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**STABLE MONO-ARENium IONS OF POLY-FLUORINATED [2.2]
PARACYCLOPHANES**

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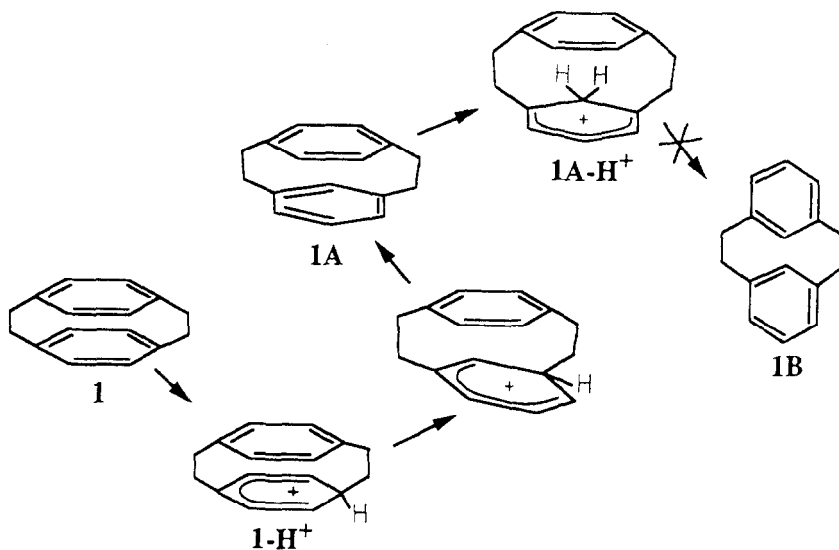
SUMMARY

Stable Monocations (σ -complexes) of tetrafluoro[2.2] paracyclophane and octafluoro[2.2] paracyclophane are generated by ipso protonation in superacid media and their NMR parameters are compared with the σ -complex of protonation of the parent [2.2] paracyclophane.

INTRODUCTION

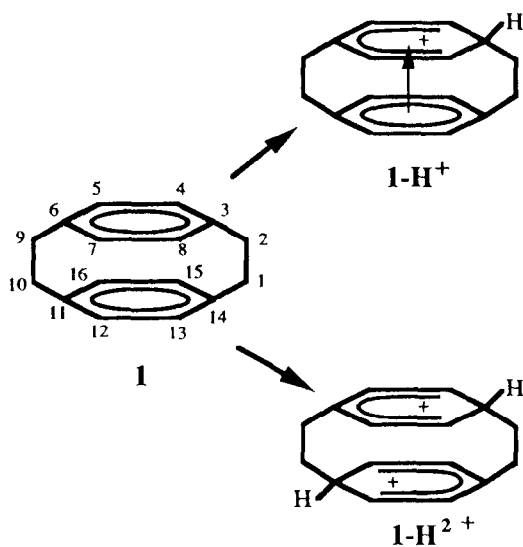
As first demonstrated by Cram and Hefelfinger [1], the parent [2.2] paracyclophane **1** is ipso mono-protonated in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ solvent system to give a stable σ -complex **1**- H^+ at low temperature. Upon protonation, angle deformation decreases and π - π repulsion is transformed into the more favorable charge-transfer (CT) interactions. Cation **1**- H^+ rearranges to the

thermodynamically more stable meta benzenium ion at higher temperatures (AlCl_3/HCl) and on deprotonation furnishes [2.2] metaparacyclophane 1A. The higher basicity of the 'inert' benzenium ion $\underline{1A}\text{-H}^+$ prevents its rearrangement to [2.2] metametacyclophane 1B (Scheme I).



Scheme I. Protonation and Skeletal Rearrangement of [2.2] Paracyclophane.

Recently, Hopf *et al.* [2] succeeded in deprotonation of 1 and its mono and dimethyl derivatives with magic acid/ SO_2ClF at very low temperature (-110°C). Whereas $\underline{1}\text{-H}^+$ is bright red in color, the dication $\underline{1}\text{-H}^{2+}$ is pale yellow. Charge-charge repulsion in the dication is compensated by a further decrease in angle deformation by double ipso protonation (Scheme II). Ions $\underline{1}\text{-H}^+$ and $\underline{1}\text{-H}^{2+}$ were studied by high field proton NMR.



Scheme II. Mono- and Di-Protonation of [2.2] Paracyclophane in Superacid Media.

