Mass Spectral and Theoretical (AM1) Study of Cations Derived from Janusene. Evidence for Interannular Proton Transfer

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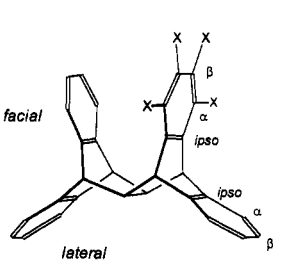
Received February 23, 1993

A previous failure to find clear evidence for protonation of janusene in superacid solutions, coupled with evidence for radical cation formation, led to the current mass spectral and theoretical study. The janusene radical cation $JAN^{\bullet+}$ generated by EI/MS undergoes cycloreversion to give the anthracene radical cation with high selectivity over the dibenzobarrelene cation. Cycloreversion of tetrafluorojanusene radical cation $F_4JAN^{\bullet+}$ is also selective toward $AN^{\bullet+}$ formation, with lesser amounts of $F_4AN^{\bullet+}$, $DBB^{\bullet+}$, and $F_4DBB^{\bullet+}$ cations being formed in order of decreasing relative abundance. In contrast, protonated janusenium ion $(JAN{\cdot}H)^+$ and $(F_4JAN{\cdot}H)^+$ undergo cycloreversion with a preponderance of $(DBB{\cdot}H)^+$ as the charged fragment. Acetylation (with $MeCO^+$), trimethylsilylation (with TMS^+), and trifluoroacetylation (with CF_3CO^+) of JAN and F_4JAN, and fragmentation of their resulting cations, were also studied by tandem mass spectrometry. Remarkably, the acylated cations also gave predominantly $(DBB{\cdot}H)^+$ as the cycloreversion cation, thus indicating interannular proton transfer. The stabilities of protonated and oxidized janusenes, and several model compounds, were calculated by the AM1 molecular orbital method. For JAN, β-facial protonation is preferred over lateral protonation by about 4 kcal/mol, whereas in F_4JAN preference for facial versus lateral protonation is less (2.5 kcal/mol). The AM1 calculations lend support to the concept of rapid interannular proton transfer between facial rings, which may help to explain the observation of broad NMR lines in attempts to protonate janusene in superacids.

Introduction

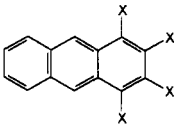
The synthesis and properties of compounds with face-to-face aromatic rings that are held within the normal van der Waals distance (3.4 Å) remains a subject of considerable investigation. We have previously investigated the chemical behavior in superacid media of two prototypical face-to-face systems: [2.2]paracyclophane and janusene.[1,2] Our findings on polyfluoro[2.2]paracyclophanes[1] confirmed earlier studies on the parent molecule that σ complex formation occurs via ipso protonation to provide considerable relief of the angle strain in the [2.2]paracyclophane framework.[3] Surprisingly, we found that janusene, which has virtually undistorted (i.e., planar) aromatic rings,[4] did not give clear evidence for σ complex formation.[2] NMR signals were broad, and oxidation to the janusene radical cation and formation of coupled products occurred. A tetrafluorojanusene behaved similarly.

The objective behind our current study was to investigate further the behavior of janusene toward electrophiles and in oxidation via mass spectral and theoretical studies. In regard to protonation, it had been expected that a σ-complex could be observed in superacid solution because Cristol's initial study of the janusene system demonstrated activation toward electrophiles with electrophilic nitration and bromination occurring predominantly at C_β of a facial ring rather than in a lateral ring.[5] In Cristol's study, janusene (JAN or 1) was prepared by a Diels–Alder reaction



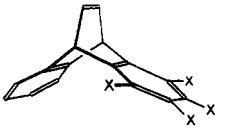
JAN (or **1**); X = H

F_4JAN (or **11**); X = F



AN (or **4**); X = H

F_4AN; X = F



DBB (or **21**); X = H

F_4DBB; X = F

between anthracene (AN or 4) and dibenzobarrelene (DBB or 21).[6] In the mass spectral study reported here, we examine the gas-phase behavior of the janusene radical cation, $JAN^{\bullet+}$, protonated janusene, $(JAN{\cdot}H)^+$, adducts with other electrophiles, and their cycloreversion to species related to AN and DBB. The behavior of the facially tetrafluorinated derivative, F_4JAN, first synthesized by Filler et al.,[7] is also examined. We shall use the letter designations, such as $(JAN{\cdot}H)^+$, when describing the MS results because the detailed structures may not be certain and use the number designation, such as 1, when discussing particular structures and theoretical calculations.

(1) Laali, K.; Filler, R. *J. Fluorine Chem.* **1989**, *43*, 415.
(2) Laali, K. K.; Gelerinter, E.; Filler, R. *J. Fluorine Chem.* **1991**, *53*, 107.
(3) (a) Hefelfinger, D. T.; Cram, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 4754. (b) Hopf, H.; Shin, J. H.; Volz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 564.
(4) Macintyre, W. M.; Tench, A. H. *J. Org. Chem.* **1973**, *38*, 130.
(5) Cristol, S. J.; Lewis, D. C. *J. Am. Chem. Soc.* **1967**, *89*, 1476.
(6) Systematic names for janusene and dibenzobarrelene are 5,5a,6,11,11a,12-hexahydro-5,12:6,11-di-*o*-benzenonaphthacene and dibenzobicyclo[2.2.2]octatriene, respectively.
(7) Filler, R.; Cantrell, G. L. *J. Fluorine Chem.* **1987**, *36*, 407.

