Tetrahedron 60 (2004) 2259–2265

Tetrahedron

Influence of the H/F replacement on the homoaromaticity of homotropylium ion: a GIAO/DFT theoretical study

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Received 14 October 2003; revised 9 January 2004; accepted 12 January 2004

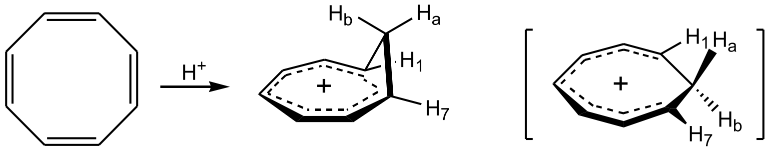
Abstract—The problem of homoaromaticity in mono-, di- and polyfluorinated- homotropylium cations is addressed by the B3LYP/6-311++G** DFT method. The energetic, structural and magnetic criteria are used for this purpose. They convincingly show that the ground state equilibrium species are aromatic, or in other words that the homoaromaticity is preserved by the (poly)fluorination. In contrast, a considerable decrease in the aromatic stabilization is observed in the transition structures (TS). According to the NICS(0) index, they vary form strongly antiaromatic, via weakly and non-aromatic to slightly aromatic transition states. However, the hierarchy of the aromaticity in fluorinated homotropylium ions predicted by NICS(0) is completely unrelated to that obtained by using the energy criterion assuming a kinetic definition of aromaticity. On the other hand the latter is closely related to geometric parameters of the equilibrium and transition structures.

1. Introduction

The concept of homoaromaticity was introduced by Winstein in 1959.[1–3] According to Winstein: “the aromatic stabilization of conjugated systems with $(4n+2)$ π-electrons may not be destroyed by the insertion of one or more intervening groups”.[4] The paradigm of homoaromaticity is the homotropylium ion (**1**) [also called homotropenylium cation, systematic name: (deloc-1,2,3,4,5,6,7)-2,4,6-cyclooctatrien-1-ylium] that can be obtained by protonation of cyclooctatetraene (COT).

It is useful to summarize the most important experimental characteristics of **1**:[1–5] (i) In ^1H NMR the following signals were observed: −0.67 (H_b), 5.10 (H_a) and 6.42 ppm (H_1 and H_7). (ii) The geometry of **1** is not known, but from other compounds it can be estimated that the non-bonded contact $C_1\cdots C_7$ is 2.28 Å, whereas all the ‘aromatic bonds’ (from C_1–C_2 to C_6–C_7) show almost perfect C–C bond equalization exhibiting the same bond length (no alternation). (iii) The inversion barrier, through planar **2**, amounts to 93.3 kJ mol^{-1}.

The homotropylium cation has been the subject of many theoretical studies.[4] The most important, in chronological order, are those of Haddon,[6] Cremer,[7–9] Schleyer.[9,10] and Lepetit–Silvi–Chauvin.[11] The second publication of Schleyer[10] offers an excellent summary of the situation. The main characteristics of the geometry of **1** are ‘aromatic’ C–C bonds around the perimeter of ~1.40 Å, except C_1–C_8=C_7–C_8=1.479. The non-bonded distance gives rise to a very sharp bond angle $C_1\cdots C_7$=1.906 Å, C_1–C_8–C_7=80.1° [MP2(full)/6-31G*]. Other methods give for the C_1–C_7 distance, 2.031 Å (MP4sdq/6-31G*) and 2.149 Å (B3LYP/6-311+G**).[10] The calculated inversion barrier is 104.0 [MP4sdq/6-31G*//MP2(full)/6-31G*] and



COT Homotropylium ion (**1**) Transition state (**2**)

Keywords: Homoaromaticity; NMR; GIAO; DFT.

