

MNDO Study of the (Anti)aromaticity of Fluorine-Containing Cyclopentadienyl, Indenyl, and Cyclopenta[*b*]naphthyl Cations*

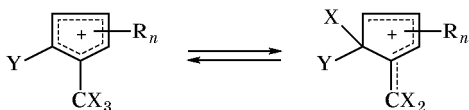
L. N. Shchegoleva, V. M. Karpov, and V. E. Platonov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia

Received April 18, 2001

Abstract—MNDO calculations were performed to estimate the aromaticity (antiaromaticity) of a series of fluorine-containing cyclopentadienyl, indenyl, and cyclopenta[*b*]naphthyl cations in terms of the Dewar–Breslow criterion which utilizes the difference in the enthalpies of formation of isomeric cations with closed and open π -systems as aromaticity index. The aromaticity is strongly determined by both the structure of the carbon skeleton and the number and position of fluorine atoms. A linear correlation was revealed between the aromaticity index and the energy of the lowest singlet–singlet excitation for cations having a cyclic π -system.

For studying the degree of aromaticity of cyclic conjugated systems in terms of the Dewar–Breslow criterion [1, 2], we previously proposed to use model compounds formally capable of existing as isomers with both closed and open conjugation chain [3], e.g., like those shown below:



Such models make it possible to compare the stability of ions. From the viewpoint of quantum-chemical calculations, an advantage of these models is that they provide the possibility for direct comparison of the total energies of isomers without introducing errors due to addition of extra atoms to compounds with an open conjugation chain.

In terms of the proposed approach, quantum-chemical estimation of the difference in the enthalpies of formation of fluorine-containing methylcyclopentadienyl cations and their isomers with an open π -system [4] showed that substituents could strongly affect the degree of aromaticity. Nevertheless, the examined substituted cyclopentadienyl cations retain


their antiaromatic character: cations with a cyclic π -system have higher energy than their “open” isomers. However, the situation may change in going to fluorinated derivatives of the other antiaromatic system, indenyl cation. According to the experimental data, perfluoroalkylindenyl cations [3, 5] and poly-fluoroalkylindenyl cations having chlorine atoms in the five-membered ring [6] (generated in solution) are thermodynamically more stable than isomeric alkylideneindanyl ions having an open π -system. In this connection we thought it reasonable to estimate the difference in the enthalpies of formation of fluorinated methylindenyl cations and their “open” isomers, alkylideneindanyl cations, and to relate the obtained aromaticity indices (Dewar–Breslow) to electronic structure parameters of indenyl and other cations having a cyclopentadienyl fragment.

The calculations were performed in the MNDO approximation using MOPAC 7.0 software package [7]; graphical representations of the orbital electron density distribution were generated with the aid of MOLDEN program [8]. Some data for cyclopentadienyl cations were taken from our previous publication [4]. The aromaticity indices of fluorinated methylcyclopentadienyl, methylindenyl, and methylcyclopenta[*b*]naphthyl cations were calculated by the formula

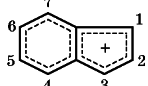
$$\Delta = \Delta H_f(\text{closed}) - \Delta H_f(\text{open}).$$

* This study was financially supported by the Russian Foundation for Basic Research (project no. 99-03-32876).

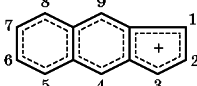
Table 1. Enthalpies of formation, aromaticity (antiaromaticity) indices, and energies of the lowest singlet excitations for model cations having a cyclopentadienyl fragment (all quantities are given in kcal/mol)