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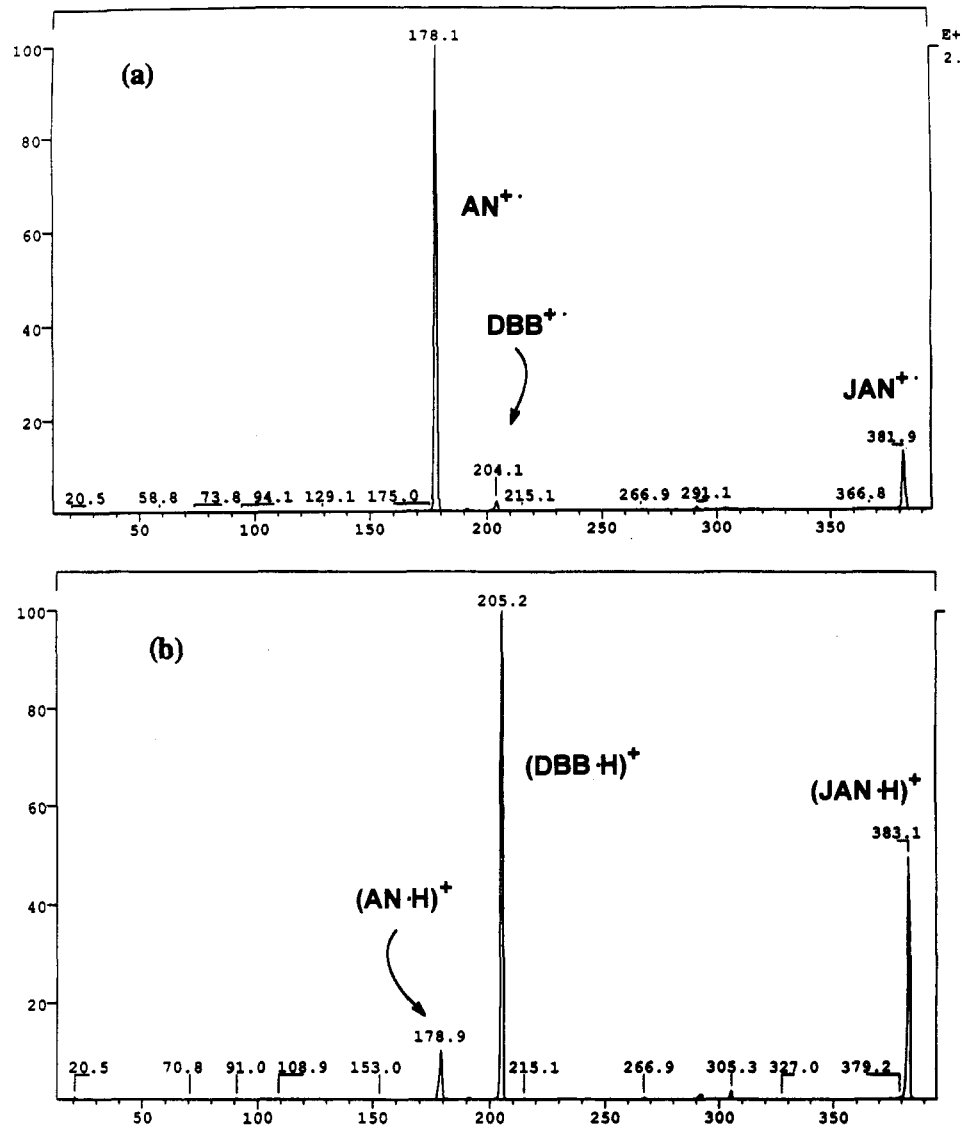


Figure 1. Product ion scans of (a) $JAN^{\bullet+}$ (m/z 382) and (b) $(JAN{\cdot}H)^+$ (m/z 383).

Results

MS Study of Janusene Cations. The 70-eV EI mass spectrum of janusene shows the radical cation $JAN^{\bullet+}$ (m/z 382; 9.7) and the products of its cycloreversion, i.e., $AN^{\bullet+}$ (m/z 178; 100) and $DBB^{\bullet+}$ (m/z 224; 6). The preponderance of m/z 178 over m/z 224 suggests that cleavage of $JAN^{\bullet+}$ proceeds with high selectivity to produce $AN^{\bullet+}$ with loss of DBB rather than $DBB^{\bullet+}$ with loss of anthracene. Collisionally induced decomposition (CID) of $JAN^{\bullet+}$ also led to a highly specific cycloreversion forming $AN^{\bullet+}$ (m/z 178; 100) as the major charged product, whereas the $DBB^{\bullet+}$ peak was very small (m/z 204; 2) (Figure 1a).

The isobutane CI mass spectrum of janusene shows a high abundance of $(JAN{\cdot}H)^+$ (m/z 383; 100). No significant diprotonation was achieved (very weak m/z 192). Abundant product ions were $(AN{\cdot}H)^+$ (m/z 179; 50) and $(DBB{\cdot}H)^+$ (m/z 205; 16). Interestingly, the decomposition (CID) of $(JAN{\cdot}H)^+$ produced the reverse relative populations of these two ions: $(DBB{\cdot}H)^+$ was the base peak (m/z 205; 100) with $(AN{\cdot}H)^+$ being a minor product (m/z 179; ~12) (Figure 1b).

Reaction of JAN with $MeCO^+$ (acetone/CI)[8-10] produced the acetylated janusene adduct $(JAN{\cdot}COMe)^+$ in good abundance (m/z 425; 65), other prominent ions being $(JAN{\cdot}H)^+$ (100) and $AN^{\bullet+}$ (74). No doubly acetylated janusene cations could be detected in the acetone/CI mass spectrum of JAN. Collisional decomposition of $(JAN{\cdot}COMe)^+$ gave $MeCO^+$ as the major product (m/z 43; 100), together with $(DBB{\cdot}H)^+$ (m/z 205; 28), $(DBB{\cdot}COMe)^+$ (m/z 247; 15), $(AN{\cdot}COMe)^+$ (m/z 221; 11), and $JAN^{\bullet+}$ as minor products.

Janusene was similarly reacted with Me_3Si^+ ion (generated via TMS/CI)[11,12] to give abundant $(JAN{\cdot}SiMe_3)^+$ cation (m/z 455). Decomposition of m/z 455 produced a strong Me_3Si^+ ion (m/z 73; 100) with $JAN^{\bullet+}$ (m/z 382) being barely visible. Some $(JAN{\cdot}SiMe_3)^+$ remained unreacted (m/z 455; 20).

Trifluoroacetylation of JAN with CF_3CO^+ generated from trifluoroacetic anhydride (TFA/CI) gave $(JAN{\cdot}COCF_3)^+$ (m/z 479) in low abundance (17). Remarkably, collisional decomposition of the latter produced $(DBB{\cdot}H)^+$

(8) Wang, G.; Sha, Y.; Xu, Z.; Pan, J. *Anal. Chem.* **1985**, *57*, 2283.
(9) Vairamani, M.; Kumar, K. V. S.; Rao, G. K. V. *Org. Mass Spectrom.* **1990**, *25*, 363.
(10) Vairamani, M.; Saraswathi, M.; Kumar, K. V. S. *Org. Mass Spectrom.* **1992**, *27*, 27.
(11) Clemens, D.; Munson, B. *Org. Mass Spectrom.* **1985**, *20*, 368.
(12) Chizhov, O. S.; Kadentsev, V. I.; Stomakhin, A. A. *Org. Mass Spectrom.* **1991**, *26*, 757.

(m/z 205) as the nearly exclusive product with no CF_3CO^+, $(AN{\cdot}COCF_3)^+$, or $(DBB{\cdot}COCF_3)^+$ being formed.

MS Study of Tetrafluorojanusene Cations. The EI/MS of F_4JAN yielded $F_4JAN^{\bullet+}$ (m/z 454; 18) together with the cycloreversion products $AN^{\bullet+}$ (m/z 178; 100), tetrafluoroanthracene radical cation $F_4AN^{\bullet+}$ (m/z 250; 24), $DBB^{\bullet+}$ (m/z 204; 17), and a tiny peak at m/z 276 for tetrafluorodibenzobarrelene $F_4DBB^{\bullet+}$. The preponderance of $AN^{\bullet+}$ relative to other cycloreversion cations illustrates that cycloreversion leading to loss of F_4DBB is most preferred, whereas loss of AN is least favored. A small but distinct oxidation dication F_4JAN^{+2} (m/z 227; M + 1 227.5) was aso observed; a dication was not observed in the EI/MS of JAN.

