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JANUSENE AND TETRAFLUOROJANUSENE IN SUPERACID MEDIA; RADICAL CATION FORMATION AND CHEMISTRY

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SUMMARY

Both janusene **1** and the facial tetrafluorojanusene **2** undergo one electron oxidation in $FSO_3H.SbF_5$ (1:1) 'magic acid'/SO_2ClF and in $HF.SbF_5$ (1:1)/SO_2ClF at low temperature to give persistent radical cations. Rapid dimerization ⟶ polymerization follows. Stable σ-complexes of protonation were not observed at all. In the less oxidizing milder superacid FSO_3H/SO_2, neither **1** nor **2** are fully protonated or oxidized.

Radical cation-mediated condensation of **1** is much more rapid than for the fluorinated analog. Two structurally different dimeric compounds could be isolated in quenching experiments.

The extent of transannular donor-acceptor interactions in the facially fluorinated janusenes were compared with those for the tropylium-containing janusene, fluorinated [2.2] paracyclophane and its stable σ-complex.

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MMX calculations were used to determine the minimum energy structures of 1 , 2 as well as the elusive 3 and the octafluorojanusene 4. Whereas facial arrangements of the phenyl rings were confirmed in all cases, deviations from complete periplanar arrangement were observed depending on the structure. Structural perturbations imposed by fluorines seem to indicate lateral ring participation, which correlates with NMR observations of shielding of the donor-ring protons.

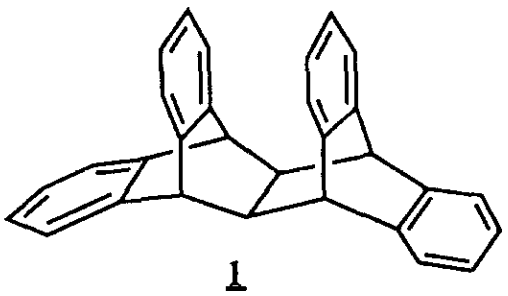
INTRODUCTION

Study of transannular interactions in structurally restricted 'stacked' π-systems, namely cyclophanes and their metallocene analogs continues to be an area of substantial interest [1,2].

Earlier syntheses of both tetrafluoro- 5 and octafluoro [2,2]paracyclophane 6 (Scheme 1) by one of us [3,4], UV-studies indicating the presence of attractive transannular interactions between the fluorinated and non-fluorinated rings in 5 and a dramatic reduction of such effects in the more flexible [4.2]paracyclophanes [5], provided an impetus to study the electrophilic chemistry of 5 [6].

A remarkable deactivation toward electrophilic substitution of the non-fluorinated deck was observed. Such deactivation was almost absent in an open-chain analog [7], arguing against an inductive deactivation mechanism through the Tedder reaction.

We subsequently generated stable σ-complexes of both tetrafluoro- 5-H^+ and octafluoro[2.2]paracylophane 6-H^+ by monoprotonation in superacid media [8]. NMR studies allowed an



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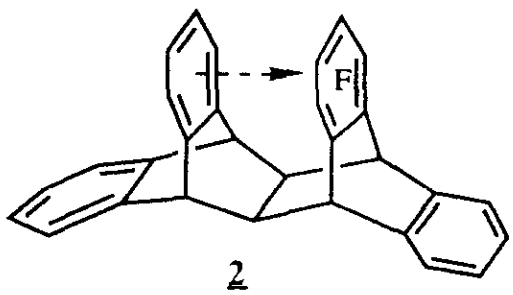

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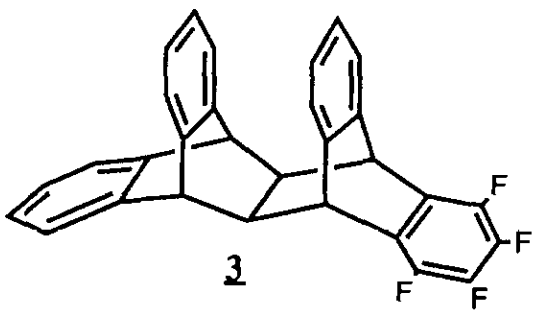

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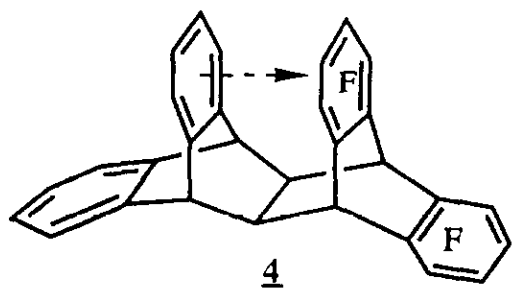