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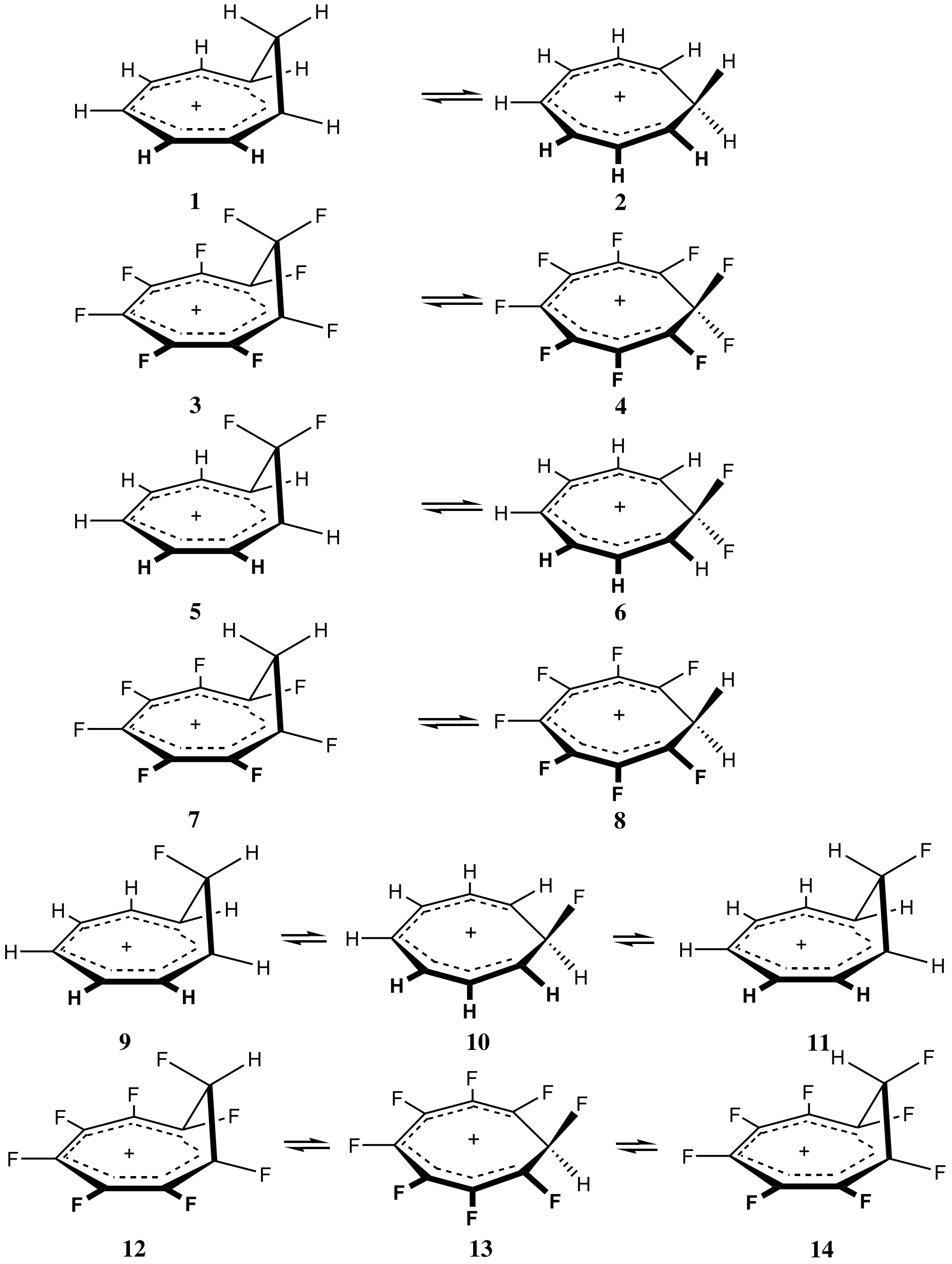
doi:10.1016/j.tet.2004.01.031



Scheme 1. The 14 molecules that have been studied.

89.3 kJ mol^{-1} [B3LYP (6-311+G**)+ZPE (RHF/6-31G*)]. In this work we consider the structure and properties of protonated COT and some of its polyfluorinated analogous with particular emphasis on their homoaromaticity.

