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THE GENERATION OF POLYFLUOROINDENYL CATIONS

ON THE AROMATICITY OF POLYFLUOROINDENYL CATIONS[1]

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Abstract—A number of polyfluoroindenyl cations has been generated by the interaction of polyfluoroindenes with SbF_5. In particular perfluoro-2-methylindenyl cation has been generated from perfluoro-2-methylindene ("open-chain" perfluoro-2-indenylmethyl ion has not been fixed). On this basis it has been proposed, that perfluoro-2-methylindenyl cation has an aromatic character (according to the Dewar and Breslow's criterion of the aromaticity).

It is well known, that the indenyl anion has an aromatic character, but the indenyl cation has an antiaromatic one.[2–4] Generation of their polyfluorinated analogs is of great interest owing to investigation of the influence of F atoms on the properties of aromatic and antiaromatic systems. In particular polyfluoroindenyl cations would become more stable than their nonfluorinated analogs in consequence of possible resonance stabilization of cations by F atoms. The resonance stabilization of carbocations by F atoms and atoms of other halogens is known.[5] The stabilizing influence of Cl atoms has been also detected in the case of the pentachlorocyclopentadienyl cation, however, its anti-aromatic character remains.[3,6] Taking into account these data, it was difficult to expect the change of antiaromatic character of indenyl cation to an aromatic one when introducing F atoms as substituents. In this connection the generation of number of polyfluorinated indenyl cations is described and the attempt has been made to estimate their degree of aromaticity.

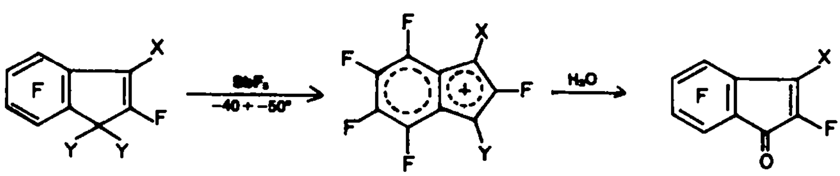
The salts of polyfluoroindenyl cations were formed when polyfluoroindenes were dissolved in the SbF_5–SO_2 system. Thus, heptafluoroindenyl cation **2a** was generated from octafluoroindene **1a**. Analogously 1-chlorohexafluoroindenyl cation **2b** and 1,3 - dichloropentafluoroindenyl cation **2c** were generated from 3 - chloroheptafluoroindene **1b** and 1,1,3 - trichloropentafluoroindene **1c**, respectively.

The salt of 1-H-hexafluoroindenyl cation **2d** is formed when 3 - H - heptafluoroindene **1d** was solved in the SbF_5–SO_2ClF system. Resinous products were formed when indene **1d** was solved in the SbF_5–SO_2 system, though the ^{19}F NMR spectrum revealed ion **2d** generation at the early stages of reaction. Perhaps such behavior of indene **1d** under these conditions is due to the incomplete change of equilibrium to the ion **2d** and the latter reacts with the initial compound **1d** giving resinous products.

The ^{19}F NMR spectroscopy data and some chemical transformations demonstrate the generation of polyfluoroindenyl cations when polyfluoroindenes react with antimony pentafluoride. Thus, when the solutions of cation **2b** and **2c** salts interact with water 3 - chloropentafluorindone **3** forms. It is known that corresponding ketones are formed by hydrolisis of salts of polyfluorinated arenonium ions.[7]

In the ^{19}F NMR spectra of polyfluoroindenyl cations, there are some characteristic features, which had been previously observed for other polyfluorinated cations (in Fig. 1 as an example is given spectrum of perfluoro - 2 - methylindenyl cation **2e**). Thus, the downfield shift of most of signals is observed as compared to the precursor in ^{19}F NMR spectra of polyfluoroindenes solutions in SbF_5 (Table 1, see Refs. 7,8). All spectra consideration of generated pohufluoroindenyl cations permits us to ascribe rather strictly the signals of F atoms in the positions 1, 2, 3. The signals of 1(3)-F atoms are the most downfield. F atom signal in position 2 is in upfield. The signals of the other F atoms have not been simply classified.