I–VIII



IX–XX



XXI–XXV

Comp. no.	Substitution pattern	ΔH_f	Δ	$\Delta E(S_0 \rightarrow S_1)$	Comp. no.	Substitution pattern	ΔH_f	Δ	$\Delta E(S_0 \rightarrow S_1)$
1-CH ₃					1-CF ₃				
I	–	240.8	21.5	19.3	V^a	–	118.7	24.6	19.2
II	2,5-F ₂	150.8	10.8	32.0	VI	2,5-F ₂	25.5	13.4	31.9
III	3,4-F ₂	153.4	16.7	24.5	VII^a	3,4-F ₂	38.1	24.5	20.8
IV	F ₄	75.9	15.2	20.9	VIII	F ₄	–47.2	17.6	25.1
2-CH ₃					2-CF ₃				
IX	–	230.1	10.0	33.6	XI	–	99.6	7.9	36.3
X	F ₆	–21.3	–0.1	45.7	XII	F ₆	–147.5	2.6	48.6
					XIII	1,3-F ₂	9.6	2.2	43.7
					XIV	1,3,4,7-F ₄	–73.1	0.6	50.0
1-CH ₃					1-CF ₃				
XV	–	228.7	4.8	34.8	XVIII	–	105.7	7.0	32.3
XVI	F ₆	–14.4	–0.3	39.7	XIX	F ₆	–134.1	5.3	37.4
XVII	2-CF ₃ ,F ₅	–113.0	–1.9	47.0	XX	2-CF ₃ ,F ₅	–228.7	–1.5	42.3
2-CH ₃					2-CF ₃				
XXI	–	236.4	3.2	47.0	XXII	F ₈	–224.4	–3.0	58.5
					XXIII	1,3,4,5,8,9-F ₆	–148.0	–4.4	56.5
1-CH ₃					1-CF ₃				
XXIV	–	235.9	–4.6	45.5	XXV	F ₈	–211.9	–2.8	49.2

^a The cation has an asymmetric structure as a result of the Jahn–Teller pseudoeffect.

Here, $\Delta H_f(\text{closed})$ and $\Delta H_f(\text{open})$ are the enthalpies of formation of isomeric cations with closed and open π -systems, respectively (Table 1). In keeping with the given data, the degree of aromaticity (antiaromaticity) strongly depends on both the structure of the carbon skeleton and the substituents; it ranges from 10.8 to 24.6, from –1.5 to 10, and from –4.6 to 3.2 kcal/mol for the series of substituted cyclopentadienyl, indenyl, and cyclopenta[*b*]naphthyl cations, respectively. The Δ values for cations of the first series are always positive, whereas the aromaticity index for fused

cations changes its sign, depending on the substitution pattern, i.e., cyclic π -system becomes energetically more favorable than its open analog. This is consistent with the experimentally observed [5] displacement of the equilibrium between perfluorinated “open” alkylideneindanyl and “cyclic” alkylindenyl cations toward the latter.

The antiaromatic character of the parent cyclic $C_5H_5^+$ cation results from incomplete population by electrons of the degenerate e_1'' π -MO of highly symmetrical D_{5h} structure [$(e_1'')^2$ electron configuration].

Therefore, the ground state of $C_5H_5^+$ is triplet, and the lowest singlet state is degenerate. Introduction of substituents eliminates degeneracy. However, such substituents as F, Me, and CF_3 weakly perturbate the π -system. According to the MNDO [4] and non-empirical MP2/6-31G* [9] calculations, the structures of frontier MOs of fluorine-substituted cyclopentadienyl and methylcyclopentadienyl cations are similar to the e_1'' components of the $C_5H_5^+$ MO (Fig. 1). The mode of splitting of e_1'' -MO (i.e., which of the components, ϕ_s or ϕ_a , is populated in the ground state of substituted cation) is determined by electronic effects of the substituents. The methyl and trifluoromethyl groups act in the opposite directions: in the ground state of methylcyclopentadienyl cation (**I**), ϕ_a -MO is populated, i.e. mesomeric effect is crucial. By contrast, the HOMO in trifluoromethylcyclopentadienyl cation corresponds to ϕ_s , while ϕ_a is the lowest unoccupied molecular orbital. The effect of fluorine atoms on the splitting of e_1'' -MO is determined by their mesomeric effect [4]: in the ground state of $C_5F_nH_{5-n}^+$ cations that of the ϕ_s -MO and ϕ_a -MO is populated which is localized on carbon atoms attached to fluorine to a lesser extent. Here, the degree of splitting depends on the difference in localization of ϕ_s -MO and ϕ_a -MO in the substituted positions. On the basis of the above qualitative considerations, the maximal splitting of e_1'' -MO could be expected for the cation 1-Me-2,5-F₂C₅H₂⁺ (**II**). It should be noted that this cation is characterized by the smallest value of Δ in the series of substituted cyclopentadienyl cations (Table 1).

