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Bridged [14]Annulenes in Superacids: Protonation and Oxidation to Dications. Transannular Interaction and Homoaromaticity

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^{13}C and ^{1}H NMR spectra show that the 1,6:8,13-propanediylidene, 1,6:8,13-butanediylidene, and *syn*-1,6:8,13-bismethano derivatives of [14]annulene yield structurally similar symmetrical, monoprotonated ions in mixtures of $SbF_5/HFSO_3$ and $ClSO_2F$ at −80 °C. Over a period of weeks at −80 °C, or more rapidly at higher temperatures, these ions are oxidized into the respective unprotonated dications, stable at room temperature. The behavior of 1,6:8,13-ethanediylidene[14]annulene under similar conditions is quite different. At −80 °C a mixture of ions is produced that converts in a matter of hours to a single, unsymmetrical monoprotonated ion. Warming this solution results in the formation of a complex mixture of products. The ethano-bridged annulene also behaves differently in solutions of a weaker acid (CF_3COOH) than does the propano-bridged annulene. The different behavior on protonation is rationalized in terms of variations in the degree of transannular interaction due to structural differences in the hydrocarbon skeletons.

1,6:8,13-Bridged [14]annulenes are a class of compounds that have yielded a wealth of information about the relationships between structure and aromaticity. By varying the nature of the bridging substituents, the anthracene-like ring system can be perturbed in a systematic fashion. The effects on the conjugation and the aromatic characteristics of the 14-carbon perimeter have been studied by ESR,[2a] photoelectron,[2b] optical,[3] and NMR[4] spectroscopy and X-ray crystallography.[5] These studies have established the importance of the 1,6:8,13 transannular interactions in determining the spectroscopic properties of this class of hydrocarbons. We were interested in finding out how the transannular interaction is reflected in the chemical reactivity of [14]annulenes, in particular protonation by strong acids.

In the following report, we describe NMR studies of 1,6:8,13-bismethano[14]annulene (1), 1,6:8,13-ethanediylidene[14]annunulene (2), 1,6:8,13-propanediylidene[14]annulene (3), and 1,6:8,13-butanediylidene[14]annulene (4) in strong acid and superacid solutions.

Experimental Section

The annulenes used in this study were prepared by using procedures previously described.[6-9] The 1:4 SbF_5/HSO_3F mixture and $ClSO_2F$ were purchased from Aldrich Chemical Co. and used without further purification, as were trifluoroacetic acid and trifluoroacetic acid-*d*. Spectra were run on Varian SC-300 and XL-300 instruments equipped with standard variable temperature units.

The samples were prepared by adding the hydrocarbon (10–30 mg) to the mixture of SbF_5–FSO_3H–SO_2ClF at −78 °C followed by transfer of the sample to the precooled probe of the spectrometer.

Results

1,6:8,13-Propanediylidene[14]annulene (3). The decoupled six-line ^{13}C NMR spectrum of the pure hydrocarbon in $CDCl_3$ is shown in Figure 1A and the corresponding ^{1}H NMR spectrum in Figure 2A. Note the upfield resonances for the bridge carbons and hydrogens in particular. Addition of the annulene to the superacid solvent at −78 °C gives a dark orange solution and the ^{13}C and ^{1}H spectra are shown in Figures 1B and 2B, respectively. The new species has ten ^{13}C resonances and is designated **3A**.

If this solution is allowed to stand for several months at −100 °C, it turns violet and the peaks of **3A** are replaced by the six resonances of a new species (**3B**), shown in Figures 1C and 2C. This change can be effected in minutes if the solution is warmed to room temperature, where the violet species is stable. The peak assignments shown in Figures 1C and 2C were obtained by single frequency decoupling. The data are summarized in Table I.

If the solution of **3A** is quenched in cold methanol saturated with sodium bicarbonate, the starting annulene is recovered cleanly. When the annulene is treated at ambient temperatures in $CDCl_3$ with a large excess of CF_3COOD, the solution turns from yellow to green and the aromatic protons are substituted by deuterons at different rates (2 > 3 ≫ 7). No deuterium incorporation is observed for the bridge protons. If a mixture of CF_3COOH and $CDCl_3$ is used as a solvent (1:1), no change is observed for the aliphatic protons while the fine structure of the multiplet labeled 2,3 is lost.

1,6:8,13-Bismethano[14]annulene (1). Figure 3A shows the ^{1}H NMR spectrum for the pure annulene in $CDCl_3$ at room temperature. Addition to the superacid solvent at −78 °C gives a green solution and the NMR spectrum shown in Figure 3B. These signals slowly convert into those of a new species at −100 °C as shown in Figure 3C.