The approximation to the first order structure permits us to interpret the fine structure of signals in ^{19}F NMR ions **2b,d** spectra. It follows from ^{19}F NMR spectra of generated cations that some spin-spin coupling constants of F atoms increase as compared to the precursors (as in case of polyfluorinated arenonium and benzyl cations[7,8]). The highest values of spin-spin coupling constants have been observed in most downfield signals of F atoms. For example, values of these constants for cation **2b** are 65 Hz (F atoms at δ_F −131.6 and −64.3 ppm) and 51 Hz (F atoms at δ_F −131.6 and −71.9 ppm) and for cation **2d** are 74 Hz (F atoms at δ_F −160.2 and −92.7 ppm) and 67 Hz (F atoms at δ_F −160.2 and −64.4 ppm). The complete analysis of ^{19}F NMR spectra of polyfluoroindenes was not carried out. However it follows from the estimates of the fine structure signals in approximation to the first



1a–d **2a–d** **3b, c**

(a) X = Y = F; (b) X = Cl, Y = F; (c) X = Y = Cl; (d) X = H, Y = F

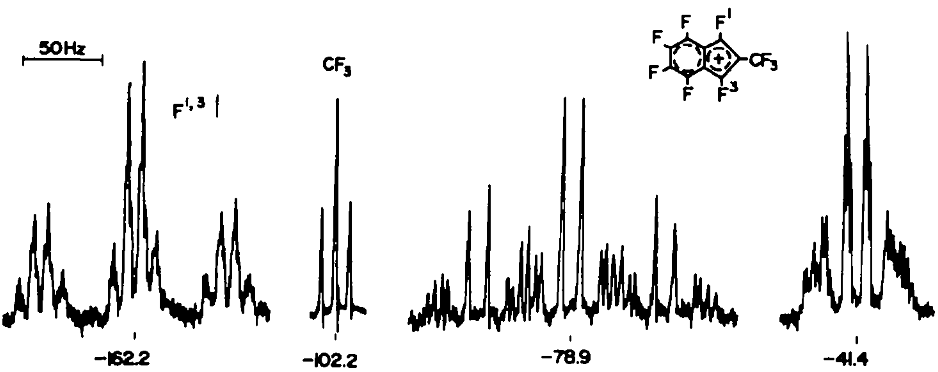


Fig. 1. ^{19}F NMR spectrum of the perfluoro-2-methylindenyl cation 2e (in SbF_5–SO_2 solvent system).

Table 1. ^{19}F NMR spectra of polyfluoroindenyl cations and their precursors

Ion	Chemical shifts, ppm[a,b]			Precursor	Chemical shifts, ppm[a,c]	
	$F^{1,3}$	F^2	other atoms (intensity)		CF_2	other atoms (intensity)
2a	142.0	11.9	75.6(2), 36.9(2)	1a	38.0	24.8(1), 17.8(1), 17.4(1), 15.4(1), 10.9(1), 4.9(1)
2b	131.6	23.1	71.9(1), 64.3(1) 39.1(1), 31.6(1)	1b	38.2	24.5(1), 23.3(1), 15.2(2), 9.9(1)
2c	-	33.1	61.4(2), 33.3(2)	1c	-	28.2(1), 22.8(1), 13.1(2), 8.7(1)
2d[d]	160.2	30.4[e]	92.7(1), 64.4(1), 57.1(1), 22.3(1)[e]	1d	35.9	30.0(1), 22.8(1), 16.8(1), 14.0(1), 7.5(1)
2e	162.2	102.2 (CF_3)	78.9(2), 41.4(2)	1e	45.5	102.2(3), 55.8(1), 25.3(1), 22.0(1), 16.0(2)

[a] Downfield chemical shifts from internal C_6F_6. [b] For solutions in SbF_5–SO_2 (−40°).
[c] For solutions in CCl_4. [d] For solution in SbF_5–SO_2ClF (−50°). [e] Proposed attribution.

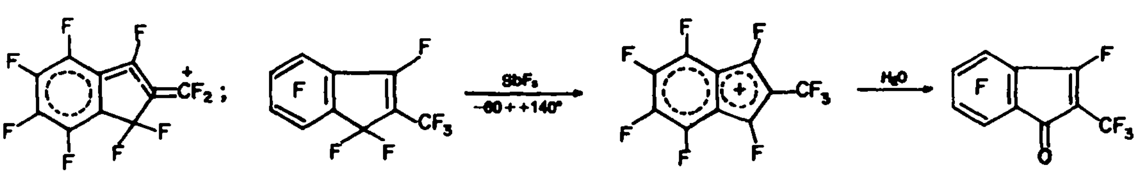
order structure, that the values of constants in these compounds do not exceed 20–30Hz.

Formally ($4n = 8$ π-electrons) polyfluoroindenyl cations are antiaromatic. Accordingly, heptafluoroindenyl cation 2a had been previously classified as an antiaromatic.[9] For estimating the degree of aromaticity of polyfluoroindenyl cations, it seemed reasonable to employ the aromaticity criterion which is used in the works of Dewar[4] and Breslow[2,3] and resides in comparing the energy characteristics (for example, heats of formation[4]) of cyclic and corresponding open-chain ions.

