Theoretical investigation of [2.2]paracyclophane as a donor toward a $Cr(CO)_3$ group

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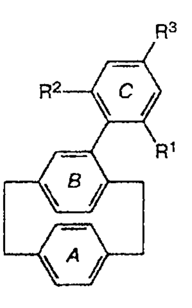
A comparative molecular orbital study of [2.2]paracyclophane and simple arenes as ligands toward a $Cr(CO)_3$ group was performed with the aim of accounting for the observed coordination patterns. While the inter-ring repulsion is an important factor in [2.2]paracyclophane activation, it is not the only one. The molecular orbitals of two arene rings stacked parallel to each other were analyzed in some detail. The inward hybridization (toward the other ring) of the $(arene)_2$ HOMO was shown to reduce the strength of consequent bonding with the $Cr(CO)_3$ fragment. The overall stabilization of [2.2]paracyclophane complex with $Cr(CO)_3$ is enhanced by a reduction of the inter-ring repulsion and strengthening of the Ar—Cr bond, and reduced by weakening of the intra-ring carbon—carbon bonds. The inter-ring repulsion increases with approach of the arenes to each other, as appears to happen in the structure of [2.2]paracyclophane complex with $Cr(CO)_3$. This explains the high donor ability of the free ring of the $(arene)_2Cr(CO)_3$ complex toward another $Cr(CO)_3$ fragment. It was proposed that the stabilization of the [2.2]paracyclophane complex with $Cr(CO)_3$ results ultimately from the relaxation of the strained framework of [2.2]paracyclophane. The kinetic factor in $Cr(CO)_3$ complexation was also studied by analyzing the charges on competing arene rings in monoaryl-substituted derivatives of [2.2]paracyclophanes.

Key words: [2.2]paracyclophane, complexation with chromium, regioselectivity; molecular orbitals, interaction of π-systems.

[2.2]Paracyclophane has an intriguing and rich chemistry. The high strain of the [2.2]paracyclophane molecule makes it generally quite reactive. One would like to know if the excess energy in the molecule can be utilized to effect stronger bonding of paracyclophane with inorganic metal-containing fragments as compared to regular arenes. The particular metal-containing fragment which we are concerned with in this work is the $Cr(CO)_3$ group occurring commonly in organometallic chemistry. The complex of [2.2]paracyclophane with $Cr(CO)_3$ was first synthesized in 1960,[1] and its structure was established by X-ray analysis.[2] The experimental and theoretical aspects of a competing interaction of [2.2]paracyclophane and *p*-xylene with $Cr(CO)_3$ were studied recently by Dyson, Mingos, and coworkers.[3]

In the previous paper[4] the monoaryl-substituted derivatives of [2.2]paracyclophane were used to investigate the preferred sites (regioselectivity) for the complexation of $Cr(CO)_3$ within one molecular framework. The monoaryl-substituted derivatives of [2.2]paracyclophane have three possible sites for coordination with a $Cr(CO)_3$ group, namely aromatic rings labeled *A*, *B*, and *C*. The experiments showed that ring *A* is the preferred site for complexation, followed by ring *B*. Complexation of ring *C* seems to be the least favored relative to other options.



Let us attempt to rationalize the arene ring site preferences for $Cr(CO)_3$ coordination. Clearly the overall yield of a particular product in a chemical reaction is determined by the thermodynamic stability of the complex and/or the kinetic rate of its formation. Our focus here is first on the thermodynamic aspects of the reaction. Let us use the extended Hückel method (EHT), an approximate molecular orbital theory, to analyze the differences between the binding energies of [2.2]paracyclophane and *p*-xylene complexation with $Cr(CO)_3$. At the end of the article we

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will approach the kinetic aspect of the problem by analyzing the charges on competing arene rings.

From the steric point of view, it can be deduced that aromatic rings *B* and *C* having bulky substituents might be less likely to bind to $Cr(CO)_3$; following this line of reasoning, the unsubstituted ring *A* should be the most preferred site for complexation. These steric arguments are in general agreement with the experimental results.[4] Nevertheless, we think that steric considerations alone are insufficient to account for the large difference between the ease of complexation of the $Cr(CO)_3$ group with rings *B* and *C*. The strongly expressed preference for $Cr(CO)_3$ coordination to ring *B* (relative to ring *C*) indicates that the arene rings of [2.2]paracyclophane are better donors than substituted arenes.