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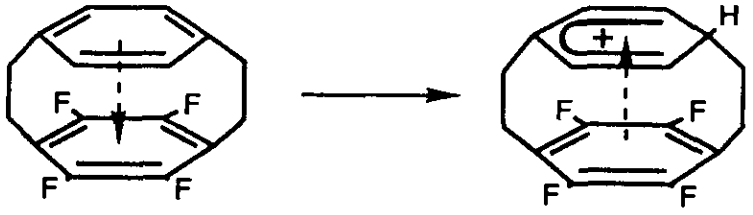
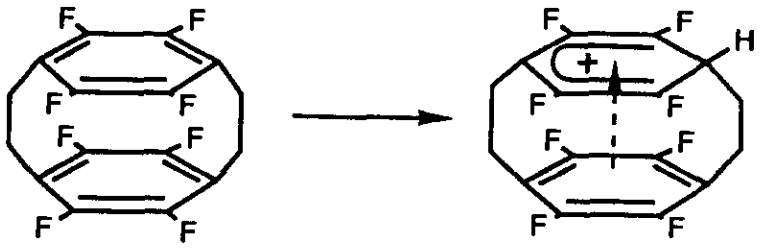


5 5-H⁺

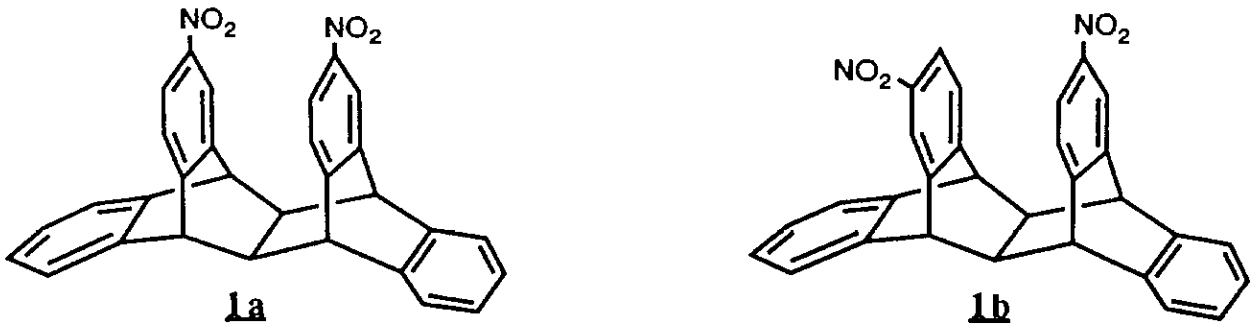


6 6-H⁺

Scheme 1. Janusene, Fluorinated Janususenes, Fluorinated [2.2]Paracyclophanes and Their σ-Complexes.

evaluation of the extent of transannular π-electron drain to be made in such systems. Protonation of **5** leads to switching of the direction of transannular π-electron drain and to shielding of the arenium ion protons by the fluorinated deck. The extent of such shielding was found to be larger in **5**-H^+ than for the mono-arenium ion of parent [2.2]paracyclophane.

In search for another model to examine transannular effects in stable σ-complexes, we focused on janusene **1** and its fluorinated analog **2**. First synthesized by Cristol via a $4\pi+2\pi$ cycloaddition between dibenzobarrelene and anthracene [9], **1** can be viewed as a [3.3]orthocyclophane having two vis-à-vis benzene rings. Mono-nitration and mono-bromination of **1** indicated strong preference for facial attack, indicative of ground state destabilization by transannular π-repulsion and transition state stabilization by π-delocalization. Further nitration of facially nitrated **1** gave a mixture of dinitro isomers, with preference for nitration at the unsubstituted facial ring. Two such isomers were isolated in equal amounts (**1a** and **1b**) (Scheme 2), one of which (**1a**) should be minimal if a resonance phenomenon involving bond formation between the facial rings is operating; pointing to a transannular polarization mechanism.



Scheme 2. Dinitro-Janusene Isomers.

