Electron density distribution in molecules of 4-aryl-substituted [2.2]paracyclophanes and regioselectivity of their complexation with $Cr(CO)_3$

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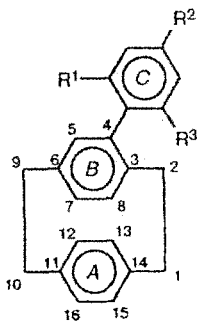
Charges on carbon atoms in the molecules of 4-aryl-substituted [2.2]paracyclophanes were estimated and the role of charge control as a kinetic factor in regioselectivity of their complexation with $(NH_3)_3Cr(CO)_3$ was investigated using electron density distribution analysis by the Bader, Weinhold—Reed (NPA), and Mulliken methods. The most plausible picture of the electron density distribution in substituted [2.2]paracyclophanes was obtained by the Bader method and compared with experimental data on the yields of reaction products. Topological analysis of the electron density distribution in the [2.2]paracyclophane molecule by the Bader method confirmed the existence of a weak antibonding interaction between the stacked benzene rings.

Key words: 4-aryl[2.2]paracyclophanes, complexation, atomic charges, *ab initio* calculations, inter-ring antibonding.

Recently,[1,2] some regularities of complexation of the acceptor $Cr(CO)_3$ fragment with aryl-substituted [2.2]paracyclophanes were discussed. Experimental data on the yields of complexes in reactions between 4-aryl[2.2]paracyclophanes and $(NH_3)_3Cr(CO)_3$ [1] indicate the following complexation pattern of the three different rings *A*, *B*, and *C* in these compounds: ring *A* (the preferred site), followed by ring *B*, and ring *C* (*i.e.*, *A* > *B* > *C*), notwithstanding individual characteristics of the regioselectivity of complexation of the compounds studied (**2**—**4**) with the $Cr(CO)_3$ fragment.



1: $R^1 = R^2 = R^3 = H$
2: $R^1 = R^3 = H$, $R^2 = Me$
3: $R^1 = R^3 = H$, $R^2 = OMe$
4: $R^1 = R^2 = R^3 = Me$

It was experimentally established[1] that compound **2** reacts with $(NH_3)_3Cr(CO)_3$ to give two complexes, a mononuclear complex with $Cr(CO)_3$ fragment coordinated to the unsubstituted ring *A* of [2.2]paracyclophane and a dinuclear one with $Cr(CO)_3$ coordinated to both rings *A* and *B*, the former complex being formed selectively (Table 1). Compound **3** also reacts with $(NH_3)_3Cr(CO)_3$ to give a mononuclear complex with $Cr(CO)_3$ coordinated to ring *A* and a dinuclear one with $Cr(CO)_3$ coordinated to both rings *A* and *B*. A mononuclear complex with $Cr(CO)_3$ coordinated to ring *B* is also formed in this case, however (see Table 1). Reaction between compound **4** and $(NH_3)_3Cr(CO)_3$ results in the formation of a complex in which the chromium tricarbonyl fragment is coordinated to the unsubstituted ring as the main product. The yields of dinuclear complexes of the types *AB* and *AC* that are also formed in this case do not exceed 3 to 5%, and the yield of a mononuclear complex with $Cr(CO)_3$ coordinated to ring *C* is less than 1% (see Table 1).

Table 1. Conditions of reactions between monoaryl-substituted [2.2]paracyclophanes **2**—**4** (L) and $(NH_3)_3Cr(CO)_3$ ("Cr") (dioxane, 100 °C) and the yields of mononuclear and dinuclear complexes*

L	"Cr"/L	Duration of reaction/h	Yields of different types of complexes (%)				
			A	*AB*	*B*	*AC*	*C*
2	1 : 1	4.0	46	24	—	—	—
	2 : 1	0.5	45	45	—	—	—
	3 : 1	1.0	17	63	—	—	—
3	1 : 1	0.5	29	9	14	—	—
	2 : 1	0.5	38	33	19	—	—
	3 : 1	0.3	10	64	6	—	—
4	2 : 1	0.5	53	1.6	—	2.7	—
	3 : 1	0.3	45	0.9	—	3.6	—
	2 : 1	1.0	66	4.6	—	5.1	0.76

* See Ref. 1.

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The theoretical analysis of regioselectivity of [2.2]paracyclophane complexation performed on the basis of calculations carried out both in the framework of the semiempirical EHT scheme[2] and by the DFT method[3] showed that a decrease in the energy due to the reduction of the inter-ring repulsion in the paracyclophane molecule upon the complexation of the $Cr(CO)_3$ group and the steric effect caused by the mutual repulsion between rings *B* and *C* are the main factors affecting the reactivity. The role of kinetic factor in complexation with $Cr(CO)_3$ was discussed[2] under assumption that (from the kinetic viewpoint) the larger the total charge on carbon atoms of a particular ring of substituted [2.2]paracyclophane, the higher the complexation rate of that ring (since paracyclophane is a donor toward the $Cr(CO)_3$ group). The magnitudes of Mulliken charges on the benzene rings calculated in the framework of the AM1 method for compounds **3** and **4** are in qualitative agreement with the experimental data on the yields of complexation products ($A > B > C$).[2] However, for [2.2]paracyclophanes **1** and **2** the negative charges decrease in the order $A > C > B$,[2] which contradicts the experimental results obtained for compound **2**. In addition, the total negative Mulliken charges (q) on the benzene rings *A*, *B*, and *C* obtained from calculations are large (from −0.42 to −0.56 *e*), which seems to be unlikely.