This idea is supported by the experimental and theoretical work of Dyson, Mingos, and coworkers[3] who compared the reactivity of unsubstituted [2.2]paracyclophane and *p*-xylene toward $Cr(CO)_6$ and found that [2.2]paracyclophane reacts slightly faster. They also found a 10 : 1 ratio of products of attack on the aryl rings of [2.2]paracyclophane and *p*-xylene, respectively, by their competing reactions with $Cr(CO)_6$. Assuming that the ratio of the respective products was obtained at equilibrium, one can estimate the difference in the free energies of these reactions as approximately 0.07 to 0.08 eV. In order to explain the experimental results, Dyson, Mingos, and coworkers[3] used density functional theory (DFT) calculations,[5] which confirmed the greater stabilization upon the coordination of $Cr(CO)_3$ with [2.2]paracyclophane compared to *p*-xylene.

Dyson, Mingos, and coworkers[3] explained the results of their calculations by considering different simpler models for [2.2]paracyclophane, and here we follow them.

Conceptually, the molecule of [2.2]paracyclophane may be imagined as being assembled from two *p*-xylene molecules in three steps (Scheme 1), a construction that might allow one to assess the influence of different steps of the assembly on the binding ability of arene rings. The first step (Scheme 1, *a*) involves the parallel approach (stacking) of two *p*-xylene molecules to a distance of 3.09 Å, the average ring separation in [2.2]paracyclophane. In the next step, the methyl groups are bent toward each other, thus forcing boat conformations (as observed in the [2.2]paracyclophane structure) of the arene rings (Scheme 1, *b*). Finally, one imagines a transformation of the methyl groups into dimethylene bridges (Scheme 1, *c*), with loss of hydrogens.

Scheme 1

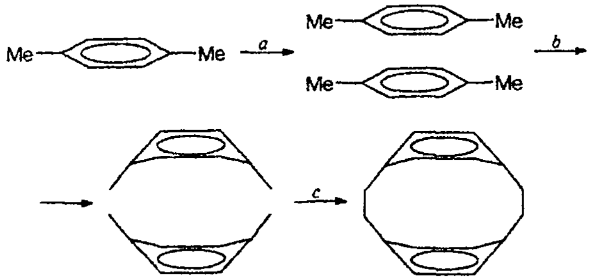

Table 1. Parameters of EHT calculations

Atom	Orbital	H_{ii}/eV	ζ (*C*)	Reference
C	2s	−21.4	1.625	6
	2p	−11.4	1.625	
O	2s	−32.3	2.275	6
	2p	−14.8	2.275	
H	1s	−13.6	1.3	
Cr	4s	−8.66	1.7	7
	4p	−5.24	1.7	
	3d	−11.22	4.95 (0.5060), 1.8 (0.6750)	

Comparing the donor ability of a separate ring with that of a "dimer" (step *a*), Dyson, Mingos, and coworkers[3] found that the two rings separated by 3.09 Å are better donors toward the $Cr(CO)_3$ group than rings with infinite separation. They attributed this effect to the reduction of the inter-ring repulsion upon the complexation of the $Cr(CO)_3$ group.

The second step of the assembly, bending of the methyl groups and arene rings, has a negligible impact on the donor ability of the arene rings.[3] The last step, the connection of methyl groups into dimethylene bridges, introduces through-bond coupling between the rings, lowering the inter-ring repulsion. As was shown by Dyson, Mingos, and coworkers,[3] the donor-enhancing effect of the first step of the assembly was partially canceled by the third step.

Calculation Procedure

All EHT calculations were performed using the Yet Another extended Hückel Molecular Orbital Package (YAeHMOP) program developed in our group by G. Landrum.* The standard parameters listed in Table 1 were used for the C, H, O, and Cr atoms. The AM1 calculations were performed using the HYPERCHEM Release 4.5 for Windows program.

Results and Discussion

Our calculations, to be detailed below, suggest that the donor ability of [2.2]paracyclophane toward the $Cr(CO)_3$ group is primarily affected by the first step of the assembly of the molecule. In this work, we focussed mainly on that step, stacking of two benzene rings (see Scheme 1, *a*). In order to explore the reasons for the additional stabilization of the complex of $Cr(CO)_3$ with two stacked arene rings relative to separate rings, let us

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* Comprehensive information can be obtained in the Internet at http://overlap.chem.cornell.edu:8080/yaehmop.html.