Compounds **2** and **3** were previously synthesized by one of us via cycloaddition reactions involving tetrafluoro- and octafluoro-dibenzobarrelene and anthracene [10]. UV studies showed a donor-acceptor band near 283-284 nm. ^{1}H NMR showed that the non-fluorinated facial ring is shielded relative to the lateral ring protons. As with **5**, transannular deactivation of the non-fluorinated facial ring should lead to electrophilic deactivation. To probe this issue, we set out to generate stable σ-complexes of protonation of **1** and **2**, determine site of protonation under stable ion conditions, and compare their NMR data with those of **5**-H$^+$.

RESULTS AND DISCUSSION

Slow addition of a slurry of **1** to a homogeneous solution of magic acid diluted in SO_2ClF at -90°C gave a dark orange solution, which upon vortex mixing and an increase in temperature (-75°C) turned red. At this point, a dark red semi-solid was also formed. A portion of the liquid was transferred into another cold NMR tube. The ^{1}H NMR spectrum of the liquid showed two broad deshielded CH absorptions centered at 3.30 (non-benzhydrylic) and 5.30 ppm (benzhydrylic) and an envelope of broad deshielded aromatic absorptions between 7.70 and 8.90 ppm. Lowering the temperature to -90°C did not result in peak sharpening. Increasing the temperature and prolonged reaction times led to more formation of solid.

Compound **2** reacted similarly with magic acid in SO_2ClF at -90°C. The ^{1}H NMR spectrum of the deep red solution which formed immediately indicated six non-equivalent (somewhat broadened)

aliphatic CH protons at 1.90, 2.10, 3.00, 3.45, 3.95, and 5.90 ppm, and once again, a broad envelope of deshielded aromatic absorptions between 7.90 and 9.0 ppm. A dark red, SO_2ClF insoluble 'polymer' began to appear. Unlike the proton spectrum, the ^{19}F NMR spectrum showed two rather sharp absorptions at -144.6 and -154.4 ppm, deshielded by 4.0 and 6.8 ppm, respectively, from the precursor, in addition to the well characterized superacid absorptions [11] and a singlet at 98.23 ppm for SO_2ClF.

In an attempt to freeze out a possible dynamic proton exchange, protonation of **1** and **2** in the highest acidity superacid $HF.SbF_5/SO_2ClF$, was studied. Once again, broad aromatic and aliphatic CH absorptions were detected and 'polymer' formation occurred. The acidity independence of line broadening pointed to radical cation formation.

We then examined the $HF.SbF_5$ solution of **1** and **2** by ESR at 200°K at 100 KHz. In both cases, broad ESR signals were detected with no observable hyperfine coupling (Fig. 1). The ESR spectrum of tetrafluorojanusene **2** showed a central line width ΔH_{pp} = 13.4 gauss and a g value of 2.0037. A weaker ESR absorption was observed for janusene **1**, presumably due to competing polymer formation in the ESR tube, with a central line width ΔH_{pp} = ca. 11.4 gauss and a g value of ca. 2.0033. Both g values are very close to that of radical cation of triptycene (g 2.0022) generated by Davies et al. via photolysis in $AlCl_3$ or in TFA/Tl(III)trifluoroacetate [12].