2. Computational details

The calculations have been carried out with the Gaussian-98 program[12] by the hybrid HF–DFT method, B3LYP,[13] initially with the 6-31G* basis set.[14] The minimum or transition state nature of the structures has been confirmed at the B3LYP/6-31G* level by the vibrational frequency calculations. Additional optimization has been carried out by the B3LYP/6-311++G** computations.[15] The nuclear shieldings have been calculated using the GIAO method at the B3LYP/6-311++G** level.[16]

3. Results and discussion

The studied systems are depicted in Scheme 1. Their energies and geometries are summarized in Tables 1 and 2, respectively. The chemical shifts for the ground state equilibrium structures of **1**, **3**, **5**, **7**, **9** and **11** are reported in Table 3.

Table 1. Energetic properties of ions **1**–**14** shown in Scheme 1. E_{total} in hartrees and ZPE and E_{rel} in kJ mol^{-1}

	B3LYP/6-31G*, E_{total}	ZPE	B3LYP/6-311++G**		
			E_{total}	E_{rel}	E_{rel}+ZPE
C_8H_9 **1**	−309.95879	92.1	−310.03235	0.0	0.0
C_8H_9 (TS) **2**	−309.92390	91.9	−309.99792	90.4	89.5
C_8F_9 **3**	−1202.95293	46.0	−1203.32190	0.0	0.0
C_8F_9 (TS) **4**	−1202.92645	45.6	−1203.29519	70.1	68.4
$C_8H_7F_2$ **5**	−508.40942	81.7	−508.54984	0.0	0.0
$C_8H_7F_2$ (TS) **6**	−508.38190	82.0	−508.52143	74.6	76.0
$C_8F_7H_2$ **7**	−1004.51589	56.4	−1004.82336	0.0	0.0
$C_8F_7H_2$ (TS) **8**	−1004.48793	56.1	−1004.79375	77.7	76.1
C_8H_8F (in) **9**	−409.17726	86.9	−409.28546	0.0	0.0
C_8H_8F (out) **11**	−409.17753	86.9	−409.28698	−4.0	−4.2
C_8H_8F (TS) **10**	−409.14234	87.3	−409.25306	89.0	90.9[a,b]
C_8F_8H (in) **12**	−1103.72744	51.3	−1104.06703	−9.7	−10.1
C_8F_8H (out) **14**	−1103.72272	51.4	−1104.06332	0.0	0.0
C_8F_8H (TS) **13**	−1103.69566	51.1	−1104.03453	75.6	74.4[a,c]

[a] With regard to the out (in and out refers to the position of the fluorine atom).

[b] The barrier for **9** is 90.9−4.2=86.7 kJ mol^{-1}.

[c] The barrier for **12** is 74.4+10.1=84.5 kJ mol^{-1}.

3.1. Energetic properties

The collection of calculated energies (Table 1, last column, E_{rel}+ZPE, kJ mol^{-1}) provides a number of important information:

(i) Let us consider the monofluorinated derivatives substituted on the sp^3 bridge first.[17] It appears that the conformer **11** with the fluorine atom sticking ‘out’ is more stable than its counterpart **9** by 4.2 kJ mol^{-1}. The opposite situation is found in a pair **12**/**14**, where the fluorine ‘in’ conformation is more favorable by 10 kJ mol^{-1}. The former finding is compatible with a known fact that the equatorially substituted fluorine yields a more stable conformer of fluorocyclohexane.[17] Note that the difference is greater in the case of **14** over **12** (10.1 kJ mol^{-1}) than in the case of **11** over **9** (4.2 kJ mol^{-1}) counting always from the less stable

Table 2. Geometries of the compounds shown in Scheme 1 (distances in Å, angles in °) optimized at the B3LYP/6-311++G** level