On the whole, substituted cyclopentadienyl cations **I–VIII** are characterized by a fairly weak splitting of the electronic energy levels because of degeneracy of the singlet state of $C_5H_5^+$. This follows [4, 9] from the existence on the potential energy surface (PES) for all the cations of stationary structures with inverted frontier MOs (electronic isomers), which are interrelated through the pseudorotation coordinate. Pseudorotation has a vibronic nature (Jahn–Teller pseudo-effect, in contrast to the Jahn–Teller effect in unsubstituted $C_5H_5^+$). Jahn–Teller pseudodistortions are observed for 1-Me-C₅H₄⁺ (**V**) and 1-Me-3,4-F₂C₅H₂⁺ (**VII**) even in the ground state. Despite symmetric arrangement of fluorine atoms with respect to the CF_3 group, the cyclopentadiene ring in these cations is asymmetric, and the frontier MOs are linear combinations of ϕ_s and ϕ_a . The structure of the HOMO of cation **VII** was reported previously [4], and the frontier MOs of cation **V** are shown in Fig. 2. Just these cations are characterized by the maximal values of Δ (Table 1).

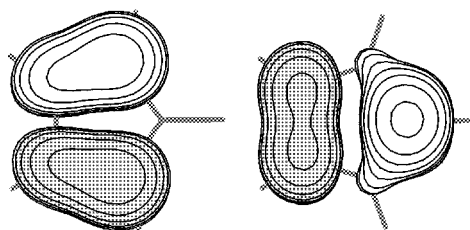


Fig. 1. Components of the degenerate e_1'' π -MO of the $C_5H_5^+$ cation (D_{5h} symmetry).

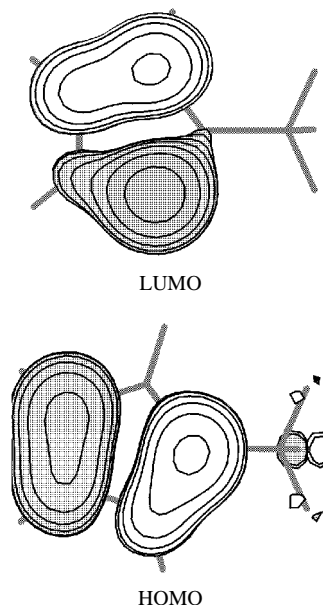


Fig. 2. Frontier molecular orbitals of the asymmetric $CF_3C_5H_4^+$ cation (**V**).

The presence of fused benzene rings induces much stronger perturbation of the π -system of cyclopentadienyl cation. Interaction between two π -systems gives rise to pairs of occupied and vacant MOs which are linear combinations of the ϕ_s and ϕ_a orbitals of the cyclopentadienyl system and orbitals of fused benzene rings. Figure 3 illustrates the resulting pattern with indenyl (**XXVI**) and cyclopenta[*b*]naphthyl (**XXVII**) cations as examples. Unlike cyclopentadienyl cations, no stationary points corresponding to electronic isomers were found on the PES of indenyl and cyclopenta[*b*]naphthyl cations. As noted above, Δ values for substituted indenyl cations **IX–XX** are on the whole smaller than those for cyclopentadienyl cations **I–VIII**; moreover, they decrease further and change their sign in going to cyclopenta[*b*]naphthyl cations **XXI–XXV**.