In this work, in order to elucidate a possible role of charge control and to interpret the experimentally observed yields of the products of reactions between $(NH_3)_3Cr(CO)_3$ and substituted paracyclophanes at a higher level of the theory, we analyzed the electron density distributions in molecules **1**—**4** on the basis of results of *ab initio* quantum-chemical calculations.

Calculation procedure

Ab initio calculations of [2.2]paracyclophane and its derivatives were carried out by the RHF method in the 6-31G basis set using the GAUSSIAN-94 program.[4] Determination of critical points (CPs) and their properties and calculations of charges on the atoms in the framework of the theory of atomic fragments in a molecule were performed using the AIMPAC program.[5] The electron density distributions were analyzed by three methods: according to Mulliken,[6] Weinhold—Reed (the NPA method),[7] and Bader.[8] Topological analysis of the electron density distribution in the molecule of [2.2]paracyclophane **1** according to the Bader method[8] was performed concurrently.

Results and Discussion

Calculation of the electron density distribution in molecules of monoaryl-substituted [2.2]paracyclophanes (2—4). The results of the calculations are listed in Table 2. Noteworthy are the large negative total charges on rings *A*—*C* obtained by the NPA and Mulliken methods. Drawbacks of the population analysis according to Mulliken are well known[9] and associated to a great extent with arbitrary partition of the electron density in the overlap regions of the atomic electron shells. This can lead not only to a strong overestimation of the calculated atomic charge,[10] but also to its wrong sign.[11]

Table 2. Total charges on benzene rings *A*—*C* in monoaryl-substituted [2.2]paracyclophanes **2**—**4** (L) calculated by the Mulliken (I),[6] Weinhold—Reed (II),[7] and Bader[8] (III) methods

L	Ring	q/e		
		I	II	III
2	*A*	−0.770	−0.980	−0.040
	B	−0.590	−0.760	−0.050
	C	−0.860	−0.990	−0.054
		$B < A < C$	$A \approx C > B$	$A \leq B \leq C$
3	*A*	−0.770	−0.980	−0.040
	B	−0.590	−0.760	−0.050
	C	−0.480	−0.720	0.480
		$A > B > C$	$A > B \approx C$	$A < B \gg C$
4	*A*	−0.770	−0.980	−0.040
	B	−0.600	−0.770	−0.060
	C	−0.540	−0.570	−0.100
		$A > B > C$	$A > B > C$	$A < B < C$

Bader's approach[8] to determination of the electron density on the atoms in a molecule is devoid of drawbacks of the Mulliken[6] and NPA[7] methods since the topological analysis[8] ignores the orbital nature and is much less dependent on the basis set used.[12] The total charges calculated in the framework of this approach are consistent with the relative electronegativities of the elements, while the calculated dipole moments of the molecules are in good agreement with the experimental data.[13] Because of this, Bader's theory of atomic fragments in molecules has found increasing use in studying the electron density distribution in organic compounds.[14—17]

According to the Mulliken and NPA calculations, ring *C* of compound **2** has the largest total charge (thereafter charge); however, the yields of complexation products of this ring are low. The absolute values of Bader's charges on the carbon atoms of rings *A*—*C* are small and lie in a narrow range (0.014 *e*). Hence, none of the three competing arene rings (*A*—*C*) can be considered to be a preferred site for coordination with the chromium tricarbonyl fragment, guided only by charge values. It should also be taken into account that the coordination of the first $Cr(CO)_3$ group leads to a rearrangement of the electronic structure of the entire molecule and the charge values listed in Table 2 become changed.

Thus, since the sterically less hindered ring *A* of molecule **2** is the first to react with $Cr(CO)_3$, a tendency for the system to weaken the destabilizing interaction between the stacked rings of [2.2]paracyclophane[2] due to its ability to act as a donor in coordination with $Cr(CO)_3$ should be considered to be the driving force of

the regioselectivity of complexation of the chromium tricarbonyl fragment with molecule **2**. Less stable complexes with a $Cr(CO)_3$ group coordinated to ring *C* are not formed at all for thermodynamic reasons.

In the case of compound **3** the large negative charges on ring *C* calculated by the Mulliken and NPA methods are inconsistent with the fact that no complexes in which the chromium tricarbonyl fragment is coordinated to ring *C* are observed among the reaction products. According to the analysis of the electron density distribution by the Bader method, ring *C* has a large positive charge, which indicates an appreciable deactivation of this ring due to the presence of a methoxy group in the *para*-position. The carbon atoms of rings *A* and *B* have small negative charges.