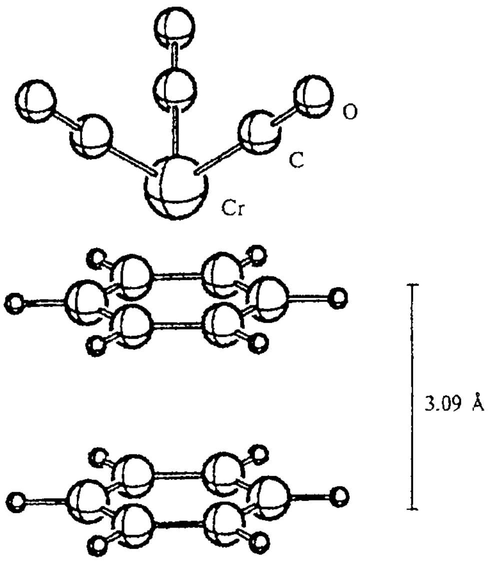


Fig. 1. $(arene)_2Cr(CO)_3$, a model of interaction between [2.2]paracyclophane and $Cr(CO)_3$.

employ an approximate molecular orbital method of the extended Hückel type.[6,8,9]

While the reduction of inter-ring repulsion upon complexation is certainly a plausible explanation for the observed theoretical and experimental outcome, there are other factors which could be at work. They come into view if one considers fragmentation of the $(arene)_2Cr(CO)_3$ system (Fig. 1) into arene and $(arene)Cr(CO)_3$. When the latter fragment is approached by the arene ring, an increase in the arene—Cr bond strength might result. This might be an alternative explanation of the higher stability of the $(arene)_2Cr(CO)_3$ complex compared to that of $(arene)Cr(CO)_3$. A change in the bonding within the benzene rings might also influence the relative donor ability of [2.2]paracyclophane and *p*-xylene.

After the complexation of the first $Cr(CO)_3$ group to [2.2]paracyclophane, the second ring might be potentially deactivated for complexation with an additional $Cr(CO)_3$ group. In order to study the donor ability of the free ring in $(arene)_2Cr(CO)_3$ toward another $Cr(CO)_3$ group, let us invoke some ideas from molecular mechanics.

Transannular interactions in two stacked arenes. One is tempted to relate bonding of [2.2]paracyclophane to $Cr(CO)_3$ to the known benzene case. The molecular orbital picture of bonding of a $M(CO)_3$ fragment to benzene and other ligands was studied by Mingos, Albright, Hoffmann, and coworkers[10,11] and has been thoroughly discussed elsewhere.[12] There are three high-lying acceptor orbitals in the $Cr(CO)_3$ fragment which are mainly responsible for bonding with the arene fragment; they are of a_1 and e symmetry. The corresponding orbitals of the arene fragment involved in the bonding are the occupied π-orbitals of a_{2u} and e_{1g} symmetry belonging to the D_{6h} point symmetry group (Fig. 2). When two benzene molecules are stacked parallel to each other, the important bonding a_{2u} and e_{1g} orbitals of the benzene rings are split into inter-ring bonding and antibonding combinations (Fig. 3) respectively of a_{1g} and a_{2u}, and e_{1g} and e_{1u} symmetry. Since both the inter-ring bonding and antibonding levels are occupied, and in the absence of any other stabilizing interactions, the net result should be a repulsion between the two benzene rings. This is a typical example of a two-orbital four-electron repulsion.

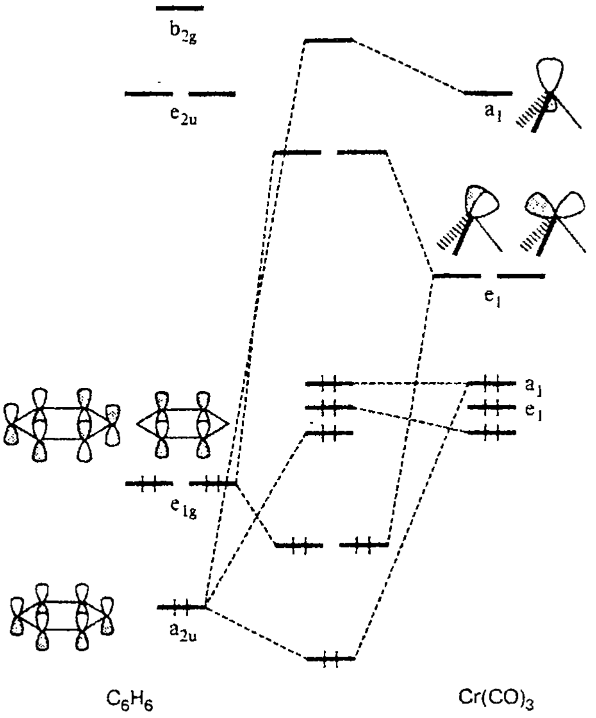


Fig. 2. Schematic interaction diagram between the frontier π-orbitals of benzene and $Cr(CO)_3$ fragment.