Taking the above stated into account, it is reasonable to presume a relation between the degree of

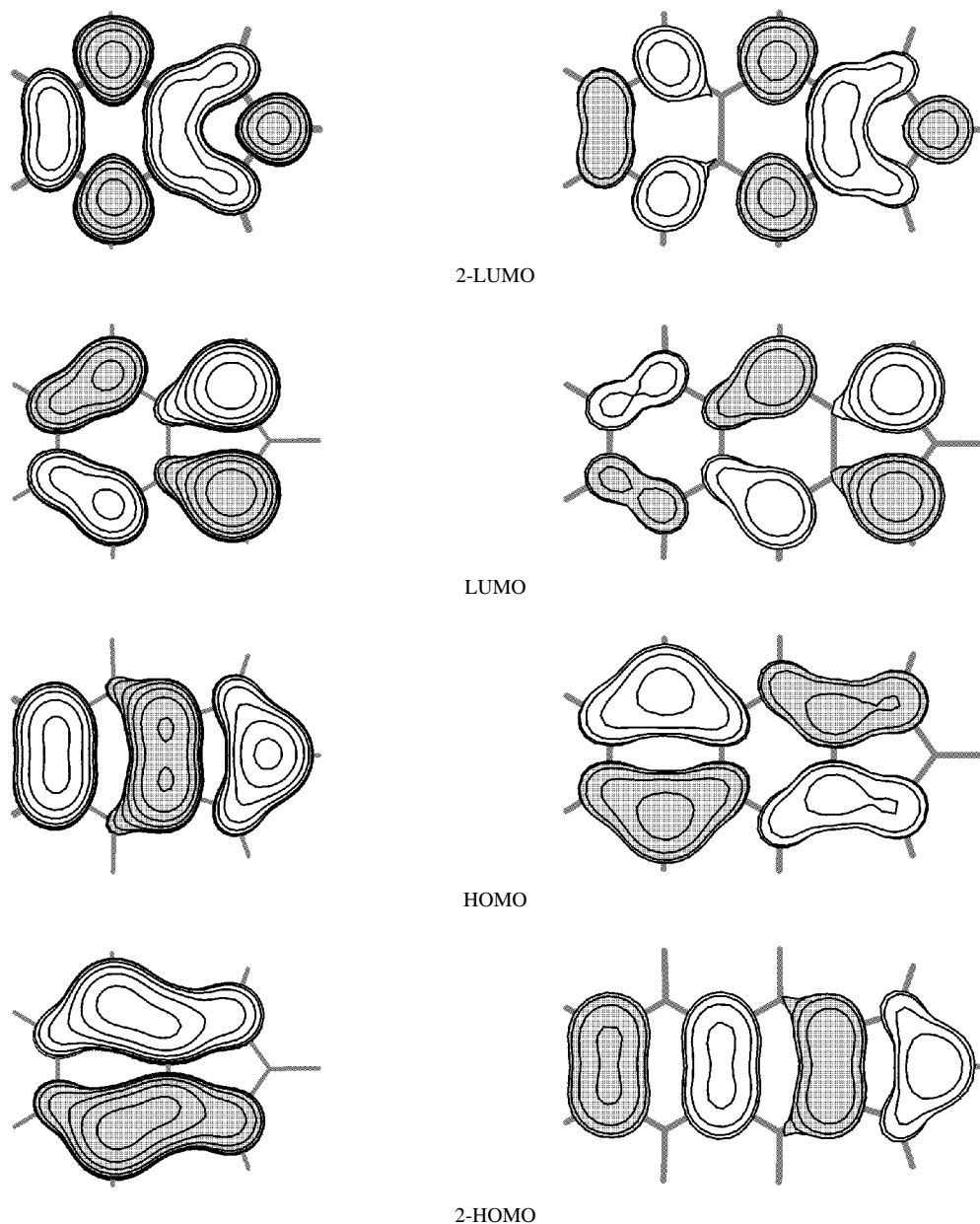


Fig. 3. Highest occupied and lowest unoccupied molecular orbitals of indenyl (XXVI) and cyclopenta[*b*]naphthyl (XXVII) cations.

aromaticity (antiaromaticity) of cyclic cations having a cyclopentadienyl fragment and splitting of the energy levels of electronic states arising from the degenerate singlet state of the parent $C_5H_5^+$ cation. The energy of excitation was calculated with account taken of configurational interaction. For cations of the cyclopentadienyl series, only electron transitions between ϕ_a -MO and ϕ_s -MO (2×2 CI) were considered; in the case of fused cations, the active space included two highest occupied and two lowest

unoccupied MOs which are significantly contributed by ϕ_a and ϕ_s (4×4 CI). The energies of the lowest singlet excitations, $\Delta E(S_0 \rightarrow S_1)$, are given in Table 1 together with Δ values.