Collisional decomposition of $F_4JAN^{\bullet+}$ was rather selective yielding predominantly $AN^{\bullet+}$ ion (m/z 178; 100). The relative abundances of $F_4AN^{\bullet+}$ (m/z 250; 30) and $DBB^{\bullet+}$ (m/z 204; 6) were much less, again illustrating preference for loss of F_4DBB. Decomposition of the dication F_4JAN^{+2}, on the other hand, produced all of the expected singly charged cycloreversion products with less discrimination, i.e., $F_4AN^{\bullet+}$ (100), $AN^{\bullet+}$ (77), $DBB^{\bullet+}$ (52), and $F_4DBB^{\bullet+}$ (43).

F_4JAN was monoprotonated (isobutane/CI) to give $(F_4JAN{\cdot}H)^+$ (m/z 455) as the base peak, together with $(AN{\cdot}H)^+$ (m/z 179; 70) and $(DBB{\cdot}H)^+$ (9). Diprotonation was not detectable (m/z 228; M + 1 m/z 228.5). Decomposition of $(F_4JAN{\cdot}H)^+$ gave $(DBB{\cdot}H)^+$ (m/z 205; 100) as the prominent product ion, with $(AN{\cdot}H)^+$ (17), $(F_4DBB{\cdot}H)^+$ (11), and $(F_4AN{\cdot}H)^+$ (6) being observed as minor products of cycloreversion. A peak at m/z 435 corresponding to HF loss from $(F_4JAN{\cdot}H)^+$ was also seen.

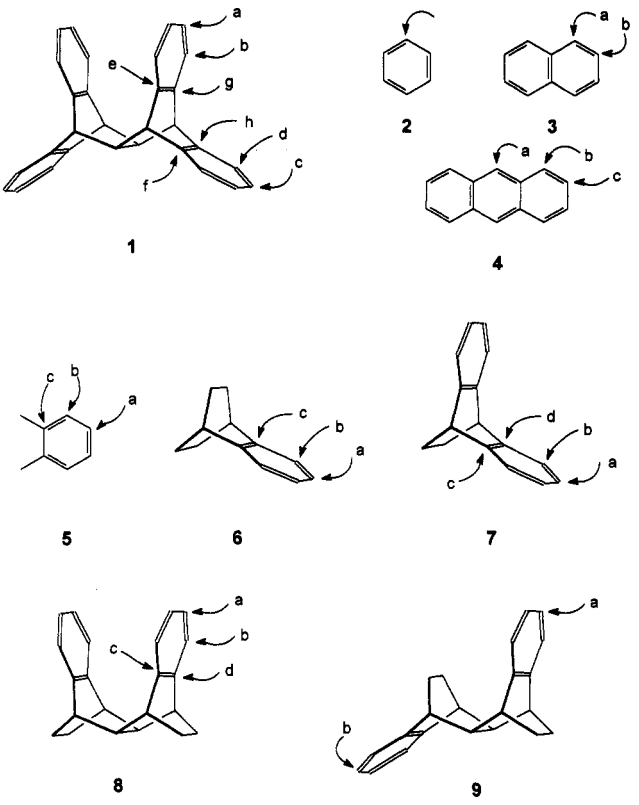
The acetone/CI–MS of F_4JAN produced the acetylated (m/z 497), protonated (m/z 455), and radical (m/z 454) ions, all in almost equal abundance. The cycloreversion cations $AN^{\bullet+}$ (100), $F_4AN^{\bullet+}$ (32), and $DBB^{\bullet+}$ (18) were also formed. Collisional decomposition of the acetylated cation gave $MeCO^+$ as the base peak whereas the $F_4JAN^{\bullet+}$ ion was negligible. Minor product ions due to $(AN{\cdot}COMe)^+$ (m/z 221), $(DBB{\cdot}COMe)^+$ (m/z 247), and $(AN{\cdot}H)^+$ (m/z 179) were also produced.

Reaction of F_4JAN with Me_3Si^+ gave a prominent silylation adduct $(F_4JAN{\cdot}TMS)^+$ (m/z 527; base peak) with weak peaks due to $F_4JAN^{\bullet+}$ and F_4AN^+. The Me_3Si^+ ion was the most intense product ion produced upon collisional decomposition of the silylated adduct (m/z 71; base peak); $F_4JAN^{\bullet+}$ was not detectable.

Trifluoroacetylation of F_4JAN with CF_3CO^+ was more effective than that of JAN, yielding the $(F_4JAN{\cdot}COCF_3)^+$ ion (m/z 551) in 50% abundance. Collisional decomposition of $(F_4JAN{\cdot}COCF_3)^+$ gave $(AN{\cdot}COCF_3)$ (m/z 275) as the main product and $(DBB{\cdot}COCF_3)^+$ (m/z 301; 22) as the minor product, with $AN^{\bullet+}$ and $DBB^{\bullet+}$ ions being barely observable; trifluoroacetylated F_4AN and/or F_4DBB ions were not detected. The preponderance of $(AN{\cdot}COCF_3)^+$ and absence of CF_3CO^+ in the product ion spectrum imply that $(AN{\cdot}COCF_3)^+$ is formed directly by cycloreversion; if so, trifluoroacetylation must have occurred at the nonfluorinated anthracene moiety of F_4JAN.

Competitive MS Study of 5 and 6. In independent experiments, equimolar mixtures of JAN and F_4JAN were reacted with $MeCO^+$, Me_3Si^+, and CF_3CO^+ in CI studies. The selectivities toward electrophiles (E^+) were determined based on the relative abundances of $JAN{\cdot}E^+/F_4JAN{\cdot}E^+$ in the CI mass spectra. These experiments can have validity as a measure of selectivity only if the relative rates of fragmentation are the same, which appears to be approximately true in the case of JAN and F_4JAN.