Previously, for revealing experimentally the degree of aromaticity (antiaromaticity) of cyclic ion, comparison was made of the energy characteristics of the cyclic and open-chain ions generated from two different precursors.[2,3,10] As some approach to solving the problem concerning the aromaticity of polyfluoroindenyl cations we suggest using one precursor, for example perfluoro-2-methylindene 1e. The degree of aromaticity of perfluoro-2-methylindenyl cation 2e could be estimated if ion 2e and perfluoro-2-indenylmethyl cation A could be generated from indene 1e and equilibrium between these two cations could be investigated taking into account various factors (solvating effects; different influence of difluoromethylene group bonded to 6-membered ring and trifluoromethyl group upon the stability of ions A and 2e, etc.).

In the literature, when studying the degree of aromaticity of ions, the experimental data obtained for solutions and gaseous phases are in good agreement (when comparing the difference in the energy characteristics of the two ions).[10,11] Moreover, the experimental data obtained for solutions are in agreement with theoretical predictions concerning the degree of aromaticity of cyclic ions.[2-4,10,11] In view of the above-stated, the applicability of the data obtained for solutions for a preliminary estimation of the degree of aromaticity of cyclic ions should be not excluded.

We have shown that when indene 1e is dissolved in the SbF_5–SO_2 system or in SbF_5, a cation 2e is generated. There are four well resolved signals in the ^{19}F NMR spectrum of cation 2e (Fig.). Perfluoro-2-methylindone 4 was formed as a result of quenching of ion 2e salt solution by water.



A 1e 2e 4

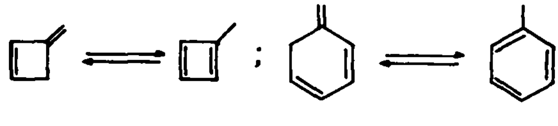
The cation 2e[a] undergoes no changes in the investigated range of temperatures from −60 to +140°. The ^{19}F NMR spectrum of the ion 2e showed no changes after the cation salt solution in antimony pentafluoride was kept at room temperature for more than two years.

If in the reaction of perfluoro - 2 - methylindene 1e with antimony pentafluoride a thermodynamic control takes place, then the fact that a cation 2e rather than an "open-chain" ion A[b] was generated from indene 1e gives grounds for doubts of the anti-aromatic nature of the cation 2e and for a suggestion that this cation is of an aromatic character.

If perfluoro-2-methylindenyl cation 2e is aromatic, then, as far as we are aware, this is the first example of "conversion" of an antiaromatic cation into an aromatic one upon introducing substituents into it and, particularly, upon introducing F atoms as such substituents. It can not be excluded that in certain other cases introducing substituents with a strong +M or −M effect into the molecule of an antiaromatic compound will allow "conversion" of this compound into an aromatic one.

We suggest that the above-discussed approach for preliminary experimental assignment of cyclic ions (both cations and anions) to an aromatic or antiaromatic system should be applied in series of other cyclic compounds, such as cyclopropene series, cyclopentadiene series, etc. using as models those compounds which are formally capable to give both cyclic and "open-chain" ions, e.g.:

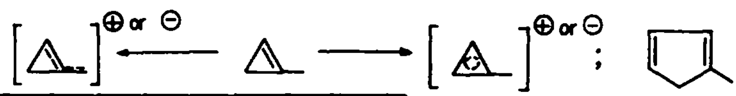
This approach can, evidently, be extended to uncharged substances as well, e.g.:



According to this, first equilibrium should be changed to the left, and the latter—to the right, since methylcyclobutadiene must be an antiaromatic compound,[2-4] but toluene is an aromatic substance. Indeed, 3 - methylenecyclobutene - 1 does not tend to isomerize to methylcyclobutadiene,[13] and 5 - methylenecyclohexadiene - 1,3 irreversibly isomerizes to toluene.[14]

Similar equilibria, evidently, must be studied in the case of heterocyclic compounds, e.g.:

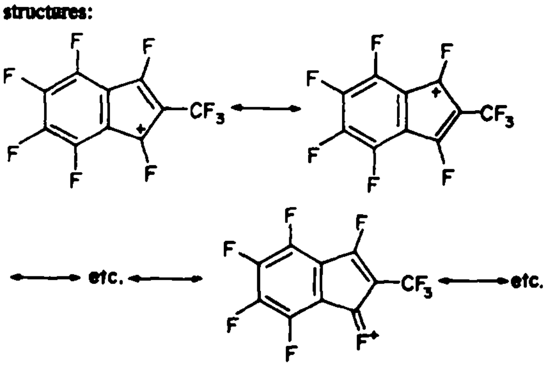
The tautomeric equilibria have been suggested for determination of "aromatic resonance energy" of heteroaromatic systems.[15,16] The difference between resonance energies of a cyclic compound and its "open-



etc.

chain" analogs has been estimated in some cases by investigating their equilibrium.[16]

[a]The representation of perfluoro - 2 - methylindenyl cation by the formula 2e shows all C atoms to be included in the π-system of ion and it can be represented formally as a set of resonance structures:



The distribution of electron density with participation of C and F atoms will depend on the most stable structure of the ion. However, the distribution of the π-electron density will not be even.

[b]It could be expected that the rupture of C–F bond in CF_3 group in indene 1e, which lead to the formation of cation A, could take place in principle under reaction conditions, since 1 - (p - anisyl) - tetrafluoroallyl cation[12] and even polyfluorinated benzyl cations[8] can be generated under similar conditions.

EXPERIMENTAL

^{19}F and ^{1}H NMR spectra were recorded on a "Varian A-56/60A" instrument. Neutral compounds spectra were recorded for solns in CCl_4 (11 mol. %). The internal standard-C_6F_6 and TMS, respectively. $(CH_3)_4NBF_4$ (3.1 ppm from TMS) has been used as internal standard when recording ^{1}H NMR spectrum of ion 2d. Shifts in ^{1}H NMR spectra are given in δ scale. IR spectra were recorded on "UR-20" for solns in CCl_4. UV spectra were measured on "Specord UV VIS" for solutions in heptane. Molecular weight of indone 4 was determined on "MC 3301" instrument.

Preparation of salts solutions of polyfluoroindenyl cations

(a) To the soln of SbF_5 (0.30 g, 1.4 mmol) in SO_2ClF (~0.5 ml) placed in an ampoule for recording of NMR spectra 0.35 mmol of 1a–e was added at −45 to −65°. Then the soln was stirred and after appearance of an intensive green colour, ^{19}F and ^{1}H NMR spectra were recorded at −40 to −60°. There were no changes in spectra when the second record of spectra was performed in 2–3 hr.

The ^{1}H NMR spectrum of 2d contains one multiplete at 7.3 ppm. The spectrum of 1d (in CCl_4) contains proton signal at 6.2 ppm.

(b) By a procedure similar to that described, 1e (0.13 g 0.42 mmol) and SbF_5 (0.91 g, 4.2 mmol) a salt of cation 2e was obtained at room temp. (intensive green colouring appeared). The ^{19}F NMR spectra of this salt soln were recorded at different temps. It is shown by ^{19}F NMR spectra the ion 2e exists in the investigated range of temps from +40 to +140°. It is shown by separate experiment that the changes of ^{19}F NMR spectra during exposure of ion 2e salt soln in SbF_5 at room temp. during 25 months have not been detected.

The hydrolysis of the salt of fluoroinated indenyl cations

(a) By a procedure similar to that described, 1b (0.18 g) the soln of the salt of ion 2b was obtained. The soln was poured into water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and CH_2Cl_2 was evaporated. The result was 0.14 g of a product whose IR and ^{19}F NMR spectra were identical with spectra of authentic 3.[17]

(b) By a procedure similar to that described, 1c (0.25 g) a mixture (0.20 g) was obtained. This mixture according to ^{19}F NMR spectrum contained 3 and 1c in the ratio ~3:2, respectively.

(c) Analogously 4 (0.07 g) was obtained from 1e (0.11 g). The substance was purified by sublimation (65–70°, 760 mm), m.p. 79–80.3° (in sealed tube). Mass spectrum: $M^+ = 288$. The ^{19}F NMR spectrum of 4 contained five signals at −101.9 (CF_3, doublet with $J_{CF_3-F^3} = 13.6$ Hz, *cf*[18]), −69.3 (F^3), −29.8, −24.6, −18.8 ppm in an intencity ratio 3:1:1:1:2, respectively. IR spectrum: 1746, 1678 (C=O, C=C), 1508 (fluorinated aromatic nucleus), 1443 cm^{-1}. UV spectrum, λ_{max}, nm (log ϵ): 319 (3.41), 332 (3.45), 344 (3.30, shoulder), *cf*[17] (Found: C, 41.7; F, 53.0. Calc. for $C_{10}F_8O$: C, 41.7; F, 52.8%).

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