Although the $(arene)_2$ fragment possesses the same D_{6h} point symmetry group as benzene, the horizontal mirror plane of the D_{6h} group in this fragment no longer passes through each benzene ring separately. Therefore, the σ and π systems of benzene are allowed to interact by symmetry, and some σ—π-hybridization occurs. This mixing of orbitals is of importance in the subsequent analyses of the interaction of $(arene)_2$ with the $Cr(CO)_3$ fragment, and we discuss it next.

Consider, for instance, the important e_1 arene orbitals. Bonding combinations of σ orbitals of e_1 symmetry can mix in with these π-orbitals. One pair of these σ-orbitals contains mainly carbon 2s orbitals, while the other pair contains mainly carbon 2p orbitals and hydrogen s orbitals. In Fig. 4, only the interaction of π-orbitals with 2s-type σ-orbitals, judged to be most

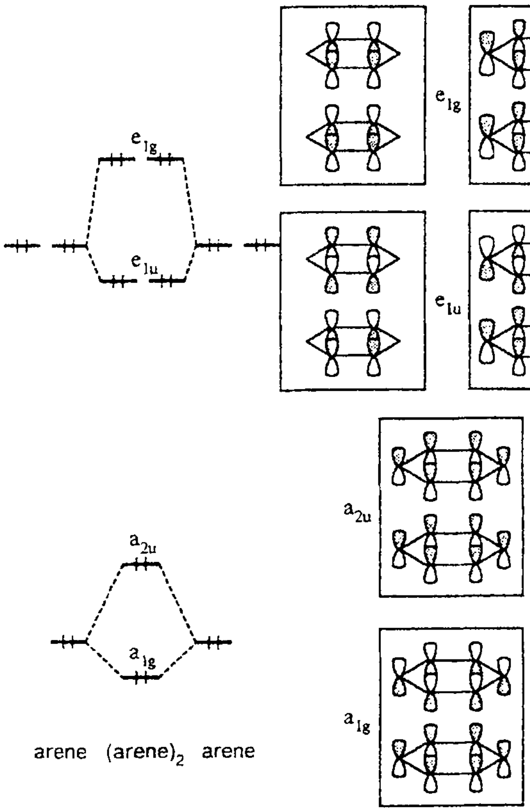


Fig. 3. Schematic interaction diagram between the occupied π-orbitals of two stacked benzene rings.

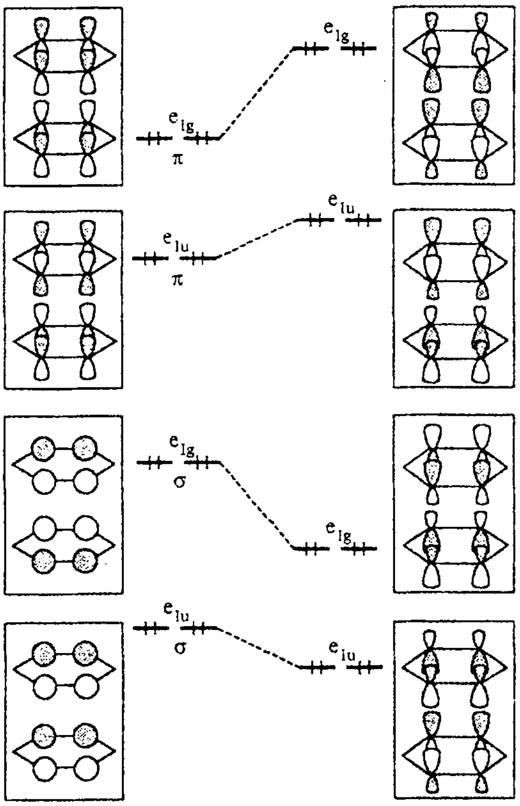


Fig. 4. Interaction of the (benzene)$_2$ e$_{1g}$ and e$_{1u}$ π-orbitals with low-lying σ-orbitals (mainly containing carbon 2s AOs) of the corresponding symmetry. Only one of the two degenerate orbitals is shown in each case.

important in giving an in-out directionality to the π-orbitals of [2.2]paracyclophane, is shown.