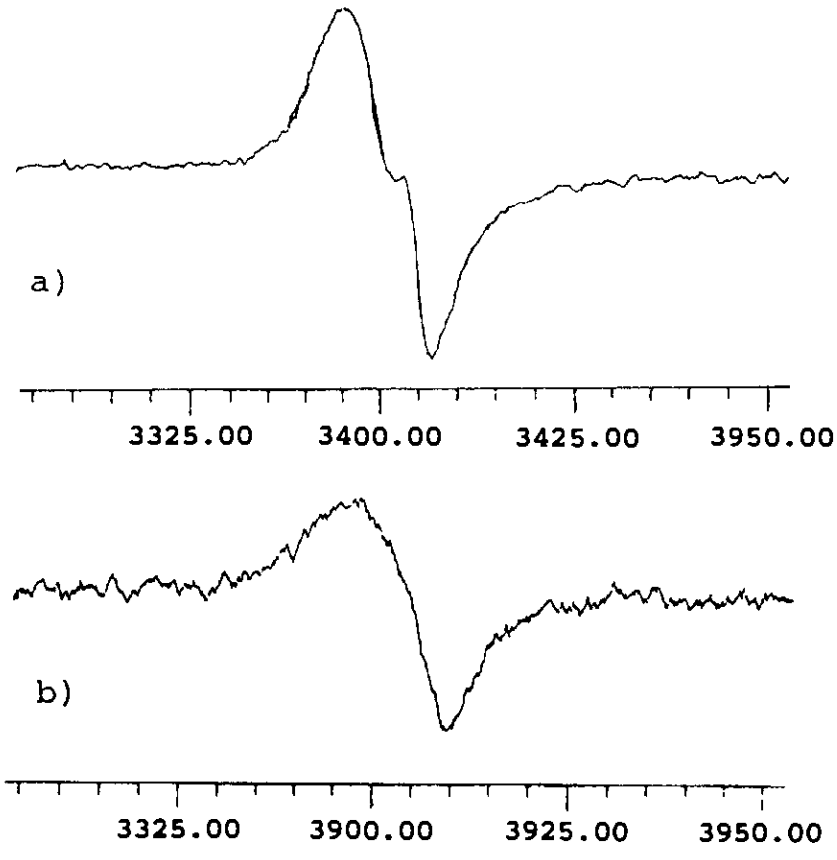


Fig.1. ESR Spectra of 2 (a) and 1 (b) in $HF.SbF_5$(1:1)/SO_2ClF at 200K.

Although lack of hyperfine coupling precluded exact structure determination of the radical cations, the presence of sharp fluorine absorptions in the NMR spectra is indicative of oxidation in a non-fluorinated ring.

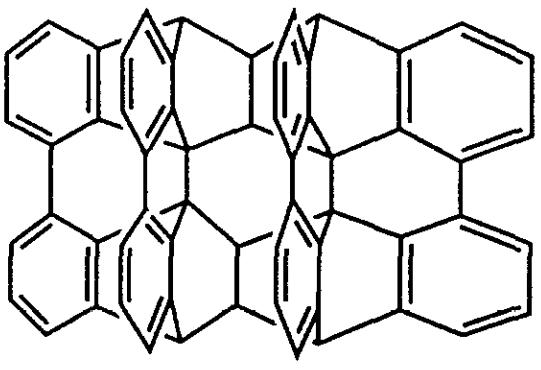
We showed previously [8] that, despite substantial shielding of the benzenium ion protons, in the stable σ-complex 5-H^+, deshielding of the fluorines on the opposite deck was rather small. Thus, the observed small $\Delta\delta_{^{19}F}$ values for 2 cannot be used as evidence for selective oxidation of a lateral ring.

In an attempt to prevent oxidation and observe a stable σ-complex, protonation of 2 was studied in FSO_3H/SO_2ClF. A bright yellow solution formed at -75°C. Addition of CD_2Cl_2 gave two

layers which became miscible at >-40°C. The ^{1}H NMR spectrum showed unchanged 2. Prolonged storage of the sample (-20°C) led to ring fluorosulfonation (appearance of low field multiplet absorptions at 7.7 and 7.5 ppm in the NMR of the quenched product mixture) and unidentified oxidative cleavage products.

Quenching Experiments

Quenching of the heterogeneous reaction mixture formed by low temperature reaction of 1 with magic acid produced a light green flaky solid which was partially soluble in CD_2Cl_2. The ^{1}H NMR spectrum of the soluble portion showed two CH absorptions appearing as slightly broadened singlets at 2.70 (non-benzhydrylic; ca. 4H) and 4.65 ppm (benzhydrylic; 4H), an aromatic triplet at 6.97 (J= 8Hz; 8H) and an aromatic doublet at 7.65 (J= ca 8 Hz; 16H). The presence of aliphatic CH (2958, 2922, 2849), aromatic CH (3105, 3075, 3032) and aromatic CC absorptions (1671, 1605, 1525, 1437) was also confirmed by the infrared spectrum, which by comparison with that of authentic 1 [9] showed differences in the position of a number of bands. Based on the spectral data, structure 7 is proposed (Scheme 3).



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Scheme 3. Suggested Structure of a Dimer of 1 formed via its Radical cation.

Study of molecular models suggests that while the proposed dimeric structure, with eleven fused 6-membered rings and two almost parallel biphenyl rings is quite rigid, it suffers little strain. Formation of 7 may be explained by a radical cation dimerization/deprotonation/aromatization sequence.