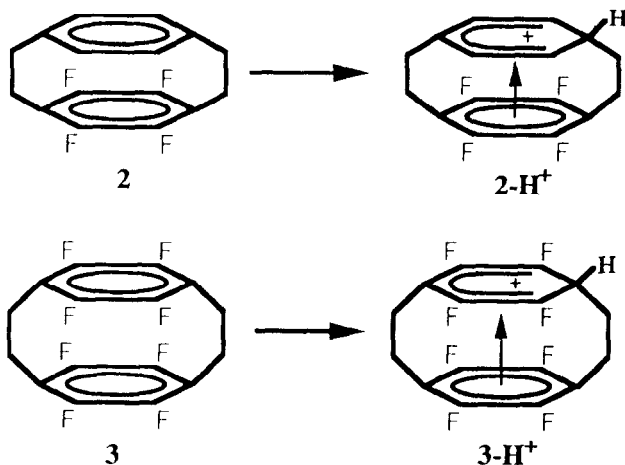
To our knowledge stable σ -complexes of other cyclophanes have not been studied [3], especially those of the polyfluorinated analogues.

One of us reported the first synthesis of tetrafluoro [2.2] paracyclophane **2** and octafluoro [2.2] paracyclophanes **3** [4,5]. The corresponding [4.2] paracyclophanes were also subsequently synthesized [6]. UV studies strongly suggested the presence of attractive transannular donor-acceptor interactions between the non-fluorinated and fluorinated rings, with probable stabilization by electrostatic, induction, and dispersion forces [6a], rather than by charge-transfer. The effect was greatly reduced in the more flexible [4.2] paracyclophanes.

The electrophilic (Friedel-Crafts) chemistry of tetrafluoro [2.2] paracyclophane is remarkable; introduction of fluorines in

one ring causes a substantial decrease in reactivity of the non-fluorinated ring, indicative of transannular π electron drain [7]. Under the conditions where the parent 1 undergoes facile rearrangement (AlCl_3/HCl), tetrafluoro [2.2] paracyclophane was recovered unchanged. Acylation and bromination similarly failed. Hydrogen-deuterium exchange studies (DCl/AlCl_3) with 2 indicated that eventually all the ring hydrogens can be exchanged (^1H NMR integrations), providing evidence for the formation of a σ -complex.

It was, therefore, thought of interest to study the protonation of 2 and 3 in superacid media by multinuclear NMR at low temperature to see if stable σ -complexes could be obtained under long lived ion conditions (Scheme III). This would then allow an examination of the extent of transannular interactions for cyclophanes in which a long lived σ -complex interacts transannularly with a 'neutral' tetrafluorobenzene ring on the opposite deck.



Scheme III. Mono-Protonation of Tetrafluoro- and Octafluoro [2.2] Paracyclophane.

RESULTS AND DISCUSSION

Mono-protonation of Tetrafluoro[2.2]Paracyclophane 2

Slow addition of a cold solution of excess magic acid/SO₂ClF to a suspension of 2 at ethanol/liquid nitrogen temperature (ca. -110°C) gave a pale yellow viscous (turbid) mixture. In order to homogenize the solution by vortex mixing, it was necessary to let the temperature rise slowly while vigorously mixing. However, at ca. -85°C, the yellow color immediately turned bright red*. Attempts to reduce viscosity at ethanol/liquid nitrogen temperature by dilution with SO₂ClF were not successful. Similar results were obtained with the strongest superacid HF-SbF₅ (1:1). Therefore, we concentrated our efforts on low temperature NMR studies of the bright red monocations.

The ¹H NMR spectrum (300 MHz) of the ion solution consisted of two low field (somewhat broadened) doublets at 7.77 (H-4,H-8) and 7.05 (H-5,H-7)ppm ($\Delta\delta_{1H}$ 0.93 and 0.21 ppm respectively), a broad singlet at 3.45 ppm (ipso proton) and the methylene bridge absorptions as three multiplets at 2.86, 2.61 and 2.10 ppm. The ¹³C NMR spectrum (75.5 MHz) exhibited the C-6 (para) carbon at 200 ppm, the C-4, C-8 (ortho) at 181.6 (d, 167 Hz) and the C-5, C-7 (meta) at 138.9 (d, 168 Hz). The sp³ carbon was observed as

* In line with the observations of Hopf et al. [2], we believe the yellow solution is a dication in which the second protonation (ipso attack on the fluorinated ring) is a rapid equilibrium (not a frozen dication). Raising the temperature pushes the equilibrium completely to the monocation side (bright red color).