Scheme I

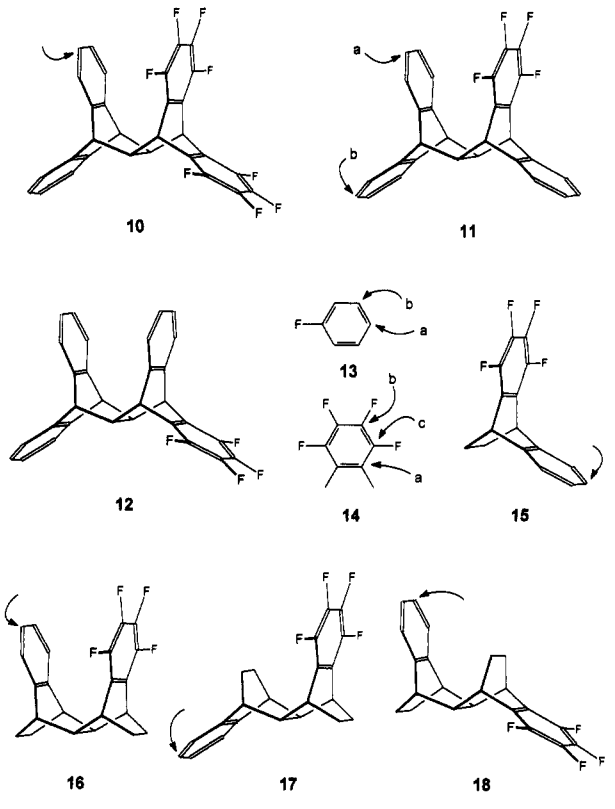


In competitive acetylation, a $k_{JAN}/k_{F4JAN} = 2.1$ was measured; i.e., fluorination of one facial ring reduces the overall relative rate of $MeCO^+$ attachment in the gas phase by roughly 2-fold. Similar competitive experiments for reactions with Me_3Si^+ and CF_3CO were unselective, giving selectivities of 1.1 and 0.9, respectively. The values near unity imply rather indiscriminate electrophilic attack due to reactive electrophiles and an activated substrate.

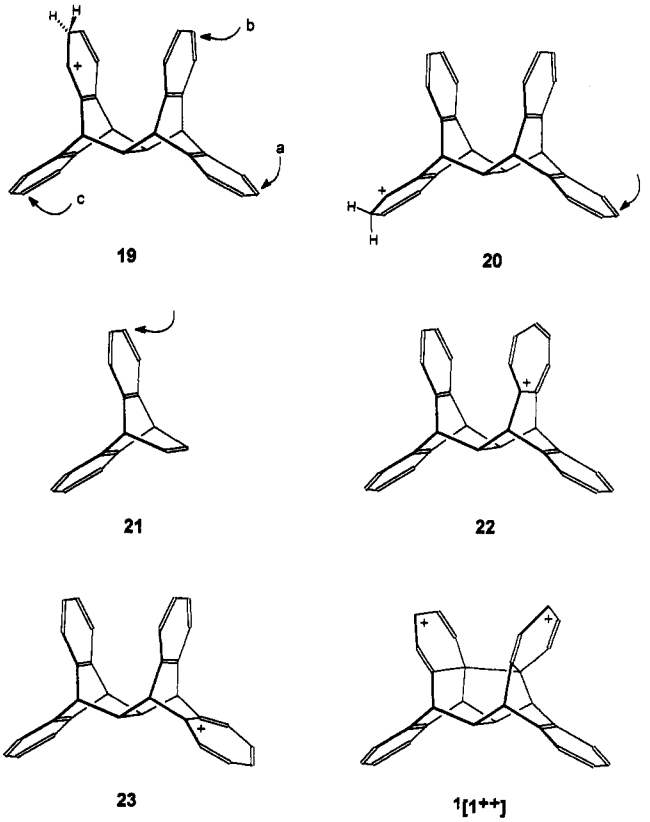
AM1 Calculations on Janusene and Related Structures. Extensive calculations were carried out in the AM1 semiempirical molecular orbital method[13] with full geometry optimization on janusene, protonated janusenes, oxidation cations of janusene, and on a variety of related structures and model compounds. The molecules calculated are shown in Schemes I–III; arrows indicate alternative sites of proton attachment to form arenium ions, with the letters indicating the predicted order of arenium ion stability from most to least stable. Table I gives the ionization potentials for uncharged molecules and heats of formation for all structures. The AM1 approach was chosen over ab initio methods primarily because of the large size of the janusene framework. However, the choice of AM1 is also justified by the findings by Gano that AM1 calculations correctly predicted features of the photoelectron spectra of a stilbene with cofacial benzene rings[14] and by Katzenellenbogen that an AM1 geometry matched up well with experiment for a 1,2-diarylindano[a]indan

(13) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(14) Gano, J. E.; Park, B.-S.; Subramanian, G.; Lenoir, D.; Gleiter, R. *J. Org. Chem.* **1991**, *56*, 4806.
(15) Anstead, G. M.; Srinivasan, R.; Peterson, C. S.; Wilson, S. R.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 1378.

Scheme II



Scheme III



with cofacial aromatic rings.[15] The AM1 calculation on janusene reproduces reasonably well the key geometric feature of the facial ring placement determined in an X-ray study of a dibromo derivative:[4] the dihedral angle between the cofacial rings is 26.6° (24.5° AM1), and the distances are 2.99 Å (3.05 Å AM1) for C_{ipso}–C_{ipso} and 4.09 Å (4.07 Å AM1) for C_β–C_β. In addition, the calculations predict that the facially tetrafluorinated janusene, 11, is more stable than the lateral tetrafluoro isomer, 12, in keeping with the exclusive formation of 11 in a Diels–Alder reaction.[7] (The predicted difference in stability of isomers is only 1 kcal/mol; the transition state was not probed.)

Discussion

In our previous NMR study of janusenes in superacid solution, clear evidence for protonation to form arenium ions was not obtained because signals were broad and concomitant and subsequent oxidation to arene radical cations occurred.[2] In the present mass spectral study, oxidation products were produced under EI conditions, while protonation and adducts with other electrophiles (in acetylation, trimethylsilylation, and trifluoroacetylation) were studied under CI conditions. The dissociation pathways of the resultant cations were followed by CID in a tandem mass spectrometer.

In solution, janusene is preferentially attacked at C_β of the facial rings in electrophilic aromatic substitution.[5] Some clues emerge regarding the structure of ions due to the attack of electrophiles in the mass spectrometer, but not specifically the preferred carbon of attachment in a possible σ-complex. In protonation, one of the most interesting results is the contrast between the preference for $(AN{\cdot}H)^+$ over $(DBB{\cdot}H)^+$ as the predominant product cation in the initial CI spectrum of janusene and the reverse preference for $(DBB{\cdot}H)^+$ over $(AN{\cdot}H)^+$ in the CID product spectrum of the $(JAN{\cdot}H)^+$ ion. One possibility is that competing pathways for decomposition are possible in the CI source, with the site of the proton attack or attachment having a large influence on the rate and mechanism of cycloreversion. The CI and CID experiments also differ in the amount of internal energy deposited in the ion even if the site of protonation is the same.