A structurally different dimer was obtained from a quenching experiment on 2. A light brown solid material was isolated after quenching of the magic acid solution, ^{1}H NMR of which showed major CH absorptions at 2.65, 4.65 and 4.80 (1:1:1) with the latter two appearing as multiplets, indicative of fluorine coupling. In addition, three other CH absorptions were present, one of which appeared as a broad singlet centered at 3.68 and the other two as doublets at 3.95 (J=29 Hz) and 4.21 (J=20 Hz). The aromatic region consisted of a complex multiplet between 7.3 and 7.78 ppm. The spectrum is best interpreted as an open dimer, adopting a conformation in which through-space coupling occurs between the benzhydrylic protons of one unit with fluorines of the other unit. In addition, further downfield shifts of the aromatic protons are indicative of ring fluorosulfonation. The IR spectrum showed CH absorptions (2963, 2925, 2849), aromatic bands (1719, 1677, 1605, 1501) and CF absorptions (1096, 1025), confirming that in comparison with the IR spectrum of authentic 2 [10], a number of bands have shifted in the dimeric structure.

NMR Studies of the Substrates and a Qualitative Comparison of Transannular Interactions with Model Systems

Complete NMR data for 1 and 2 are shown in Table. As previously pointed out [10], 1 shows four distinct aromatic multiplets, the two most upfield of which are assigned to the

TABLE

NMR Parameters for 1 and 2 in $CDCl_3$ Solvent at 24°C

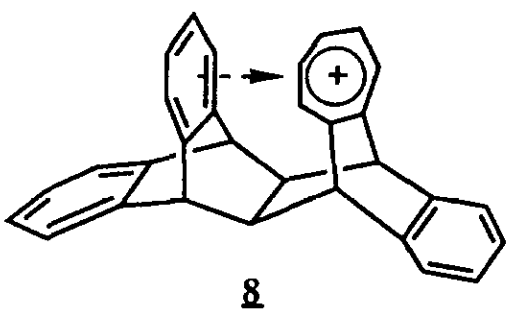
	^{1}H NMR (300.52 MHZ)	^{13}C NMR (75.57 MHz)[a]			^{19}F NMR (282.75 MHz)
		Bridgehead	Aromatic		
			ipso	Non-ipso	
1	6.67 (m; 4H) 6.83 (m; 4H) 6.97 (m; 4H) 7.18 (m; 4H)	45.05 (d; 138.3) 49.03 (d; 137)	140.37(s) 140.39(s)	122.8 (d; 157.2) 125.36 (d; 160) 125.54 (d; 159) 125.66 (d; 159.4)	
2[b]	6.89 (m; 2H) 6.99 (m; 2H) 7.07 (m; 4H) 7.22 (m; 4H)	40.78 (d; 142.62) 44.14 (d; 142.7) 48.37 (d; 141)	144.71(s) 143.10(s) 140.0 (s)	123.13 (d; 159.8) 123.52 (d; 159) 124.63 (d; 160) 125.75 (d; 159.9) 126.28 (d; 160) 126.92 (d; 159)	-148.50(2F;S) -161.2 (2F;S)

[a]Multiplicities and coupling constants (Hz) in brackets.

[b]Two tiny doublets at 124.75 (J = 250 Hz) and 125 ppm (J = 250 Hz) were observed in the ^{13}C spectrum, assigned to two non-equivalent facial CF.

facial rings due to their enhanced electron density, analogous to the parent [2.2] paracyclophane. However, the facial rings in **1** are inherently more deshielded than [2.2]paracyclophane. With **2**, despite transannular π-electron drain, the facial protons are shielded (ca 0.2 ppm upfield compared to **1**), a trend which is opposite to the observed deshielding (0.34 ppm) of the non-fluorinated deck in **5**. Comparison between **2** and **5** [8] shows more shielded fluorines in **2** as compared to **5**. Using **8** [13] as a model, whereas CT interactions lead to shielding of the facial tropylium protons, the protons of the facial donor ring are still more shielded (by ca 0.30 ppm) as compared to **1**. Transannular π-electron drain into the tropylium cation in **8** is manifested not only in its UV spectrum, but also in its increased reduction potential and pK_R^+ value. Comparison of the ^1H NMR shifts of the facial phenyl ring protons in **8** with the mono-arenium ion of parent [2.2]paracyclophane [8], again shows more shielded facial protons for **8**, despite the presence of transannular electron drain in both systems.

Interestingly comparison of the reported [13] ^1H shifts for **8** with those of **1** shows an average deshielding of the lateral ring protons, when a tropylium cation is facial.



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Scheme 4. Tropylium-Janusene.