	C1–C2	C2–C3	C3–C4	C1–C8	C1···C7
C_8H_9 **1**[a]	1.377	1.404	1.399	1.490	2.149
C_8H_9 (TS) **2**	1.356	1.427	1.390	1.498	2.685
C_8F_9 **3**	1.370	1.425	1.403	1.517	2.428
C_8F_9 (TS) **4**	1.366	1.432	1.398	1.517	2.707
$C_8H_7F_2$ **5**	1.368	1.412	1.397	1.493	2.279
$C_8H_7F_2$ (TS) **6**	1.357	1.423	1.391	1.496	2.700
$C_8F_7H_2$ **7**	1.370	1.419	1.405	1.491	2.353
$C_8F_7H_2$ (TS) **8**	1.361	1.433	1.397	1.494	2.673
C_8H_8F (in) **9**	1.376	1.405	1.397	1.491	2.142
C_8H_8F (out) **11**	1.373	1.405	1.400	1.487	2.198
C_8H_8F (TS) **10**	1.358	1.424	1.391	1.497	2.688
C_8F_8H (in) **12**	1.370	1.423	1.402	1.500	2.380
C_8F_8H (out) **14**	1.371	1.419	1.408	1.504	2.369
C_8F_8H (TS) **13**	1.365	1.432	1.396	1.516	2.662
	C1–C8–C7	C2–C1–C8	C3–C2–C1	C4–C3–C2	C3–C4–C5
C_8H_9 **1**	92.3	124.1	128.0	130.7	129.6
C_8H_9 (TS) **2**	127.3	138.3	134.5	137.0	133.3
C_8F_9 **3**	106.3	126.2	128.7	132.8	131.4
C_8F_9 (TS) **4**	126.2	138.5	134.9	136.4	134.1
$C_8H_7F_2$ **5**	99.5	125.0	129.7	131.9	130.7
$C_8H_7F_2$ (TS) **6**	129.0	137.1	134.8	136.6	134.0
$C_8F_7H_2$ **7**	104.2	125.5	126.0	131.9	130.6
$C_8F_7H_2$ (TS) **8**	127.0	139.2	133.7	136.6	134.1
C_8H_8F (in) **9**	91.9	124.9	129.8	130.8	130.0
C_8H_8F (out) **11**	95.3	124.1	127.3	131.1	129.9
C_8H_8F (TS) **10**	127.9	137.7	134.8	136.6	133.7
C_8F_8H (in) **12**	105.0	127.2	128.1	132.6	131.3
C_8F_8H (out) **14**	103.9	124.1	125.7	131.8	130.8
C_8F_8H (TS) **13**	122.8	138.6	134.2	135.9	133.1

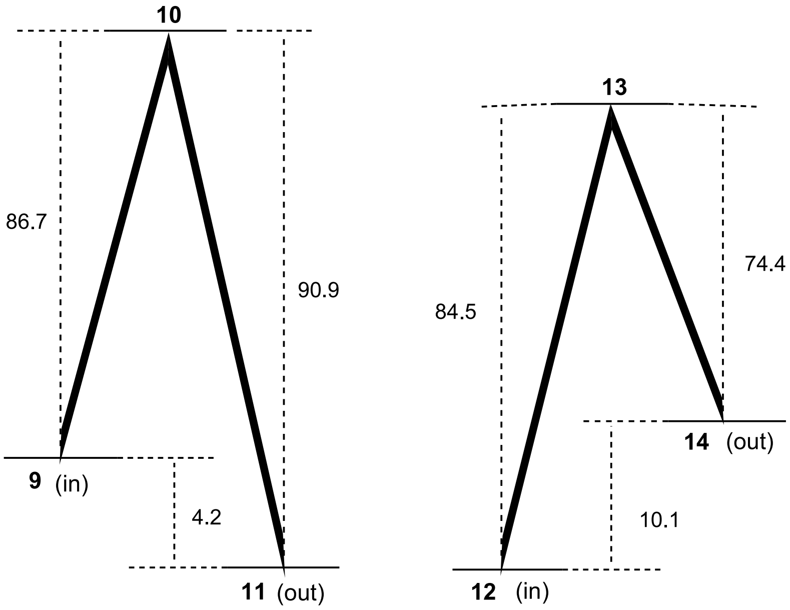
[a] The optimized geometry of **1** (Table 2) is practically identical to that calculated at the B3LYP/6-311+G** by Schleyer et al.:[10] aromatic C1–C2, C2–C3 and C3–C4 bonds are of 1.377/1.404/1.399 Å, respectively, whereas C1–C8=C$_7$–C$_8$=1.490, C1···C7=2.149 Å and the sp^3 carbon atom bond angle C1–C8–C7=92.3°. The same holds for the inversion barrier (Table 1) is 90.4 kJ mol^{-1} as compared to 89.5 kJ mol^{-1} calculated by ZPE (B3LYP/6-311++G**).[10]

