisive as it also affects the bond order, being in benzene 1.394 Å, BO 1.67, and in carborane 1.623 Å, BO 0.74, but it also influences in *o*-benzyne 1.244 Å, BO 2.71, and *o-carboryne* 1.356 Å, BO 1.84. Upon the reaction with two units of alkyne, the *o-carboryne* and the *o*-benzyne lead to structurally similar cycloaddition compounds but the *o-carboryne* and *o*-benzyne revert to the comfort geometry, the C–C distances and BO of their original parents, *o*-carborane and benzene. Whereas benzene leads to an aromatic compound, the *o*-carborane leads to a local, the carborane, aromatic compound. This has been fully confirmed with cyclotrimerization of *o*-benzyne, phenanthryne and *o-carboryne*. With no exception, no 3D aromatic *o*-carborane when bonded to four π electron fragments enabled to produce a 6π fragment as a global aromatic compound, only keeping the aromaticity of the original 3D fragment. Conversely, global aromaticity is obtained in similar circumstances with a Hückel[28] 2D original fragment. As said above, this is a consequence of the very dissimilar C–C distance that creates a bond order difference about one unit. Indeed, the *o-carboryne* is in reality an *o*-carborene and therefore should be termed as *o*-carborene. This would explain all reactivity of [2+2+2] in which the first one is one alkene and the other two alkynes,[29] in this case it would lead to a cyclohexadiene and would express that it is impossible to generate a global aromatic in the fusion of a 3D- and a 2D-aromatic. On the other hand, this study has shown that when a triple bond is produced in benzene or a double bond in *o*-carborane, the aromaticity remains either constant or somehow reduced, that would be due to a pinning of the electronic delocalisation in favour of this triple or double bond, which reverts to total delocalisation once the generated σ is broken. These studies do not seem to support the isosterism of carborane and benzene, but it is another aromatic compound to develop new lead compounds.

Methods

All calculations were performed with the Gaussian 09 package[30] by means of the B3LYP[31] hybrid density functional and the 6–311++G(d,p) basis set.[32] The geometry optimizations were carried out without symmetry constraints (Table S1 in the Supporting Information). Analytical Hessians were computed to characterize the optimized structures as minima (zero imaginary frequencies). Aromaticity was evaluated by means of the nucleus-independent chemical shift (NICS),[2a,b,e,f,33] proposed by Schleyer and co-workers as a magnetic descriptor of aromaticity. NICS is defined as the negative value of the absolute shielding computed at a ring center or at some other point of the system. Rings with large negative NICS values are considered aromatic. NICS values were computed using the gauge-including atomic orbital method (GIAO).[34] Multicenter indices (MCI)[35] and delocalization indices (DI)[22] were computed with the ESI-3D program using Atoms-in-Molecules (AIM) partition of space.[35c,36] Reported ring currents were computed

Table 3. NICS (in ppm) and MCI (in a.u.) of the systems involved in the cyclotrimerization of *o*-benzyne, 9,10-phenanthryne and *o-carboryne.* Formation energy (in kcal mol^{-1}) and bond lengths (in Å) are also included.

system	ring	NICS(0)	MCI	△E	d(C═C)	d(C–C)^{new}
o-benzyne	6MR	−18.1	0.077		1.244	
o-benzyne^{x3}	6MR$^{central(C)}$	−2.1	0.008	−283.4	1.417	1.463
	6MR$^{terminal(T)}$	−7.5	0.051			
9,10-phenanthryne	6MR$^{mid(M)}$	−13.8	0.018		1.225	
	6MR$^{terminal(T)}$	−8.8	0.048			
9,10-phenanthryne^{x3}	6MR$^{central(C)}$	−1.0	0.025	−248.5	1.405	1.434
	6MR$^{terminal(T)}$	−7.1	0.049			
	6MR$^{mid(M)}$	−0.5	0.009			
o-carboryne	B_4C	−40.5			1.356	
	center	−35.4				
o-carboryne^{x3}	6MR$^{central(C)}$	−4.9	0.001	−233.7	1.686	1.536
	B_4C	−31.9				
	center	−26.4				

with the GIMIC program using the GIAO procedure at the same level of theory.[37] Canonical and localized molecular orbitals have been depicted with ADF software package.[38]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: benzyne · carboryne · carborane · non-conventional double bond · 3D aromaticity

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