Structural Considerations and MMX

Examination of molecular models show that despite a rigid structure in janusene and the facial arrangements of phenyls with 2.5 Å separation, distortion of fused bicyclooctane rings are possible at the expense of facial ring separation (repulsion). This is found in the X-ray structure of a janusene dicarboxylic anhydride [9] showing a 3-4.0 Å separation of the facial rings. Regarding **2**, attempts to obtain a suitable crystal for structural analysis were unsuccessful [14].

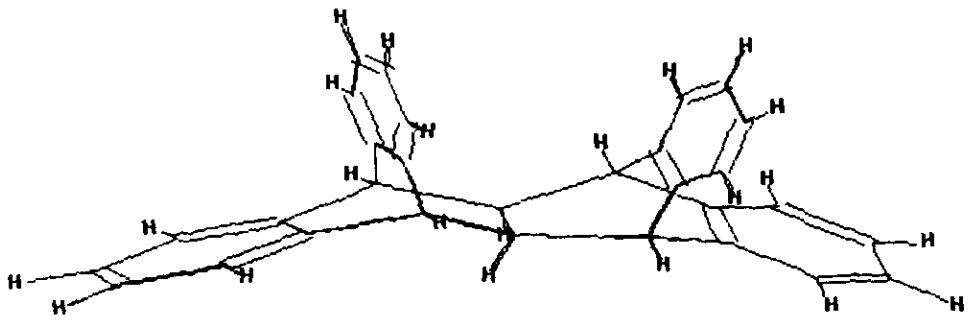
Therefore, we calculated by MMX (PCMODEL) the minimum energy structures for **1-4**, compared crucial bond angles and obtained their MMX energy and van der Waals drawings of the minimized structures (Schemes 5-7).

With **1**, the lateral rings are tilted out of plane (typically at a 155-156° angle with the adjacent bicyclooctane). The vis-à-vis rings deviate from a complete periplanar arrangement (outside pole angles of 101-102° and the inside pole angles of ca 114°).

Introduction of four fluorines onto a facial ring (**2**) does not noticeably alter the orientation of the lateral ring (still 155-157°), but leads to increased leaning of the non-fluorinated face away from the fluorinated face (125°) and towards its corresponding lateral ring (109°). This suggests that transannular deshielding may be partly compensated through CT by a lateral ring and could explain the observed NMR shielding of facial protons relative to **5** (Scheme 6).

Further fluorination of a lateral ring (**4**) flattens both lateral rings (172-173°), with the fluorinated-face at ca 100° and the non-fluorinated face at ca 111°. Flattening of the lateral rings probably reflects ArF-ArF repulsion (Scheme 7).

a)



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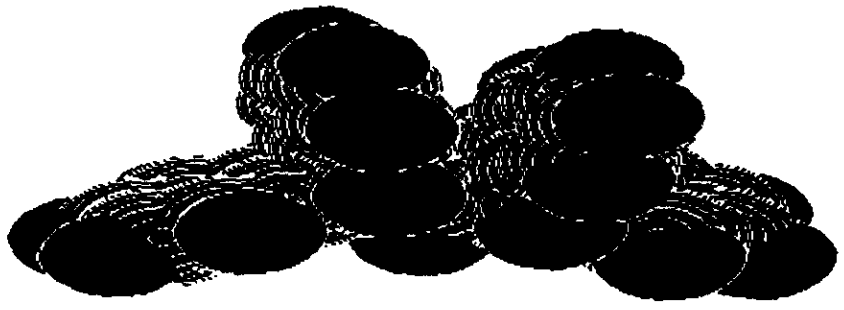


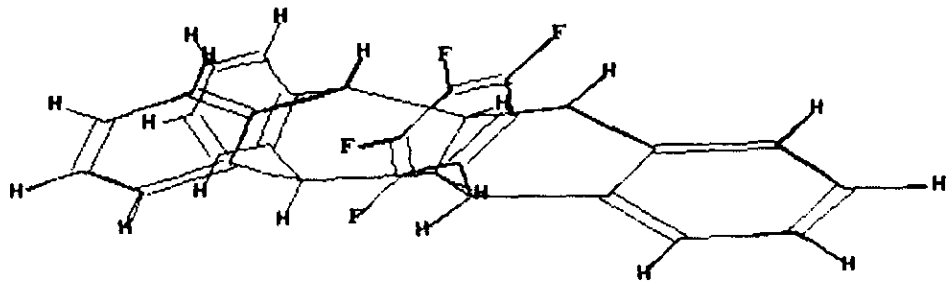
c)