A similar change in relative proportions of the major product ions from the CI to the CID spectrum occurred in the protonation of tetrafluorojanusene. In this case, however, the dominance of the $(DBB{\cdot}H)^+$ and $(AN{\cdot}H)^+$ product ions over the $(F_4DBB{\cdot}H)^+$ and $(F_4AN{\cdot}H)^+$ ions implies that the proton was attached to the nonfluorinated anthracene moiety in $(F_4JAN{\cdot}H)^+$. Similarly, the preponderance of the $(AN{\cdot}COCF_3)^+$ product ion from the $(F_4JAN{\cdot}COCF_3)^+$ ion indicates that trifluoroacetylation must have occurred at the nonfluorinated anthracene moiety. For the acetylation and trimethylsilylation adducts, the decompositions were not so informative, as the $COCH_3^+$ and $SiMe_3^+$ ions dominated. Possibly π-complexes rather than σ-complexes are involved in the latter cases; both types have been invoked in studies of arene/TMS^+ association complexes.[16] However, in a competitive experiment, $COCH_3^+$ exhibited a selectivity of about 2.1 for janusene over tetrafluorojanusene. Combining these results, it appears that the facial tetrafluoro substituents deactivate the tetrafluorinated anthracene moiety relative to the nonfluorinated anthracene side and deactivate the entire molecule relative to janusene.

In the remainder of the Discussion below, the features of protonated janusenes, oxidation to radical cations and dications, and cycloreversion from cationic species are considered in light of AM1 calculations. Of course, it is

(16) (a) Wojtyniak, A. C. M.; Stone, J. A. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 59. (b) Fornarini, S. *J. Org. Chem.* **1988**, *53*, 1314. (c) Stone, J. A. *Res. Chem. Intermed.* **1991**, *16*, 257.

Table I. AM1 Ionization Potentials, Heats of Formation, and Relative Energies of Protonation for Janusenes and Model Compounds

compd	IP, eV	H_f, kcal/mol	ΔE,[a] kcal/mol	compd	IP, eV	H_f, kcal/mol	ΔE,[a] kcal/mol
1	8.915	126.6		8b·H$^+$		210.7	−13.6
1a·H$^+$		296.2	−14.5	8c·H$^+$		215.4	−8.9
1b·H$^+$		297.3	−13.3	8d·H$^+$		220.7	−3.6
1c·H$^+$		300.3	−10.3	8·H$^+$ (bridge)		235.4	
1d·H$^+$		302.1	−8.5	8·H$^+$ (cofacial)		227.6	
1e·H$^+$		302.1	−8.5	9	9.163	39.1	
1f·H$^+$		306.9	−3.8	9a·H$^+$		212.2	−10.9
1g·H$^+$		307.2	−3.5	9b·H$^+$		212.3	−10.8
1h·H$^+$		307.4	−3.3	10	9.444	−215.4	
1$^{+\bullet}$		319.4		10·H$^+$		−36.1	−4.7
^{1}[1^{2+}]		578.0		11	9.245	−45.7	
^{3}[1^{2+}]		576.5		11a·H$^+$		129.2	−9.1
2	9.653	22.0		11b·H$^+$		131.7	−6.6
2·H$^+$		206.0	*0.0*	12	9.180	−44.8	
2·H$^+$ (bridge)		228.9		13	9.545	−23.3	
3	8.711	40.6		13a·H$^+$		160.9	0.2
3$^{\bullet+}$		232.3		13b·H$^+$		168.9	8.2
3a·H$^+$		213.2	−11.4	14	9.715	−163.9	
3b·H$^+$		216.8	−7.8	14a·H$^+$		35.3	15.2
4	8.123	62.9		14b·H$^+$		36.7	16.6
4$^{\bullet+}$		241.4		14c·H$^+$		37.2	17.1
4a·H$^+$		221.3	−25.6	15	9.630	−123.5	
4b·H$^+$		229.6	−17.3	15·H$^+$		58.8	−1.7
4c·H$^+$		233.8	−13.1	16	9.253	−132.6	
5	9.183	7.4		16·H$^+$		43.0	−8.4
5a·H$^+$		184.6	−6.8	17	9.436	−132.6	
5b·H$^+$		185.5	−5.9	17·H$^+$		45.3	−6.1
5c·H$^+$		190.7	−0.7	18	9.458	−132.9	
6	9.226	5.5		18·H$^+$		45.2	−5.9
6a·H$^+$		180.3	−9.2	19a·H$^+$		520.6	40.4
6b·H$^+$		181.8	−7.7	19b·H$^+$		532.3	52.1
6c·H$^+$		187.0	−2.5	19c·H$^+$		536.6	56.4
7	9.154	48.1		20·H$^+$		522.1	37.8
7a·H$^+$		222.6	−9.4	21		83.6	
7b·H$^+$		224.3	−7.8	21$^{\bullet+}$		283.8	
7c·H$^+$		229.2	−2.9	21·H$^+$		258.7	−8.9
7d·H$^+$		229.7	−2.3	22		301.9	
8	8.848	40.3		23		305.8	
8a·H$^+$		209.7	−14.6				

[a] For isodesmic reaction 1, i.e., energy of protonation relative to benzene.

recognized that reactions in the CI source of a mass spectrometer do not necessarily occur under equilibrium conditions, whereas the AM1 data refer to equilibrium structures.

Protonated Janusenes. AM1 calculations (Table I) predict that protonation of Cβ of the facial ring in janusene is preferred, giving 1a·H$^+$ (see Scheme I), in agreement with the preferred site of electrophilic aromatic substitution.[5] Although only broad NMR signals were observed in attempts to protonate janusene under superacid conditions,[2] the σ-complex may have been present. A rapid degenerate equilibration by 1,2-hydride shifts between adjacent β positions would almost certainly lead to signal averaging and possible kinetic line-broadening at the observation temperature (−90 °C and higher), in analogy to the behavior of the benzenium ion, 2·H$^+$.[17] Equilibration might well involve the α positions as well, since 1b·H$^+$ is predicted to be only 1.2 kcal/mol less stable than 1a·H$^+$.