Table 3. GIAO-B3LYP/6-311++G** calculation of absolute shieldings (σ ppm) of the methylene bridge

Compound	In[a]	Out[a]	$\Delta\sigma$ (in−out)	C8 (^{13}C)[b]
C_8H_9 **1**	32.70 (^{1}H)	26.85 (^{1}H)	5.85 (^{1}H)	142.3
C_8H_9 (TS) **2**	27.28 (^{1}H)	—	—	134.3
C_8F_9 **3**	302.16 (^{19}F)	302.36 (^{19}F)	−0.20 (^{19}F)	72.8
C_8F_9 (TS) **4**	199.43 (^{19}F)	—	—	67.2
$C_8H_7F_2$ **5**	288.18 (^{19}F)	286.75 (^{19}F)	1.43 (^{19}F)	63.8
$C_8H_7F_2$ (TS) **6**	118.18 (^{19}F)	—	—	63.8
$C_8F_7H_2$ **7**	30.76 (^{1}H)	27.67 (^{1}H)	3.09 (^{1}H)	149.6
$C_8F_7H_2$ (TS) **8**	27.49 (^{1}H)	—	—	142.9
C_8H_8F (in) **9**	369.71 (^{19}F)	24.74 (^{1}H)	5.57 (^{19}F)	103.0
C_8H_8F (out) **11**	29.55 (^{1}H)	364.14 (^{19}F)	4.81 (^{1}H)	82.8
C_8H_8F (TS) **10**	25.17 (^{1}H)	208.20 (^{19}F)	—	96.2
C_8F_8H (in) **12**	397.25 (^{19}F)	25.49 (^{1}H)	3.59 (^{19}F)	101.3
C_8F_8H (out) **14**	28.82 (^{1}H)	393.66 (^{19}F)	3.33 (^{1}H)	102.0
C_8F_8H (TS) **13**	326.08 (^{19}F)	24.81 (^{1}H)	—	97.5

[a] For the transition states, the in/out description is irrelevant.

[b] These chemical shifts depend essentially on the number of fluorine atoms on C8, each F atom diminishes the chemical shift by about 45 ppm, but if two F atoms are present simultaneously, there is an increase of 15 ppm.

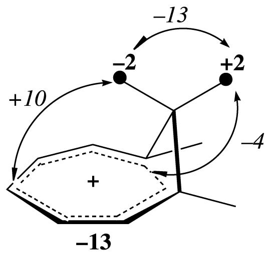


Scheme 2. The energy profiles of **9**–**10**–**11** and **12**–**13**–**14** equilibria. Notice that the zero energy origin is different in the left and right parts of the scheme.

isomer (Scheme 2). Schneider was the first to point out that electron poor arenes (phenyl groups bearing ammonium substituents) interact with anions.[18] Subsequently, this was extended to hexafluorobenzene,[19] and others to *s*-triazines and polynitrobenzenes.[20] We showed that polar neutral molecules led to stabilizing interactions with perfluoroaromatic compounds.[21] This explains why the interaction of the fluorine in is stabilizing in the case of **12** and destabilizing in the case of **9**.

(ii) A statistical analysis of the barriers, taking into account the presence of fluorine atoms on the periphery of the ring and on the bridge in positions in and out, reveals that the barrier depends not only on the principal factors (**bold**, periphery −13, in; −2, out +2 kJ mol^{-1}), but also on the interaction between them (italic, in-periphery +10, out-periphery −4, in–out −13 kJ mol^{-1}) as illustrated in Scheme 3.

The +10 kJ mol^{-1} term corresponds to the attractive interaction between the F in and the fluorinated periphery that stabilizes the equilibrium ground state structure thus increasing the barrier. One of the largest term, −13 kJ mol^{-1}, means that the presence of two fluorine atoms in the bridge, decreases considerably the



Scheme 3. Representation of the main effects of the fluorine atoms on the inversion barrier.