Scheme 5. a) Minimum Energy Structure of 1; MMX Energy = 78 Kcal/mol;

b) Van der Waals Drawing of All Atoms in the Minimized Structure;

c) Van der Waals Drawing of Heavy Atoms Only.

a)



b)

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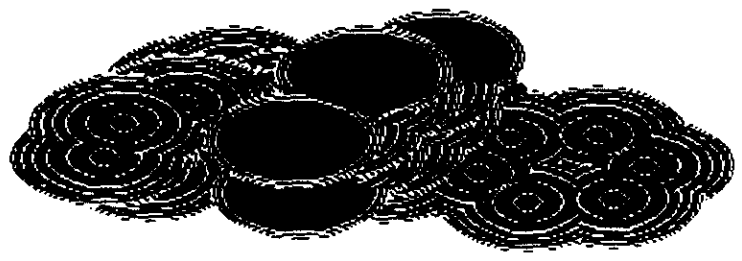
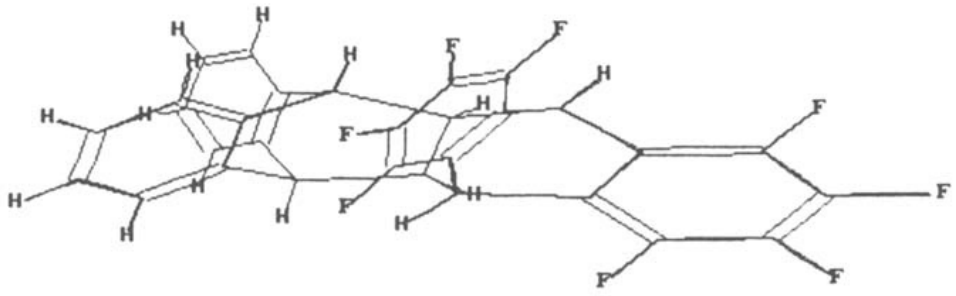


Scheme 6. a) Minimum Energy Structure of 2; MMX Energy = 84.8 Kcal/mol;

b) Van der Waals Drawing of All Atoms in the Minimized Structure;

c) Van der Waals Drawing of Heavy Atoms Only.

a)



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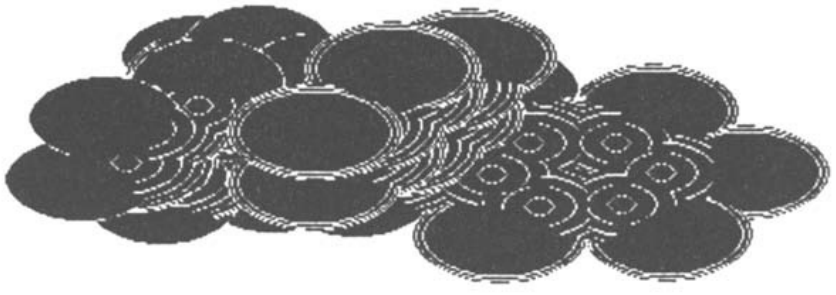
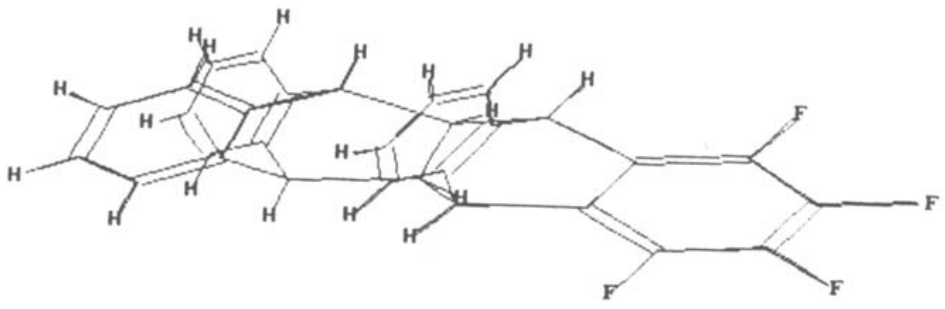


Scheme 7. a) Minimum Energy Structure of 4; MMX Energy = 100.86 Kcal/mol;
b) Van der Waals Drawing of All Atoms in the Minimized Structure.