The e$_{1u}$ π-orbitals of the (arene)$_2$ fragment (see Fig. 4) are bonding between the arene rings. The low-lying e$_{1u}$ σ-orbitals mix in with these π-orbitals out-of-phase. As a consequence, the lobes of the π-orbitals become hybridized *outward* (defined from this point on as bigger lobes pointing away from the other ring). Corresponding out-of-phase mixing of the inter-ring antibonding e$_{1g}$ π-orbitals of the (arene)$_2$ fragment with the low-lying e$_{1g}$ σ-orbitals leads to *inward* hybridization of the lobes of the π orbitals relative to the other ring (see Fig. 4). The phenomenon is analogous to what happens in the σ-orbitals of a simple molecule such as N$_2$. It is important to note that *outward* hybridization of the frontier orbitals (here e$_{1u}$ and e$_{1g}$) *is not* a universal consequence of s—p-mixing.

The electronic features of (arene)$_2$ bonding to the Cr(CO)$_3$ fragment. In the previous section, we analyzed in some detail those π-orbitals of the (arene)$_2$ system which are mainly responsible for bonding with the Cr(CO)$_3$ group. Let us discuss next the coordination of the Cr(CO)$_3$ fragment itself. The diagram of the interaction between the (arene)$_2$ fragment and Cr(CO)$_3$ fragment is shown in Fig. 5. The orbitals of the acceptor Cr(CO)$_3$ fragment are of a$_1$ and e symmetry of the C_{3v} point symmetry group. The (arene)$_2$Cr(CO)$_3$ molecule (see Fig. 1) also has C_{3v} symmetry, which means that the g and u symmetry indices of an isolated benzene no longer distinguish the orbitals.

Both occupied e$_{1g}$ and e$_{1u}$ π-orbitals of (arene)$_2$ (see Fig. 4) interact with the acceptor e-orbitals of the Cr(CO)$_3$ fragment. It is well known from perturbation theory that the strength of a particular interaction is roughly proportional to the square of the overlap and inversely proportional to the difference between the energies of interacting orbitals. The differences between the energies of the e orbitals of the Cr(CO)$_3$ fragment and the inter-ring antibonding e$_{1g}$ π-orbitals of (arene)$_2$ are smaller than the corresponding differences between the energies of the e orbitals of the Cr(CO)$_3$ fragment and the intra-ring bonding e$_{1u}$ orbitals. Thus, from the energetic point of view the inter-ring antibonding e$_{1g}$ orbitals should interact more strongly with the e orbitals of the Cr(CO)$_3$ fragment than the intra-ring bonding e$_{1u}$ orbitals.

Our detailed analysis of the overlaps between the corresponding orbitals shows that two factors play an important role — the magnitude of the orbital coeffi-

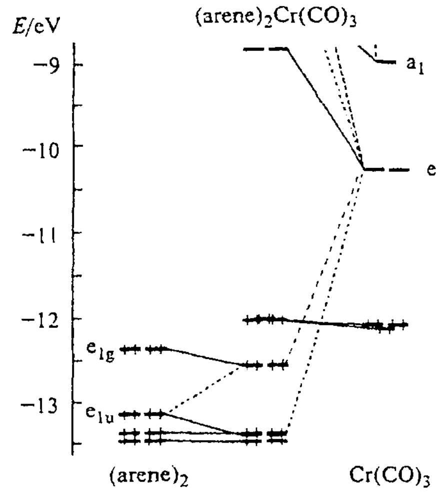


Fig. 5. Interaction diagram between the (arene)$_2$ fragment stacked at 3.09 Å and Cr(CO)$_3$ group. Only the frontier orbitals are shown.