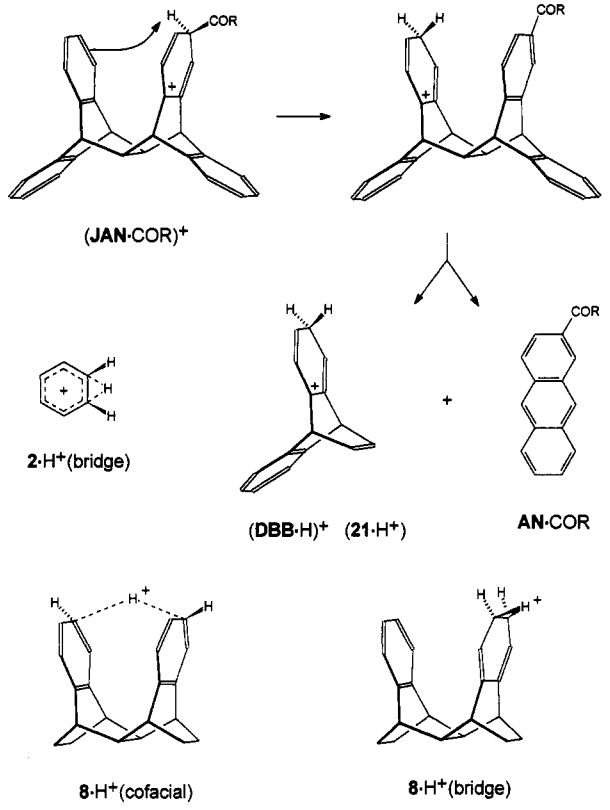
It is intriguing to speculate that the proton might also be passed intramolecularly from one facial ring to the other in a σ-complex in solution and thereby contribute to kinetic line-broadening in the NMR. Strong evidence for such proton transfer in the gas phase comes from the formation of (DBB·H)$^+$ in CID spectra of (JAN·COCH$_3$)$^+$ and (JAN·COCF$_3$)$^+$. Interannular proton transfer before cycloreversion can account for the formation of (DBB·H)$^+$, as shown in Scheme IV. (DBB·H)$^+$ is the nearly exclusive ion product in the decomposition of (JAN·COCF$_3$)$^+$ and is the major cycloreversion product from (JAN·COCH$_3$)$^+$. In these cases, H$^+$ transfer to the second facial ring would result in a more stable σ-complex, as positive charge would reside in a moiety which is not substituted with the electron-withdrawing acetyl or trifluoroacetyl group. There is no evidence for interannular proton transfer in (F$_4$JAN·COCH$_3$)$^+$ or (F$_4$JAN·COCF$_3$)$^+$ where H$^+$ transfer would be to a ring deactivated by polyfluorosubstitution.

Although semiempirical calculations generally overestimate the energy content of H-bridged (nonclassical) carbocations,[18] it is interesting to note that the predicted energy to reach the interannular H-bridged transition state 8·H$^+$ (cofacial) from 8a·H$^+$ (ΔH_f = 17.9 kcal mol^{-1}) is substantially lower than for the 1,2-hydride shift with 8·H$^+$(bridge) as the transition state (ΔH_f = 25.7 kcal mol^{-1}). The smaller structure 8 serves as a good model for janusene (see below). For comparison, the AM1 calculated barrier for 1,2-hydride shift in the benzenium ion (from 2·H$^+$ to 2·H$^+$(bridge)) is 22.9 kcal mol^{-1}, whereas the experimental E_a is only about 10 kcal mol^{-1} or less.[17,19] Thus, it is tempting to conclude that the barrier for interannular proton transfer in protonated janusene might well be less

(17) Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299.

(18) For one example, see discussions of H-bridging in cyclopentyl cations: (a) Botkin, J. H.; Forsyth, D. A.; Sardella, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 2797. (b) Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1989**, *111*, 5475.

Scheme IV



than 10 kcal mol^{-1}. Interannular proton transfer might also occur between α or ipso positions, following 1,2-hydride shifts to the less stable ions **1b**·H$^+$ and **1e**·H$^+$.

There is ample precedence for gas-phase interannular proton transfer in related cations, such as (ω-phenylalkyl)-benzenium ions.[20] Most notably, a recent study of proton transfer in thermal arenium ions from the gas-phase alkylation of 1,2-diphenylethane has shown that the Arrhenius parameters and the H/D kinetic isotope effect for the interannular shift[21] are very close to those for intraannular 1,2-shifts[22] (both have an E_a of about 8 kcal/mol). In solution, there is kinetic evidence for intermolecular proton transfer between arenium ions and arenes[23] but apparently none for ring-to-ring intramolecular transfers.[20b]

Lateral protonation is calculated to be less favorable than facial protonation by about 4 kcal/mol, but β protonation is also predicted for the lateral ring to give **1c**·H$^+$. Ipso protonation should be least favorable, but remarkably, the ipso site in the facial ring which appears least accessible by direct attack, i.e., **1e**·H$^+$, is predicted to be the favored ipso site, possibly because it allows bending of the protonated ring away from the other facial ring or because of some weak interannular bonding to the proton from the other facial ring.

Janusene is predicted to be more easily protonated than benzene by −14.5 kcal/mol. In Table I, comparison of ease of protonation is made with many model compounds (Scheme I) to help establish the reasons for the preferred site of protonation and lowered energy for formation of the σ-complex of janusene. The comparative energies of protonation are shown relative to formation of **2**·H$^+$ from benzene, i.e., ΔE for the isodesmic reaction (1). Janusene

$$\mathrm{Ar} + \mathrm{C_6H_7^+} \rightleftharpoons \mathrm{ArH^+} + \mathrm{C_6H_6} \qquad (1)$$

is actually predicted to be slightly more easily protonated than naphthalene, **3**, but substantially less easily protonated than anthracene, **4**; both **3** and **4** form stable σ complexes in superacid.[17]

A preference for electrophilic attack at the β position of 1,2-dialkyl benzenes, such as tetralin, is well known[24] and is reflected in the AM1 calculations. Both *o*-xylene, **5**, and benzobicyclo[2.2.2]octane, **6**, show the preference for β protonation in the calculations.[25] Thus, the preference for protonation of the β position in janusene is not unusual. Having the benzo group fused to the bicyclooctyl ring in **6** also accounts for about two-thirds of the lowering of the energy of protonation relative to that for benzene. A second benzo ring on the same bicyclooctyl ring system, as in **7**, has a very slight additional effect. However, having only two benzo rings but placed in a face-to-face arrangement, as in **8**,[26] fully accounts for the protonation pattern and energies in janusene. The facial–lateral placement of the benzo rings in **9** is predicted to be about 3.6 kcal/mol less susceptible to protonation than in either **1** or **8**. Thus, roughly one-quarter of the lowering of the energy of protonation of janusene relative to benzene, and the entire preference for facial (**1a**·H$^+$) over lateral (**1c**·H$^+$) protonation, can be attributed to an interaction between the facial rings.

What is the nature of the stabilizing interaction between facial rings in the σ complex? Possibilities include charge transfer, incipient covalent bonding via either a cofacially bridging proton or C_{ipso}–C_{ipso} bond formation, and polarization of the uncharged ring. Previous studies of janusene and related cofacial molecules have ascribed weak, long wavelength absorptions in UV spectra to intramolecular charge-transfer transitions.[5,27] A particularly relevant example is the pair of tropylium-containing janusene analogs, **22** and **23**.[28] Besides exhibiting a longer wavelength λ_{max}, the facial isomer **22** had more shielded tropylium ring carbons in ^{13}C spectra and greater stability as indicated by lower electron affinity and increase in pK_{R^+} by 2.3 pK units.