Statistical treatment of the results showed that there is no common correlation for the whole series of cations under study. We can speak only of a general tendency to reduction of the degree of antiaromaticity as the energy gap between the ground and the lowest excited singlet state increases. However, particular

linear dependences exist for symmetric (I–IV, VI, VIII, IX–XVI, XXI–XXIII) and asymmetric (V, VII, XV–XX, XXIV, XXV) cations with fairly high correlation coefficients, $r = 0.976$ and 0.968 , respectively (Figs. 4a, b).

Insofar as the selection rules for mixing electronic configurations for symmetric and asymmetric cations are different, the lack of a single correlation may be due to limited consideration of configurational interactions. It should also be noted that the energies of excitation calculated in the one-configuration approximation do not correlate with Δ because of similar energies of electronic states in the systems under study. Also, there is no correlation between Δ and $(E_I - E_A)/2$ (here, E_I is the ionization energy, and E_A is the electron affinity). The latter quantity reflects the absolute rigidity and was used [10] as a measure of aromaticity of benzoid hydrocarbons.

Our results indicate that the Dewar–Breslow index Δ of cations having a cyclopentadienyl fragment changes its sign (which corresponds to appearance of an aromatic character) when the energy gap between the ground and lowest excited singlet state exceeds 52 kcal/mol for symmetric structures or 42 kcal/mol for asymmetric ones. With the goal of comparing with the true aromatic systems, analogous calculations were performed for methylcyclopentadienyl anion and its “open” isomer, as well as for toluene and isomeric 5-methylene-1,3-cyclohexadiene which is known [11] to undergo irreversible transformation into toluene. The obtained values, $\Delta = -18.9$, $\Delta E(S_0 \rightarrow S_1) = 83.1$ kcal/mol (4×4 CI) for methylcyclopentadienyl anion, and $\Delta = -21.9$, $\Delta E(S_0 \rightarrow S_1) = 92.8$ kcal/mol (4×4 CI) for toluene, are well consistent with the correlation for symmetric cations (Fig. 4a). Inclusion of these points in the statistical treatment leads to a linear relation with similar parameters but higher correlation coefficient:

$$\Delta = 29.94 - 0.58 \Delta E(S_0 \rightarrow S_1);$$

$$s = 1.87, n = 17, r = 0.989.$$

However, one should keep in mind that the transition $S_0 \rightarrow S_1$ has different natures for cyclopentadienyl cations and monocyclic aromatic systems. In the first case, the excitation involves ϕ_s and ϕ_a orbitals originating from the same pair of degenerate MOs of the parent $C_5H_5^+$ cation, and the quantity $\Delta E(S_0 \rightarrow S_1)$ reflects the degree of degeneration of electronic states. The $S_0 \rightarrow S_1$ excitation of monocyclic aromatic systems involves orbitals originating from different degenerate MO pairs of the parent system (HOMO and LUMO).