cients and the directionality of the lobes of the (arene)$_2$ fragment orbitals. The orbital coefficients are larger on the inter-ring antibonding orbitals, as is usually the case with the antibonding orbitals.[12] Therefore, the orbital coefficients also favor the interaction between the inter-ring antibonding e$_{1g}$ orbitals of the (arene)$_2$ fragment with the e orbitals of the Cr(CO)$_3$ fragment. However, as was discussed above, the lobes of the highest occupied e$_{1g}$ molecular orbitals (HOMOs) are actually hybridized *inwards* (away from the Cr(CO)$_3$ group), while the lobes of lower-lying e$_{1u}$ orbitals are hybridized *outwards* (toward the Cr(CO)$_3$ group). Therefore, the σ—π hybridization reduces the overlap of the frontier inter-ring antibonding e$_{1g}$ orbitals of the (arene)$_2$ fragment with the e orbitals of the Cr(CO)$_3$ group. Of course, the opposite is true for the inter-ring bonding e$_{1u}$ orbitals of the (arene)$_2$ fragment.

It turns out that in this case the energetic and the orbital size considerations outweigh the hybridization effect. The e$_{1g}$ orbitals of the (arene)$_2$ fragment in the end interact more strongly with the e orbitals of the Cr(CO)$_3$ group compared to the e$_{1u}$ orbitals of (arene)$_2$ fragment.

The stronger interaction of the inter-ring *antibonding* e$_{1g}$ orbitals of the (arene)$_2$ fragment with the acceptor orbitals of Cr(CO)$_3$ group implies their larger depopulation compared to the inter-ring bonding e$_{1u}$ orbitals of the (arene)$_2$ system. In the absence of a Cr(CO)$_3$ group there is a repulsive and antibonding interaction between the arene rings separated by 3.09 Å as evidenced by the negative overlap population (*OP*) between the two arene rings: *OP*(arene—arene) = −0.068. Upon coordination of the Cr(CO)$_3$ group with the (arene)$_2$ fragment this value is decreased by 13% (*OP* = −0.059).

As we mentioned earlier, it is possible to fragment the (arene)$_2$Cr(CO)$_3$ complex into arene and (arene)Cr(CO)$_3$. When one of the benzene rings is drawn from infinity to a distance of 3.09 Å (the center-to-center or C to C distance) from the (arene)Cr(CO)$_3$ molecule, the arene—Cr overlap population is very slightly increased (approximately by 0.6%), since the HOMO of the (arene)$_2$ system is hybridized *inward* (away from Cr(CO)$_3$). Hybridization offsets strengthening of the arene—Cr bond due to the influence of the second ring; however, coordination of two stacked arene rings with Cr(CO)$_3$ remains preferable as compared to that of a separate arene molecule.

The third important factor is the change in the strength of the intra-ring carbon-carbon bonds. When the two benzene rings are drawn together to 3.09 Å from infinity (without the Cr(CO)$_3$ fragment), the population of the overlap between the neighboring carbon atoms within the rings is increased by 0.02 (an increase that may be traced mainly to the benzene π-system). The inter-ring benzene—benzene π-interaction is repulsive because the coefficients on the antibonding orbitals are larger than on the bonding orbitals. The bonds within the benzene rings are strengthened for the same reason, *i.e.*, the inter-ring antibonding orbitals are bonding within the rings and their orbital coefficients become larger.

Therefore, there exists a correlation between the strength of the repulsion between the arene rings and the strength of the C—C bonds within the rings. Since the interaction with Cr(CO)$_3$ decreases the repulsion, it also decreases the strength of the C—C bond within the rings. The change in bonding within the rings lowers the tendency of the two stacked arene rings to coordinate with Cr(CO)$_3$ as compared to separate arene molecules.

The final outcome of our calculations is a stronger binding of the Cr(CO)$_3$ fragment with two stacked benzene rings (compared with two separate benzene rings), by approximately 0.04 eV. This value is nearly the same as that obtained when the binding abilities of [2.2]paracyclophane and two separate *p*-xylene molecules toward Cr(CO)$_3$ are compared. Therefore, the earlier assertion (by Dyson, Mingos, and coworkers)[3] about the relative importance of the first, second, and third steps in the assembly of the [2.2]paracyclophane molecule on the donating ability toward Cr(CO)$_3$ is also confirmed by our EHT calculations.