Our AM1 calculations indicate that **22** is more stable than **23** by 3.9 kcal mol^{-1}, sufficient to account for the difference in pK_{R^+} values. This energy difference is essentially the same as that between facially and laterally protonated janusenes, and therefore the same stabilization

(19) Mason, R.; Fernandez, M. T.; Jennings, K. R. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 89.
(20) (a) Kuck, D.; Bäther, W.; Grützmacher, H.-F. *J. Am. Chem. Soc.* **1979**, *101*, 7154. (b) Kuck, D. *Mass Spectrom. Rev.* **1990**, *9*, 187.
(21) Cacace, F.; Crestoni, M. E.; Fornarini, S.; Kuck, D. *J. Am. Chem. Soc.* **1993**, *115*, 1024.
(22) Cacace, F.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* **1992**, *114*, 6776.
(23) Koptyug, V. A. In *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: Berlin, 1984; Vol. 122, p 119.
(24) Galley, M. W.; Hahn, R. C. *J. Org. Chem.* **1976**, *41*, 2006.
(25) Note that in superacid solutions, protonation of *o*-xylene leads to rearrangement to the *m*-xylenium ion by methyl and hydride shifts: Brouwer, D. M. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 611.
(26) This molecule has been synthesized and properties have been reported: Grimme, W.; Kammerling, H. T.; Lex, J.; Gleiter, R.; Heinze, J.; Dietrich, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 205.
(27) (a) Prinzbach, H.; Sedelmeier, G.; Kruger, C.; Goddard, R.; Martin, H.-D.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 271. (b) Ibuki, E.; Ozasa, S.; Fujioka, Y.; Mizutani, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 845. (c) Mataka, S.; Takahashi, K.; Hirota, T.; Takuna, K.; Kobayashi, H.; Tashiro, M. *J. Chem. Soc., Chem. Commun.* **1985**, 973. (d) Fessner, W.-D.; Sedelmeier, G.; Spurr, P. R.; Rihs, G.; Prinzbach, H. *J. Am. Chem. Soc.* **1987**, *109*, 4626.
(28) Komatsu, K.; Takahashi, K.; Okamoto, K. *Tetrahedron Lett.* **1979**, *49*, 4747.

Table II. Total Charge[a] on Aryl Rings in Janusene, Protonated Janusenes, and Janusene Radical Cation

	ring			
compd	F[b]	F′	L[c]	L′
1	−0.087	−0.087	−0.109	−0.109
1a·H$^+$	0.688[d]	−0.111	−0.010	−0.036
1c·H$^+$	0.048	−0.054	0.660[d]	0.012
1$^{\bullet+}$	0.257	0.257	0.004	0.004

[a] Sum of charges on six aryl carbons plus the attached hydrogens. [b] Facial ring. [c] Lateral ring. F and L pair are in one anthracene unit, and F′ and L′ are in the other. [d] Protonated ring.

mechanism is likely operative in both types of ions. Thus, stabilization of **1a**·H$^+$ via an incipient, cofacial proton bridge may be ruled out. There is no geometric evidence in the AM1 structure of **1a**·H$^+$ for a proton bridge nor for covalent bond formation between cofacial C_{ipso} atoms; the interring distances are only slightly shorter in **1a**·H$^+$ than in **1**, at 3.01 and 3.03 Å vs 3.05 Å for C_{ipso}–C_{ipso} (compare to 1.60 Å in ^{2}[**1**]$^{2+}$, described below).

Division of the stabilization of **1a**·H$^+$ between the remaining choices of through-space electron donation from the facing phenyl ring (charge transfer) and simple polarization of the facing phenyl ring is difficult. However, the facing ring of **1a**·H$^+$ is certainly polarized in the AM1 calculation, with each carbon picking up negative charge and each hydrogen becoming positively charged compared to janusene itself. The sum of gross atomic charges for each ring in **1**, **1a**·H$^+$, and **1c**·H$^+$ are given in Table II. The net change for the six carbons plus the four hydrogens of the facing phenyl in going from **1** to **1a**·H$^+$ is to become slightly more negative (−0.024), despite any electron donation to the protonated ring. Furthermore, the facially protonated ring in **1a**·H$^+$ is actually predicted to carry more of the positive charge than the laterally protonated ring in **1c**·H$^+$. Thus, while there is clear AM1 evidence for polarization, no obvious effect of through-space electron transfer from the facial ring emerges for the ground state of **1a**·H$^+$. There is some calculated electron drain from both lateral rings in **1a**·H$^+$, but this likely reflects the polarization of electron density toward the protonated ring. Our theoretically based analysis supports the conclusion of Cristol that the interaction between the rings in electrophilic aromatic substitution is a general polarization phenomenon rather than a resonance phenomenon involving specific bond formation between rings in the transition state.[5]

Scheme II shows molecules that were considered in evaluating the effect of polyfluorination on σ-complex formation. The octafluorojanusene, **10**, is deactivated toward β-facial protonation to give **10**·H$^+$, compared to janusene, but it is still predicted to be easier to protonate than benzene (see Table I). In the facial tetrafluorojanusene, **11**, protonation in the other facial ring is still preferred over lateral protonation, but by a smaller margin of 2.5 kcal/mol compared to 4.2 in **1**. The lateral tetrafluoro isomer, **12**, is not known.

Calculations on model compounds support the pattern of preferred protonation in the more remote nonfluorinated anthracene moiety of **11**. The AM1 prediction of a strong preference for para protonation of fluorobenzene, **13**, is in keeping with observations, but the para position is predicted to be slightly deactivated compared to benzene, whereas a *p*-fluoro substituent is actually slightly activating in electrophilic aromatic substitution. Nonetheless, any position in a tetrafluorinated ring, as in the tetrafluoro-*o*-xylene, **14**, should be highly deactivated. The tetrafluoro substitution also deactivates other rings, with the most deactivation in the adjacent lateral ring as in the model compound **15**, which is predicted to be 7.7 kcal/mol less easily protonated than the nonfluorinated **7**. The other facial ring is deactivated by 6.2 kcal/mol in **16** compared to **8**, and the more remote lateral ring is deactivated by 4.7 kcal/mol in **17** compared to **9**. Tetrafluorination in a lateral ring deactivates the remote facial ring by 5.0 kcal/mol in the model **18** compared to **9**. The combination of these substituent effects with the original activation pattern in janusene leads to the prediction of favored β-facial protonation in **10** and **11**. These predicted substituent effects are very much in agreement with the original observations of Cristol on the effect of the deactivating nitro group on subsequent nitration in the janusene skeleton.[5]

Sufficiently strong electron-withdrawing groups in a facial ring might direct substitution to the more remote lateral ring. In a second protonation after initial β-facial protonation, lateral attachment is preferred to give the **19a**·H$^+$ dication over the difacial isomer **19b**·H$^+$.

Oxidized Janusenes. Radical cation oxidation products of JAN and F_4JAN are detected in superacid solutions.[2] Arene oxidation in the presence of SbF_5 is well known,[29,30] but it is unusual for it to compete effectively with protonation in a protic superacid such as a FSO_3H/SbF_5 mixture. SbF_5 oxidation can even give a dication if the ionization potential of the arene is low enough.[30] AM1 vertical ionization potentials (IP) are listed in Table I for janusene, **1**, and a variety of other arenes.