a slightly broad doublet at 58.67 ppm. Whereas in the mono-cation precursor 2, the ^{13}C chemical shifts at C-11 and C-14 (the fluorinated ring) are equivalent and appear as a multiplet (long range fluorine coupling) at 118.8 ppm, in the mono-cation these carbons are no longer equivalent; 118.67 and 122.13 ppm. The methylene bridge carbons are similarly all non-equivalent and appear at 39.1 (t, 143 Hz), 36.9 (t, 143 Hz), 24.86 (t, 138 Hz) and 18.86 (t, 138 Hz).

For comparison, we also prepared the monocation of the parent 1 in $\text{FSO}_3\text{H}/\text{SO}_2$ solvent and obtained its ^{13}C NMR parameters. The identity of the benzenium ion was first confirmed by ^1H NMR showing an essentially identical spectrum to that of Hopf *et al.* [2] (see Table). The ^{13}C NMR of the ion showed the C-6 (para) at 197.4 (s), the C-4, C-8 (ortho) at 178.29 (d, 169 Hz), the C-5, C-7 (meta) at 142.87 (d, 171 Hz), the sp^3 carbon (C-3) at 55.5 (d, 138 Hz), the C-11, C-14 which were originally equivalent in the precursor (138.7 ppm) appeared at 146.31 and 147.1 ppm (singlets). Four methylene bridge absorptions were observed at 43.49 (t, 137 Hz), 42.27 (t, 139 Hz), 34.39 (t, 138 Hz), and 33.29 (t, 138 Hz).

The ^{19}F NMR spectrum of 2 (CDCl_3) is a single peak at -138.1, that of $\underline{2}\text{-H}^+$ shows, apart from the well characterized absorptions due to various fluorinated species in the superacid medium [8], two singlets at -135.16 and -137.1 ppm. Thus, the observed $\Delta\delta_{19\text{F}}$ in the opposite deck is rather small (1-3 ppm).

Mono-Protonation of Octafluoro [2.2] paracyclophane 3 .

Similar addition of excess magic acid/ SO_2 to a suspension of 3 in SO_2 at dry ice/acetone temperature and vigorous vortex

TABLE
NMR Parameters for Cyclophanes 1, 2 and 3 in CDCl₃ and Their Corresponding Monocations in Magic Acid/SO₂.

Cyclophane	4,8	5,7	3	6	12,16	13,15	11	14	1	2	9	10
<u>1</u>	¹ H[1]	6.50	6.50	-	6.50	6.50	-	-	3.10	3.10	3.10	3.10
<u>1</u>	¹³ C [9]	132.8	132.8	139.1	132.8	132.8	139.1	139.1	35.7	35.7	35.7	35.7
<u>1</u> -H ⁺	¹ H	8.22	7.59	4.07	6.86	7.19	-	-	3.48	2.88	3.63	3.63
"	¹³ C	(d,8.3)	(d,8.3)	(br,s)	(d,7.6)	(d,7.6)	-	-	(m)	(m)	(m)	(m)
"	¹³ C	178.29	142.87	55.5	132.4*	133.27*	146.31 ⁺	147.1 ⁺	34.39	33.29	43.29	42.27
"	¹³ C	(d,169)	(d,171)	(d,138)	(d,163)	(d,159)	(s)	(s)	(t,138)	(t,138)	(t,137)	(t,139)
<u>2</u>	¹ H	6.84	6.84	-	-	-	-	-	2.98	3.07	3.07	2.98
"	¹³ C	(s)	(s)	(s)	(s)	(s)	(s)	(s)	(m)	(m)	(m)	(m)
<u>2</u>	¹³ C	129.62	129.62	139.05	146.4	146.4	118.8	118.8	21.99	32.92	32.92	21.99
<u>2</u>	¹⁹ F	(s)	(s)	(s)	(dm)	(dm)	(m)	(m)	(s)	(s)	(s)	(s)
<u>2</u>	¹⁹ F	-	-	-	-138.1	-138.1	-	-	-	-	-	-
<u>2</u>	¹⁹ F	(s)	(s)	(s)	(s)	(s)	(s)	(s)	(s)	(s)	(s)	(s)
<u>2</u> -H ⁺	¹ H	7.77	7.05	3.45	-	-	-	-	2.61*	2.10	2.86*	2.86
"	¹³ C	(d,8)	(d,8)	(br,s)	(s)	(s)	(s)	(s)	(br,s)	(br,s)	(br,s)	(br,s)
<u>2</u> -H ⁺	¹³ C	181.6	138.9	58.67	200.0	146.9	146.9	122.13*118.67*	24.86	18.86	39.1	36.9
"	¹⁹ F	(d,167)	(d,168)	(br,d,120)	(s)	(d,250.7)	(d,250.7)	(m)	(t,138)	(t,138)	(t,143)	(t,143)
<u>2</u> -H ⁺	¹⁹ F	-	-	-	-	-135.16*	-137.1*	-	-	-	-	-
<u>3</u>	¹ H	-	-	-	-	-	-	-	3.28	3.28	3.28	3.28
<u>3</u>	¹³ C	146.9	146.9	117.72	146.9	146.9	117.72	117.72	(s)	(s)	(s)	(s)
"	¹⁹ F	(dm,252)	(dm,252)	(m)	(dm,252)	(dm,252)	(m)	(m)	21.12	21.12	21.12	21.12
<u>3</u>	¹⁹ F	-141.2	-141.2	-	-141.2	-141.2	-	-	(s)	(s)	(s)	(s)
"	¹⁹ F	(s)	(s)	(s)	(s)	(s)	(s)	(s)	(s)	(s)	(s)	(s)
<u>3</u> -H ⁺	¹ H	-	-	4.01	-	-	-	-	2.96*	2.24	2.78*	2.96
"	¹³ C	(br,s)	(br,s)	(br,s)	(br,s)	(br,s)	(br,s)	(br,s)	(br,s)	(br,s)	(br,s)	(br,s)