Let us trace the origins of this stabilization in terms of the factors mentioned above. The contributions of (1) the reduction in inter-ring repulsion, (2) the strengthening of the arene—Cr bond, and (3) the weakening of the intra-ring bonds to the calculated energy difference are estimated to be in a ratio of roughly 4 : 1 : 2. Since the small computed preference for complexation (0.04 eV) results from the cancellation of several large effects considered, one has to be cautious in interpreting the results. Although the extended Hückel method is a very approximate one, it is encouraging that our results are of the same sign and order of magnitude as the experimental estimate (0.07 to 0.08 eV) and DFT calculations (0.15 eV).[3]

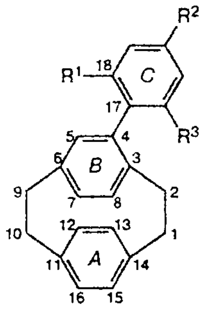
Is the uncoordinated ring of (arene)$_2$Cr(CO)$_3$ complex deactivated for complexation with an additional Cr(CO)$_3$ group? The two arene rings of [2.2]paracyclophane are located at a distance of 3.09 Å from each other. All calculations described were performed at that distance. The examination of the X-ray structure[2] of the [2.2]paracyclophane complex with the Cr(CO)$_3$ group reveals a distance of 3.03 Å between two rings,* *i.e.*, the distance between the rings has shrunk by 0.06 Å as a consequence of complexation to the Cr(CO)$_3$ group. Let us assume that this change is significant and not the result of crystal packing differences. The change of 0.06 Å seems small but affects inter-ring interaction. The negative overlap population between two arene rings increases in magnitude due to bringing together the two rings from 3.09 Å (OP(arene—arene) = −0.059) to 3.03 Å (OP(arene—arene) = −0.073) in the (arene)$_2$Cr(CO)$_3$ system. Coordination of the second Cr(CO)$_3$ group again reduces the magnitude of the negative overlap population between two arenes by 11%. Therefore, the "free" ring of (arene)$_2$Cr(CO)$_3$ is only slightly deactivated with respect to the additional complexation with another Cr(CO)$_3$ group. This conclusion agrees well with the experimentally found high yields of binuclear complexes[4] obtained even for [2.2]paracyclophanes containing bulky substituents.

By answering one question we created another: where is the energy gain coming from, if the inter-ring repulsion is restored after complexation with a Cr(CO)$_3$ group? We invoke some ideas from molecular mechanics[13] in order to propose a possible answer to this question. The molecule of [2.2]paracyclophane is a highly strained molecule. This strain may be assumed to result from two opposite forces: one pushing the arene rings apart (inter-ring repulsion), and the other pulling them together (stretched dimethylene bridges and C(arene)—C(bridge) bonds, and bent aromatic rings). In free [2.2]paracyclophane, strained as it is, these "forces" are somehow balanced. After the complexation of the first Cr(CO)$_3$ group, the inter-ring repulsion is reduced. Therefore, one can imagine that the pulling forces prevail and bring the two arene rings 0.06 Å closer. During that process the inter-ring repulsion is built up and a new balance is established at 3.03 Å separation of the rings.

One can speculate that upon complexation of Cr(CO)$_3$ to [2.2]paracyclophane the stabilization comes ultimately from relaxation of the strained [2.2]paracyclophane framework. Complexation of the second Cr(CO)$_3$ group further reduces the strain in [2.2]paracyclophane. The binding of the (arene)$_2$Cr(CO)$_3$ system to another Cr(CO)$_3$ group is also preferred by 0.04 eV compared with two separate arenes. It is appropriate here to emphasize once more the qualitative nature of our calculations and explanations.

Analysis of the kinetic factor. In the discussion above we rationalized the thermodynamic stability of the [2.2]paracyclophane complex with Cr(CO)$_3$. There is also a kinetic aspect to the problem. Dyson, Mingos, and coworkers[3] found a build-up of electron density outside of the arene rings of [2.2]paracyclophane compared to free arene rings. They attributed the higher rate of the [2.2]paracyclophane reaction with Cr(CO)$_6$ relative to *p*-xylene to the increased electron density outside of the rings. An alternative approach is to calculate the charges on different arene rings in substituted [2.2]paracyclophanes. A high negative charge on a particular arene ring might imply high reactivity of that ring toward the Cr(CO)$_3$ fragment. The assumption here is of a charge-controlled rate-determining step; a deeper analysis would involve consideration of the detailed mechanism of the reaction.

Structures for most of the [2.2]paracyclophane derivatives used in our studies[4] were not available. Therefore, we employed the AM1 semiempirical method[14] to optimize the geometries of all the ligands and to calculate the charges on different arene rings. The optimized geometric parameters of the molecules of compounds **1**—**4** containing a phenyl, *p*-tolyl, *p*-anisyl, or mesityl group in position 4 are listed in Table 2.