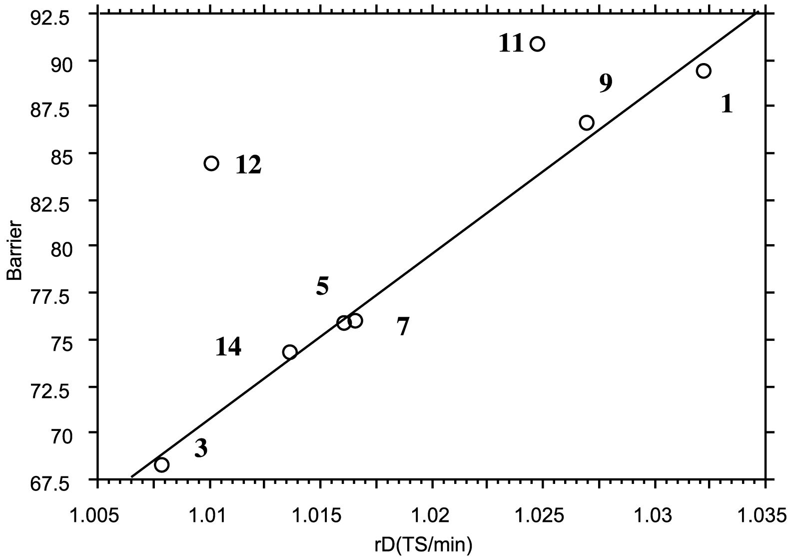


Figure 1. Plot of energy barriers (kJ mol^{-1}) vs r_D (TS/GS).

barrier, either by destabilizing the minimum or by stabilizing the TS. The latter would correspond to a decrease in the barrier due to perfluorinating the periphery.

(iii) Assuming a kinetic definition of the aromaticity (the higher the barrier, the more aromatic the compound), the aromaticity of the homotropylium ions decreases in the order **11**>**1**>**9**>**12**>**7**≥**5**>**14**>**3**. The more stable conformers, **11** and **12**, having higher barriers, appear to be more aromatic than the less stable ones, **9** and **14**.

3.2. Structural properties

Analysis of the calculated structural parameters summarized in Table 2 shows that in the ground states, the fluorination on the sp^2 carbons, increases the C1···C7 distance by 0.19 Å and the C1–C8–C7 angle by 10° on the average. The effect on the sp^3 bridge C1–C8 bond is very small, the notable exception being perfluoro derivative **3**, where an elongation of 0.027 Å is observed. Intuitively, one could therefore expect a relationship between the barriers and geometries. An examination of the C–C distances between sp^2 carbons confirms that the TS is less aromatic than the equilibrium structures[7] (or that the equilibrium structure is aromatic and TS is it not, see NICS calculations).[10] If we choose the C2–C3/C1–C2 ratio (r_D), as an aromaticity index this ratio should be large when the loss of aromaticity is large. Another point of considerable interest is the C1–C2 bond distance, which is the shortest in all compounds. This is indicative of the homoconjugative interaction with the out of plane C1–C8 and C7–C8 bonds. Fluorination has very little effect on the C1–C2 bond distance implying that it does not affect much the homoconjugation. In TS, this bond is even shorter, because of the considerable localization effect with accompanying bond length alternation. Intuitively, one could therefore expect that the barrier increases as r_D increases. That is what is observed in Figure 1.

The barriers of compounds **11** and **12** deviate and have been excluded from the regression (their inclusion lowers the correlation coefficient to very small r^2=0.62). The straight line depicted in Figure 1 corresponds to:

$$\text{Barrier (kJ mol}^{-1}) = -(824 \pm 37) + (886 \pm 37) r_D, \tag{1}$$

$$n = 6, \qquad r^2 = 0.993$$

Although we have no explanation, it should be noted that **11** and **12** correspond to the minimum energy conformers (those with highest barriers) of the equilibria shown at the bottom of Scheme 1.

3.3. Magnetic properties

The calculated absolute shieldings (σ, ppm) of the methylene bridge calculated by the GIAO-B3LYP/6-311++G** method are given in Table 3.