Removal of fluorines from the facial ring (3) removes the repulsive interaction and the fluorinated lateral ring regains its 'janusenal' orientation (156-158°) with the facial rings at ca 101° (Scheme 8).

a)



b)

Scheme 8. a) Minimum Energy Stucture of 3; MMX Energy = 84 Kcal/mol;
b) Van der Waals Drawing of All Atoms in the Minimized Structure.

CONCLUSIONS

Unlike the fluorinated [2.2]paracyclophanes, attempts at observation of long-lived σ-complexes by protonation of janusene **1** and its facially perfluorinated derivative **2** were unsuccessful due to facile oxidation to a radical cation and its resultant chemistry.

Comparison of the NMR chemical shifts of **1**, **2**, and **8** with related models of rigid vis-à-vis cyclophanes shows that, whereas in all cases CT interactions lead to shielding of the acceptor ring protons, the donor ring is shielded in the janusene skeleton and deshielded in the [2.2]paracyclophane skeleton.

MMX structure minimizations, taken together with NMR observations, point to possible contribution to the CT mechanism by the lateral rings in **2** and **8**. Such cooperative effects (not operative in **5**), may be responsible for the observed [9] preferential dinitration of a facially mono-nitrated janusene, at an unsubstituted facial ring.

Structural and theoretical/conformational studies on janusene and fluorojanusene dimers, and an evaluation of the synthetic scope of this 'one-pot' radical cation dimerization process directed towards preparation of novel host materials are underway.

EXPERIMENTAL

Compound **1** was a gift sample, kindly furnished by Prof. Cristol (to RF).

Compound 2 was prepared as previously described [10].

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. SO_2ClF was an Aldrich sample and was distilled once from SbF_5.

NMR spectra were recorded on a GN-300 wide-bore instrument, using 5 mm switchable $^1H/^{13}C$ and 5 mm ^{19}F probes. Acetone-d_6 was used for homogeneity adjustments at low temperature and CD_2Cl_2 was used as internal lock and reference. For ^{19}F NMR spectra, external $CFCl_3$/acetone-d_6 (1:3 v/v) in a 5 mm tube was used. The reported shifts are upfield from the reference.

X-band ESR spectra were obtained using an IBM 200D-SRC spectrometer with a ER 4111 temperature controller which has a precision of 1 K. The spectrometer frequency was measured using a Hewlett Packard 5351A microwave frequency counter, and the magnetic field was measured by the Hall probe of the spectrometer which had been previously calibrated near g=2 using an NMR gaussmeter. The IBM ESR software used these results to calculate the reported g and linewidth data.

IR spectra were run on a Perkin-Elmer 1600 series FTIR.

a) Low Temperature Stable Ion Studies

To a slurry of the substrate (ca 25 mg) in SO_2ClF (0.5 ml) placed inside a 10 mm NMR tube and cooled to EtOH/liquid nitrogen temperature or dry ice/acetone temperature under a nitrogen atmosphere, was added a pre-cooled solution of the superacid (ca 1 ml) diluted in SO_2ClF (ca 1ml) with efficient mixing (vortex).

Quartz NMR tubes were used for preparations involving $HF.SbF_5$. Due to an inherent higher viscosity of the latter relative to magic acid, addition was done at -75°C. 1 was initially dark orange , but a persistent dark red color developed upon raising the temperature to -65°C and a dark red semi-solid material appeared. With 2, the ion solution was deep red and 'solid' formation was slower.

A portion of the superacid solution was transferred via a cold pipet (SO_2ClF) into a 5 mm NMR tube and examined immediately. The fluorine spectra were recorded on the same sample. Another portion of the superacid solution was transferred into pre-cooled ESR tubes; some solid appeared during the ESR measurements.

b) Quenching Experiments

The NMR tubes containing cold ion solutions were carefully poured into a slurry of bicarbonate and ice with vigorous mixing, whereupon flaky solids (light-green for 1 and pale brown for 2) separated, but which partially dissolved upon addition of CH_2Cl_2 and vigorous mixing. The organic extract was separated, dried ($MgSO_4$) and the solvent removed under vacuum. The residue redissolved in $CDCl_3$ for NMR and IR assay.

c) Calculations

MMX molecular mechanics calculations were performed with the PCMODEL version of C.Still's MODEL program (Serena Software). Good convergence was achieved, usually after 100 iterations.

ACKNOWLEDGEMENTS

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