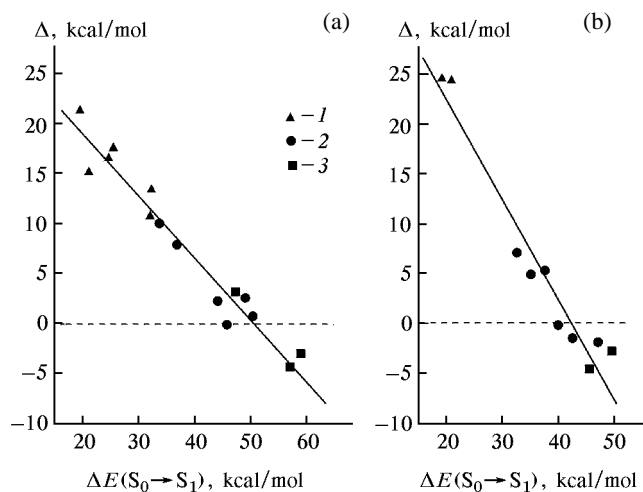


Fig. 4. Correlations between the Dewar–Breslow aromaticity index Δ and the energy of the lowest singlet–singlet excitation $\Delta E(S_0 \rightarrow S_1)$ for cations having a cyclopentadienyl fragment: (a) $\Delta = 31.35 - 0.62 \Delta E(S_0 \rightarrow S_1)$, $s = 1.85$, $n = 15$, $r = 0.976$ (symmetric cations); (b) $\Delta = 42.51 - 1.00 \times \Delta E(S_0 \rightarrow S_1)$, $s = 2.85$, $n = 10$, $r = 0.968$ (asymmetric cations); (1) methylcyclopentadienyl cations, (2) methylindenyl cations, (3) methylcyclopenta[*b*]naphthyl cations.

The existence of an inverse linear relation between the Dewar–Breslow aromaticity index and the energy of the lowest singlet–singlet excitation makes it also possible to compare (on a qualitative level) cyclic systems having no isomers with open conjugation chain. Table 2 contains $\Delta E(S_0 \rightarrow S_1)$ values which indicate increase of the aromaticity in going from indenyl cation (XXVI) to cyclopenta[*b*]naphthyl cation (XXVIII), as well as on replacement of hydrogen by fluorine. This is consistent with the data for analogous cations having a methyl or trifluoromethyl group. Thus the energy of the lowest singlet–singlet

Table 2. Enthalpies of formation and energies of the lowest singlet–singlet excitation (4×4 CI) of indenyl and cyclopenta[*b*]naphthyl cations and their perfluorinated analogs (kcal/mol)

Compound	ΔH_f	$\Delta E(S_0 \rightarrow S_1)$
Indenyl cation (XXVI)	240.7	28.0
Cyclopenta[<i>b</i>]naphthyl cation (XXVII)	247.0	41.0
Perfluoroindenyl cation (XXVIII)	-46.4	36.8
Perfluoro(cyclopenta[<i>b</i>]naphthyl cation (XXIX)	-123.1	53.0

excitation of compounds having a cyclic π -system may appear to be a universal parameter characterizing their aromaticity.

REFERENCES

1. Dewar, M.J.S., *The Molecular Orbital Theory of Organic Chemistry*, New York: McGraw-Hill, 1969.
2. Breslow, R., *Chem. Eng. News*, 1965, vol. 43, no. 26, pp. 90–99; Breslow, R., *Acc. Chem. Res.*, 1973, vol. 6, no. 12, pp. 393–398; Breslow, R., *Pure Appl. Chem.*, 1971, vol. 28, nos. 2–3, pp. 111–130.
3. Karpov, V.M., Platonov, V.E., and Yakobson, G.G., *Tetrahedron*, 1978, vol. 34, no. 21, pp. 3215–3218.
4. Shchegoleva, L.N., Karpov, V.M., and Platonov, V.E., *Zh. Strukt. Khim.*, 1996, vol. 37, no. 6, pp. 1023–1030.
5. Karpov, V.M., Platonov, V.E., Chuikov, I.P., and Shchegoleva, L.N., *Russ. J. Org. Chem.*, 1999, vol. 35, no. 1, pp. 80–84.
6. Karpov, V.M. and Platonov, V.E., *Russ. J. Org. Chem.*, 2001, vol. 37, no. 7, pp. 981–987.
7. Stewart, J.J.P., *MOPAC 7.0*, Public Domain Copy.
8. Schaftenaar, G., *QCPE-619*.
9. Shchegoleva, L.N., Karpov, V.M., and Platonov, V.E., *Zh. Strukt. Khim.*, 1999, vol. 40, no. 1, pp. 184–187.
10. Zhou, Z. and Navangul, H.V., *J. Phys. Org. Chem.*, 1990, vol. 3, no. 12, pp. 784–788.
11. Bailey, W.J. and Baylouny, R.A., *J. Org. Chem.*, 1962, vol. 27, no. 10, pp. 3476–3478.