To discuss the NMR data, we will first examine those of compound **1**, since the corresponding experimental information is available (Table 4). The ^{13}C NMR data (at −60 °C

Table 4. Calculated absolute shieldings (σ ppm) and experimental chemical shifts (δ ppm) for homotropylium cation **1**

Atom	δ (ppm)[a]	IGLO[b]	GIAO
C1/C7	122.2	105.0/119.0	133.2
C2/C6	153.7	155.9/149.6	145.6
C3/C5	143.2	143.7/150.7	149.5
C4	144.7	148.1/150.7	139.7
C8	43.7	36.2/35.1	40.2
H1/H7	6.42/6.48		6.49
H2/H6	/8.39		8.33
H3/H5	/8.57		8.72
H4	/8.27		8.25
H8a	5.10/5.13		4.94
H8b	−0.67/−0.73		−0.68
$\delta H_a-\delta H_b$	5.77/5.86	5.1	5.62

[a] ^{1}H NMR: From Ref. 24b/3b and 5b.

[b] ^{1}H NMR:[IGLO/6-31G**//MP2/6-31G*]/[MP4(SDQ) value of R(1,7), distance C1–C7].

in FSO_3H-SO_2ClF or at −78 °C in FSO_3H-SbF_5/SO_2ClF) were measured by Paquette, Olah et al.:[22b] 43.7 (C8, dd, J=159.2, 155.8 Hz); 122.2 (C1 and C7, d, J=175.8 Hz); 153.7 (C2 and C6, d, J=163.6 Hz); 143.2 (C3 and C5, d, J=165.9 Hz); 144.7 ppm (C4, d, J=165.3 Hz). We have published GIAO/B3LYP/6-311++G** calculations that are relevant for the present paper.[23] They are reported in Table 5.

Table 5. Calculated absolute shieldings (σ, ppm) and experimental chemical shifts (δ, ppm) for some relevant compounds

Compound	$\sigma\,^1H$	$\delta\,^1H$	$\sigma\,^{13}C$	$\delta\,^{13}C$
TMS	31.97	0.00	184.75	0.00
Methane	31.74	0.23	190.43	−7.0
Benzene	24.40	7.26	49.65	130.2

The data of Tables 4 and 5 together with the σ values of **1** have been used to calculate the δ values of Table 4 through Eqs. 2 and 3:

$$\delta^1H = (30.8 \pm 0.2) - (0.962 \pm 0.008)\,\sigma^1H, \qquad n = 9, \qquad r^2 = 0.999 \tag{2}$$

$$\delta^{13}C = (174 \pm 4) - (0.939 \pm 0.036)\,\sigma^{13}C, \qquad n = 8, \qquad r^2 = 0.991 \tag{3}$$

The agreement is highly satisfactory, in particular the $\delta H_a - \delta H_b$ value. It is worth noticing that Winstein using the simple Johnson–Bovey tables calculated δ=5.56 ppm.[2,24] He also reported that the effect is 5.42 ppm for H_b and −0.14 ppm for H_a, proving simultaneously the usefulness of the Johnson–Bovey approximation and the aromatic character of the homotropylium ring. It should be recalled that the Johnson–Bovey equation was calculated for benzene itself.

For the remaining compounds, we report only the atoms of the methylene bridge in Table 3. We will discuss the $\Delta\sigma$ values (ppm). It is useful to consider two things: (i) the ring-current effects are independent of the probe (^1H or ^{19}F) and depend only of the geometry.[24] (ii) The ring-current effects produced by C_6H_6 and C_6F_6 are very similar.[25] Neglecting other effects (geometries differences, anisotropies of the C–F bonds), it is expected that $\Delta\sigma$ would be similar in all cases. This is not the case although most values are in the range 3–6 ppm, compounds **3** and **5** (both having a CF_2) behave differently. Empirically, the data of Table 3 can be adjusted to a model taking into account the perfluorination of the aromatic part (Ar: 0 for 7H and 1 for 7F) and the nature of the out atom (R_{out} 0 for H and 1 for F):

$$\Delta\sigma(\text{ppm}) = -(2.4 \pm 0.3)\text{Ar} - (4.0 \pm 0.4)R_{out}, \qquad n = 8, \qquad r^2 = 0.979 \tag{4}$$