1—**4**

1: R^1 = R^2 = R^3 = H
2: R^1 = R^2 = H; R^3 = Me
3: R^1 = R^2 = H; R^3 = OMe
4: R^1 = R^2 = R^3 = Me

For comparison with the experimental data, the geometry of free [2.2]paracyclophane was optimized by the AM1 method and molecular mechanics. As can be seen, the X-ray structural data are in good agreement with the calculated geometric parameters for free compound; hence, it is possible to use the AM1 method for a reasonably good prediction of the geometry of [2.2]paracyclophane molecules.

The AM1 calculations result in a strong distortion of the geometry of molecules **1**—**4** compared with the [2.2]paracyclophane structure. For example, arene rings *A* and *B* are not parallel to each other. As expected, rings *B* and *C* are twisted about the C(4)—C(17) axis, with the largest dihedral angle in sterically hindered mesityl derivative **4**.

We estimated the donor ability of rings *A*, *B*, and *C* as a simple sum of total charges on the six carbon atoms

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* In the crystalline structure reported in Ref. 2 the two arene rings are not exactly parallel to each other and we have taken the average distance between the two rings.

Table 2. Geometric parameters (main distances (l), the C(1)—C(2)—C(3) bond angle (α), and torsion angles (φ) in the molecules) for [2.2]paracyclophane (PCP) and its derivatives **1**—**4** calculated by the AM1 method

Parameter	**1**	**2**	**3**	**4**	PCP	PCP[a]	PCP[b]
l/Å							
C(1)—C(2)	1.55	1.55	1.55	1.55	1.555	1.572	1.569
C(1)—C(14)	1.49	1.49	1.49	1.49	1.495	1.523	1.572
C(4)—C(13)	3.08	3.10	3.14	3.27	3.08	3.11	
C(8)—C(15)	3.14	3.11	3.06	3.08	3.08	3.11	3.10
C(5)—C(12)	3.04	3.08	3.06	3.22	3.08	3.11	3.10
C(7)—C(16)	3.13	3.10	3.11	3.00	3.08	3.11	3.10
C(3)—C(14)	2.72	2.72	2.72	2.72	2.70	2.80	2.79
C(6)—C(11)	2.70	2.70	2.70	2.71	2.70	2.80	2.79
α/deg	112	112	113	113	113	110	113
φ/deg							
C(5)—C(4)—C(3)—C(8)	20	19	20	23	16	14	13
C(4)—C(8)—C(3)—C(2)	9	9	9	7	8	10	11
C(5)—C(4)—C(17)—C(18)	28	30	35	56	—	—	—
C(1)—C(2)—C(9)—C(10)	15	14	17	4	0	0	0

[a] Molecular mechanics (MM+) calculations.[15] [b] X-ray analysis data.[2]

Table 3. The sums of total negative charges on the ring carbon atoms calculated by the AM1 method

Compound	$-\varepsilon$(HOMO)/eV	$-q/e$		
		Ring A	Ring B	Ring C
1	8.88	0.555	0.459	0.510
2	8.65	0.549	0.458	0.493
3	8.54	0.551	0.455	0.424
4	8.70	0.561	0.471	0.454

of the corresponding arene rings. The results are listed in Table 3. Ring A has the highest negative charge as compared to rings B and C for all the molecules studied, which is in agreement with the higher coordination ability of ring A.[4] The magnitude of the negative charges is greater for ring B compared with ring C in compounds **3** and **4**, which also agrees with the experimental data. However, for structures **1** and **2** the relationship is reversed: ring C has a larger negative charge than ring B, which contradicts the data on complexation.

* * *

Considering the results of our AM1 calculations of molecules **1**—**4**, one may suggest that the kinetic factor plays a relatively minor role in determining the ratio of yields of the products of [2.2]paracyclophane reaction with $Cr(CO)_3(NH_3)_3$.[4] It is likely that the increase in stability of [2.2]paracyclophane complexes with $Cr(CO)_3$, due mainly to the reduction of the strain in the [2.2]paracyclophane molecule, plays a crucial role. Our theoretical results are in qualitative agreement with the experimentally observed ratios of the $Cr(CO)_3$ adducts with rings A, B, and C of [2.2]paracyclophane and with the high yields of the binuclear complexes.[4]

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