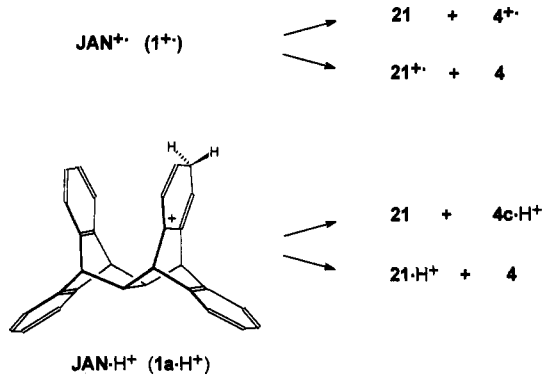
The calculated vertical IP of **1** at 8.915 eV is 0.204 eV (4.7 kcal) higher than that of the conjugated naphthalene, **3**, but the calculated adiabatic IP (**1** → **1**$^{\bullet+}$) is only 1.1 kcal/mol higher. Naphthalene gives a radical cation in SbF_5/SO_2ClF, while benzene (**2**, AM1 IP 9.653 eV) is not oxidized by SbF_5 and anthracene (**3**, IP 8.123 eV) gives a dication.[28] Presumably, the adiabatic IP of janusene is lowered over the vertical IP more than for **1**–**3** because of greater structural reorganization. The majority of the charge in **1**$^{\bullet+}$ resides in and is shared equally by the two facial rings, which more noticeably closer together (2.75 Å C_{ipso}–C_{ipso}, 3.60 Å C_β–C_β) than in **1**, according to the AM1 calculation. The triplet and singlet forms of the dication of **1** were calculated to be very similar in energy but quite different geometrically. In ^{3}[**1**$^{2+}$], the facial rings move apart due to charge repulsion (3.11 Å C_{ipso}–C_{ipso}, 4.38 Å C_β–C_β). ^{1}[**1**$^{2+}$] is predicted to form a single bond (1.60 Å) between two ipso carbons, thereby sharing the charge between the two rings, but with considerable twisting so that the two carbons bearing the most charge are 4.70 Å apart.

The AM1 calculations fail to provide an explanation for the competitive formation of radical cations of **1** and **11** in protic superacids containing SbF_5. **1** is predicted to be easier to protonate than naphthalene, which is readily protonated in such media to give **3a**-H$^+$.[17]

Decomposition Modes of Janusene Cations. Radical cations of janusene and protonated janusenes have a somewhat different outcome in collisionally induced decomposition. As shown in Figure 1, both JAN$^{\bullet+}$ and (JAN·H)$^+$ cleanly give cycloreversion products in CID

(29) Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 4086.
(30) For a recent leading reference, see: Mills, N. S. *J. Org. Chem.* **1992**, *57*, 1899.

Scheme V



spectra. However, decomposition of $JAN^{\bullet+}$ predominantly gives $AN^{\bullet+}$ with a very small amount of $DBB^{\bullet+}$, while $(JAN{\cdot}H)^+$ gives $(DBB{\cdot}H)^+$ with a small amount of $(AN{\cdot}H)^+$. Analogously, the radical cation $F_4JAN^{\bullet+}$ decomposes to give predominantly $AN^{\bullet+}$ while $(F_4JAN{\cdot}H)^+$ cycloreverts to give mainly $(DBB{\cdot}H)^+$. Thus, in addition to the selectivity as to whether the charge is preferred on an AN or DBB fragment, the F_4JAN ions show selectivity for formation of the nonfluorinated cations over fluorinated cations in the cycloreversions.

Scheme V shows the competing outcomes for the cycloreversion reactions of $JAN^{\bullet+}$ and $(JAN{\cdot}H)^+$. For $JAN^{\bullet+}$, or $1^{\bullet+}$, the observed result of **21** and $\mathbf{4}^{\bullet+}$ formation, rather than $\mathbf{21}^{\bullet+}$ and **4**, should be favored by 21.7 kcal/mol according to AM1 H_f data from Table I. For $(JAN{\cdot}H)^+$, assuming that it is ion $\mathbf{1a}{\cdot}H^+$ and that no hydride shifts are involved, the initial cation product would be either the $(AN{\cdot}H)^+$ ion $\mathbf{4c}{\cdot}H^+$ or the β-protonated $(DBB{\cdot}H)^+$, $\mathbf{21}{\cdot}H^+$. The AM1 calculations predict that the $(AN{\cdot}H)^+$ ion would be favored, in contrast with experiment, but only by 4.2 kcal/mol. Thus, at least the AM1 calculations suggest a much smaller thermodynamic preference for the protonated anthracene cation from protonated janusene than for the anthracene radical cation from the janusene radical cation. In reality, the decomposition pathways may be stepwise and not controlled by the thermodynamics of product formation. However, the preference for nonfluorinated cations is easily understood in terms of the destabilizing effect of polyfluoro substitution in cations, whether the pathway is stepwise or concerted.

Conclusions

The janusene and tetrafluorojanusene radical cations undergo a highly selective cycloreversion in collisionally induced decomposition to produce the anthracene radical cation as the charged fragment. The protonated janusenium ions cyclorevert with a high preference for formation of protonated dibenzobarrelene under CID conditions. Acylated cations also give mainly protonated debenzobarrelene, in a process likely involving interannular proton transfer. AM1 calculations indicate that face-to-face proton transfer is quite feasible. The AM1 calculations on janusenes and model compounds indicate that the preference for facial over lateral ring protonation is attributable to an interaction between the facial rings that is largely a polarization phenomenon. It is possible that the previous failure to find clear NMR evidence for protonation in superacid media was due to line broadening from rapid 1,2-hydride shifts and interannular proton transfer.

Experimental Section

Samples of JAN and F_4JAN were available from our previous stable ion study.[2]

A Finnigan-Matt 95Q hybrid mass spectrometer was used for the MS studies. Collisional activation was carried out in the "collision octapole" with translational energy of 50 eV and with air as collision gas. The pressure in the collision cell was adjusted to ca. 0.2 Pa, which corresponds to a pressure in the quadrupole analyzer region of 8×10^{-4} Pa. The acetone/CI and TMS/CI conditions were analogous to the reported procedures.[8-12]

For "TFA/CI" experiments TFA was used as CI reagent to generate CF_3CO^+ ions (m/z 96). Whereas m/z 69 ion (CF_3^+) was also formed in TFA/CI, its attachment cations with the janusenes were either weak or absent.

The aromatics were introduced as solids. In competitive experiments, an equimolar mixture of the two janusenes was prepared by weight, dissolved in chloroform, and thoroughly mixed (vortex). Homogeneous liquid samples were injection *via* a microsyringe into sample capillaries.

Molecular orbital calculations were carried out with either the MOPAC 5.0 program (QCPE) or a MOPAC 6.0 version compiled for 80486 PC's (supplied by Serena Software).

Acknowledgment. We are most grateful to Dr. Robert Lattimer for recording the mass spectra at BF Goodrich R&D Center. Partial support for this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.