3.4. The problem of the magnetic definition of aromaticity in homotropylium ions

We have mentioned earlier that if a kinetic definition of the aromaticity is assumed (measured by the inversion barrier, i.e., the difference in energy between the ground and the transition states) then the aromaticity decreases in the order **11**>**1**>**9**>**12**>**7**≥**5**>**14**>**3**. We wish now to approach this problem using as criterion Schleyer's NICS(0) (there is a problem of sign when relating NICS and aromaticity, here a + sign corresponds to aromatic compounds, for instance, benzene +8 ppm).[26,27] There is no difficulty in calculating the NICS(0) for the TSs, but this is not the case for the equilibrium structures. To calculate the NICS(0), it is necessary to carry out Bader's AIM analysis first in order to pinpoint the ring critical point (rcp).[28] It is possible to identify the rcps for the TSs **2**, **4**, **6**, **8**, **10** and **13** without any problem, but in the non-planar minima, the rcps of **7** and **14** do not exist. Consequently, we determined a geometrical center-of-gravity of carbons C1–C2–C3–C4–C5–C6–C7 (heptagon) for the equilibrium structures and of carbons C1–C2–C3–C4–C5–C6–C7–C8 (octagon) for the TSs. The largest difference in the position of the rcp and the geometrical center-of-gravity is 0.22 Å for the true minima on the potential surface and 0.11 for the TSs. The results are in Table 6.

According to Table 6 data, the equilibrium structures are aromatic and the TSs vary from strongly antiaromatic (**2**) to weakly antiaromatic (**8**, **10**) to non-aromatic (**4**, **6**) and to slightly aromatic (**13**). The barriers and the NICS(0) are completely unrelated. Even if we apply as an aromaticity criterion the difference of NICS(0), Δg, between the equilibrium and the TS, the order of aromaticity should be **1**>**7**>**9**>**11**>**3**>**14**>**5**>**12**, completely unrelated to that found previously, even excluding compounds **11** and **12**. This is not surprising since NICS are strongly perturbed by the C–F dipoles and do not reflect the aromaticity in fluorinated derivatives. Having said this, it should be

Table 6. NICS(0) (ppm) calculated at the rcp and at the geometrical center-of-gravity (g); Δg is the difference of g between the minimum and the TS

	rcp	g	Δg		rcp	g	Δg
C_8H_9 **1**	11.29	10.13	26.85	C_8H_8F (in) **9**	11.45	10.14	13.40
C_8H_9 (TS) **2**	−16.72	−16.72		C_8H_8F (out) **11**	11.00	10.04	13.30
				C_8H_8F (TS) **10**	−3.24	−3.26	
C_8F_9 **3**	9.87	9.65	9.99				
C_8F_9 (TS) **4**	−0.32	−0.34		C_8F_8H (in) **12**	9.68	9.50	7.59
				C_8F_8H (out) **14**	—	11.44	9.53
$C_8H_7F_2$ **5**	9.71	8.55	8.89	C_8F_8H (TS) **13**	1.89	1.91	
$C_8H_7F_2$ (TS) **6**	−0.32	−0.34					
$C_8F_7H_2$ **7**	—	10.17	14.03				
$C_8F_7H_2$ (TS) **8**	−3.86	−3.86					

pointed out that NICS(0) values do reflect the fact that in going from the equilibrium ground state to transition state structure a sharp decrease in the aromatic character takes place. This is in accordance with the conclusion derived by considering the variation in bond distances (vide infra).

4. Conclusion

We have shown that homoaromaticity of mono-, di- and polyfluorinated homotropylium cations is not much affected by a degree of fluorination implying that it is a persistent property of the parent homotropylium ion. In contrast, a substantial decrease in the aromaticity is detected in the transition state structures. Adopting a kinetic definition of aromaticity, it turns out that aromaticity is linearly related to geometric features of the ground state equilibrium and transition state structures. On the other hand, the hierarchy of aromaticity obtained by NICS(0) index is completely different.

Acknowledgements

Support was provided by the Spanish DGI (Project No. BQU2003-01251). One of us (Z. B. M.) would like to acknowledge Iberdrola Foundation Visiting Fellowship, which enabled his stay at the Universidad Autonóma de Madrid.

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