^a Multiplicities and coupling constants (Hz) are given in brackets.

^b * and + denote that the assignment of chemical shifts may be reversed.

mixing did not initially give a benzenium ion. Mono-protonation could only be achieved after continuous vortex while allowing the temperature to rise slowly to ca.-40°C. This resulted in the formation of a persistent bright red color. With HF-SbF₅ the protonation was more rapid. The ion was characterized by ¹H NMR showing the characteristic ipso proton as a broad singlet at 4.01 ppm and the three bridge methylenes (broad singlets) at 2.96 (4H), 2.78 (2H) and 2.24 (2H).

Model Studies; Protonation of tetrafluoro-p-xylene 4

For comparison with protonated 3, we chose to generate the stable σ -complex of protonation of tetrafluoro-p-xylene 4. However, attempted protonation in magic acid/SO₂ solvent failed to produce a stable σ -complex! The substrate was only slightly soluble in this medium and raising the temperature to -30°C had no effect. An ¹⁹F NMR monitoring of the reaction showed that the -145.54 ppm signal (sharp singlet) of the precursor appeared as a broad peak centered at -146.5 ppm. On the other hand, the stable σ -complex of ipso attack was readily obtained by protonation in HF-SbF₅. The ¹H NMR of this ion showed a broad singlet at 4.50 ppm (ipso proton) and two methyl peaks at 2.51 and 1.85 (1:1 ratio) for the para and ipso methyls respectively. The ¹³C NMR spectrum exhibited the benzenium ion absorptions at 189.14 (para), 173.5 (ortho), and 145.5 (meta) with the sp³ carbon at 45.97 (remained a singlet in a coupled spectrum) and the methyl carbons at 16.35(para) and 12.74 (ipso).

Thus, in a superacid medium (magic acid) in which 3 is protonated, 4 is not. We believe this observation to be a direct indication that the π - π repulsion inherent in 3 provides the driving force for its observed protonation in magic acid.

On the Stability of the mono-cations of 2 and 3 in Superacid Media

Cold solutions of the cations were stable for several hours without any signs of decomposition. Quenching of the ion solutions (ice/bicarbonate) regenerated the starting materials as assayed by NMR (^{19}F and ^1H). In HF-SbF_5 some decomposition was observed (10-15%; based on NMR integrations) when the solutions were kept for 24h at -60°C prior to quenching. The ^{19}F NMR spectrum of the recovered material from quenching of the benzenium ion of 3 showed apart from a major peak at -141 ppm for the unchanged precursor, small peaks at -144.1 and -145.5 ppm (a total of 10%) for by-products.