Among 4-aryl[2.2]paracyclophanes **2**, **3**, and **4**, the magnitude of charge on ring *C* calculated by the NPA method is minimum for compound **4**. Ring *C* of molecule **3** (and **4**) has the smallest charge obtained by the Mulliken method (see Table 2). Nevertheless, compound **4** forms complexes with $Cr(CO)_3$ coordinated to ring *C* (see Table 1). In the series of 4-aryl[2.2]paracyclophanes **2**—**4** the largest negative charge on ring *C* of molecule **4** obtained from the analysis of the electron density distribution by the Bader method corresponds to the observed coordination of the attacking acceptor group to this ring. However, the greater donor ability of ring *C* in compound **4** has little effect and corresponding complexes are formed in low yields. The low yields of the products of $Cr(CO)_3$ coordination to ring *B* can be explained by steric hindrances produced by a bulky mesityl substituent in ring *B*. Weakening of inter-ring interaction and the presence of a bulky substituent that sterically hinders ring *B*, thus preventing the formation of complexes of the types *AB* and *B* in high yields (as in the case of compounds **2** and **3**), remain the main factors of regioselectivity of $Cr(CO)_3$ complexation with compound **4**.

Topological analysis of the electron density distribution in the molecule of [2.2]paracyclophane (1). Topological analysis of the [2.2]paracyclophane molecule by the Bader method[8] makes it possible to reveal important characteristic features of the electron density distribution. At CPs[8] of all C—C and C—H bonds, the electron density Laplacian ($\nabla^2\rho_c$) and the density of local electronic energy[5,8] ($H(r_c)$) are negative (Table 3; data for CPs of C—H bonds are omitted). Both these parameters indicate that the electron density is concentrated in the vicinity of CPs of C—C bonds. Asymmetry of the electron density distribution along the interatomic vector is characterized by ellipticity (ε), whose value for the ordinary C(1)—C(2) bond is 3 times larger than for the C(2)—C(3) bond, which reflects the presence of an "ethane π-bond."

Topological structure of the electron density distribution in unsubstituted [2.2]paracyclophane is of interest because of the presence of all types of CPs. If the presence of CPs on the lines connecting the atoms (in general, these lines can not coincide with interatomic vectors; see the ε values) and CPs at the centers of benzene rings are readily predictable, the presence of a cage CP at the center of the molecule is not evident. As is known,[8] such a CP corresponds to a local electron density minimum and is confined in a spatial region of several rings in size (as in the case of cage molecules of the tetrahedrane type). This indicates that the two benzene rings of [2.2]paracyclophane interact with each other. The value of the electron density Laplacian in the interplane region is positive (Fig. 1), which is indicative of a repulsive interaction and corresponds to the conclusions drawn previously.[2,3] The sign of the density of local electronic energy $H(r_c)$ (see Table 3) shows that the kinetic energy dominates over the potential energy near the cage CP, whereas its small absolute value suggests a weak electron repulsion.

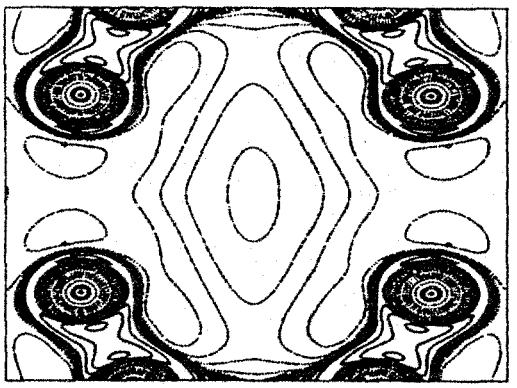

Fig. 1. Contour map of distribution of the electron density Laplacian $\nabla^2\rho$ (RHF/6-31G) in the C(1)C(2)C(3)C(6)C(9)C(10)C(11)C(14) plane of [2.2]paracyclophane. The lines correspond to the following values: $\pm1\cdot10^{-3}$, $\pm2\cdot10^{-n}$, $\pm4\cdot10^{-n}$, and $\pm8\cdot10^{-n}$ (*n* changes from −3 to +2 with an increment of 1). Bold lines connect the points at which $\nabla^2\rho < 0$ and dotted lines connect the points at which $\nabla^2\rho > 0$.

Table 3. Properties of critical points in topological structure of [2.2]paracyclophane **1**

CP type	$\rho(r_c)$ [a]	$\nabla^2\rho(r_c)$ [b]	$H(r_c)$ [c]	ε [d]
CPs of bonds				
C(1)—C(2)	0.1950	−0.2998	−0.1234	0.0309
C(2)—C(3)	0.2350	−0.4514	−0.1716	0.0102
C(3)—C(8)	0.2971	−0.7154	−0.2729	0.1441
C(8)—C(7)	0.2975	−0.7204	−0.2758	0.1461
Ring CP	0.0209	0.1791	0.0088	–
Cage CP	0.0040	0.0204	0.0006	–

[a] The electron density value at a given CP.
[b] The value of the electron density Laplacian at a given CP.
[c] The value of local electronic energy.
[d] The ellipticity value at a given CP.

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