Attempted Skeletal Rearrangement of the Mono-cations

As reported by Filler et al. [7], unlike 1, 2 is not isomerized under Friedel-Crafts conditions. In the present study we found no change in the NMR spectra of the ion solutions on warming the NMR tubes up to -30°C . When 2 was dissolved in $\text{FSO}_3\text{H/SO}_2$ at -60°C , an orange-red heterogeneous mixture resulted. Evaporation of the solvent with a fast flow of dry nitrogen and warming the sample slowly to room temperature, gave

a blue-purple solution. The sample was left overnight at r.t. while mixing under nitrogen. ^1H NMR of the organic extract after quenching the acid solution showed only the unchanged precursor.

Comparison of the ^{13}C NMR shifts of the benzenium ions of 1 and 2 shows that charge delocalization within the benzenium ions is similar in the two ions. It appears then that transannular interactions in 2- H^+ "stabilize" the resonance structures of ipso attack to such an extent that skeletal rearrangement is no longer a favorable process.

A Comparison of Transannular Interactions between the Precursors and the Monocations of Fluorinated and Non-fluorinated [2.2] Paracyclophanes

It has been shown [3,10] that proton chemical shifts of cyclophanes can be used to estimate the extent of transannular interactions in the systems. Two effects need to be considered a) shielding due to the ring current of the opposite deck and b) the transannular donor-acceptor effect. We have used this approach to obtain a qualitative estimate of the transannular effects in the benzenium ions of 1 and 2.

The ^1H NMR of the ring protons in the parent 1 is at 6.50 ppm, that of 2 is at 6.84 ppm. Thus the observed deshielding in 2 ($\Delta\delta_{^1\text{H}}=0.34$ ppm) can be ascribed to π electron drain into the fluorinated ring, assuming that the ring current effects are similar.

The ^1H shifts of the mono-cations of 1 and 2 can be compared with the ^1H shifts of the static benzenium ion reported by Olah and co-workers [11]. Subtraction of the ortho and meta proton chemical shifts yields shielding values of 1.93 (9.70-7.77) and 1.55 (8.60-7.05) ppm for 1 and 1.48 (9.70-8.22) and 1.01 (8.60-7.59) ppm for 2. This accounts for the combined shielding by the ring current of the opposite deck and the transannular effects. Alternatively, the proton shifts of the monocations of 1 and 2, can be directly compared. This yields $\Delta\delta_{1\text{H}}$ values of 0.45 (8.22-7.77) and 0.54 (7.59-7.05) for the transannular effect alone. Thus, the benzenium ion of the fluorinated cyclophane 2- H^+ is more shielded as compared to 1- H^+ , indicative of stronger transannular effects. Non-bonded interactions between the $\overset{\delta+}{\text{C}} - \overset{\delta-}{\text{F}}$ dipole and the benzenium ion may be a major contributor to the observed shielding. Other spectroscopic as well as theoretical studies are needed to establish the mechanism of this transannular stabilization.

EXPERIMENTAL

Tetrafluoro- and octafluoro [2.2] paracyclophane were prepared as previously reported [5]. Magic acid was prepared from freshly distilled FSO_3H and SbF_5 . HF-SbF_5 (1:1) triple distilled was purchased from Aldrich and used as received.

NMR spectra were recorded on a GN-300 wide-bore instrument using a 5 mm Switchable $^1\text{H}/^{13}\text{C}$ and a 5mm ^{19}F probes. A neat acetone- d_6 sample was used for homogeneity adjustments at low temperature and as an external reference. For ^{19}F NMR, an

external CFCl_3 /acetone- d_6 (1:3 v/v) 5 mm tube was used. The reported shifts are upfield from the reference. Typically, the ^1H and ^{13}C NMR spectra were run first, the probe was changed, and the ^{19}F spectra were recorded on the same sample.

Preparation of the Ions

To a slurry of the substrate (40 mg) in SO_2 or SO_2ClF (0.5 ml) cooled to ethanol/liquid nitrogen temperature or dry ice/acetone temperature was added a pre-cooled solution of the superacid (1 ml) in SO_2 or SO_2ClF (1 ml) with effective mixing (vortex). A yellow viscous solution resulted which turned bright red on raising the temperature while vortexing.

Quenching Experiments

The NMR tubes containing the ion solutions were carefully added to a slurry of bicarbonate and ice with vigorous mixing. The organic phase was extracted (CH_2Cl_2), separated and dried (MgSO_4). The solvent was removed under vacuum and the residue redissolved in CDCl_3 for NMR assay.

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