The first-formed ion is labeled **1A**, the second, stable at room temperature, **1B**. The NMR data are collected in Table I. The conversion from **1A** to **1B** is accompanied

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[2] (a) Gerson, F.; Huber, W.; Lopez, J. *J. Am. Chem. Soc.* **1984**, *106*, 5808. (b) Batich, C.; Heilbronner, E.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2288.

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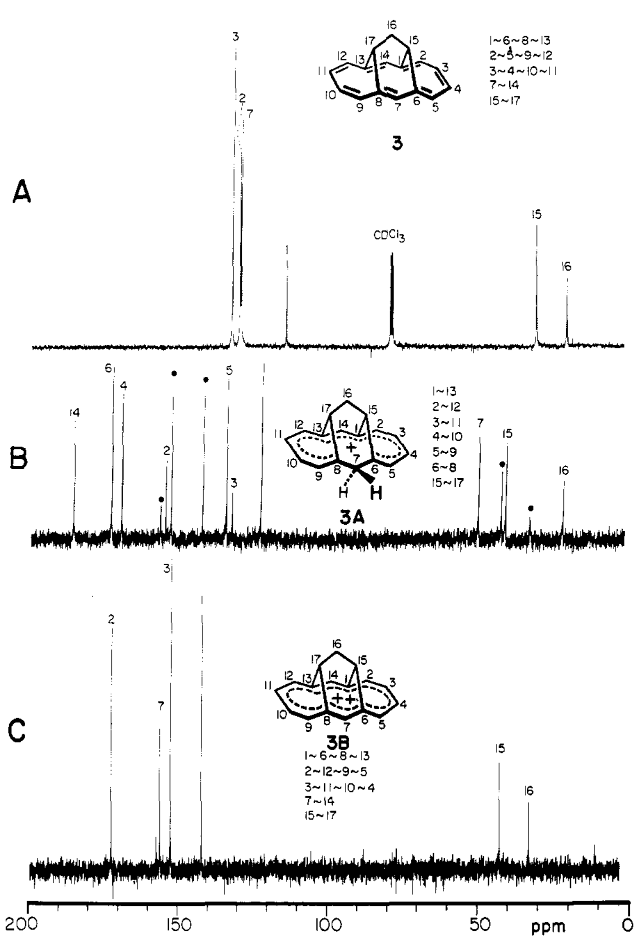

Figure 1. ^{13}C NMR spectra: (A) **3** in $CDCl_3$ at room temperature; (B) **3A** in superacid at −80 °C, traces of **3B** marked by black dots; (C) **3B** in superacid at room temperature.

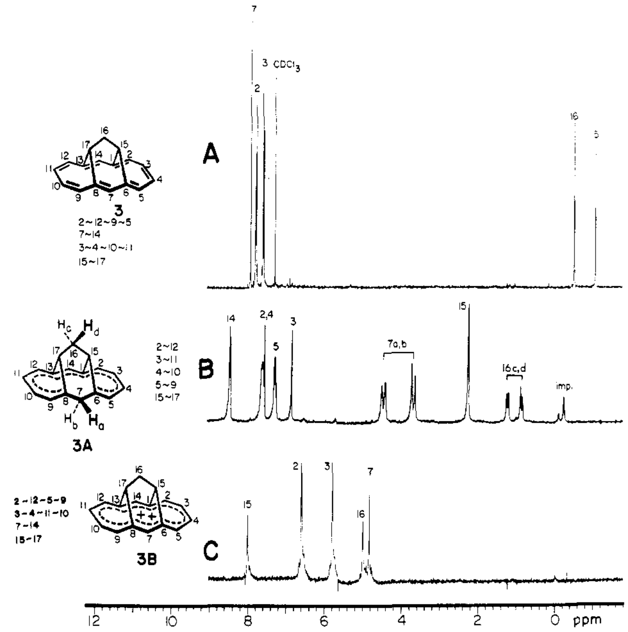

Figure 2. ^1H NMR spectra: (A) **3** in $CDCl_3$ at room temperature; (B) **3A** at −80 °C in superacid; (C) **3B** at room temperature in superacid.

by a change in color from green to violet.

1,6:8,13-Butanediylidene[14]annulene (4). This annulene behaves like the annulenes 1 and 3. At −80 °C the decoupled ^{13}C NMR spectrum ten intense peaks, due to **4A**, accompanied by a set of six resonances of lower intensity, assigned to **4B**. Upon standing at −100 °C for about 1 year, the intensity ratio of these two groups of resonances is inverted with the original ten peaks of **4A** now present at very low intensities. Corresponding changes are observed in the ^1H NMR spectrum. Table I lists the NMR data. The solution of **4B** is dark red.

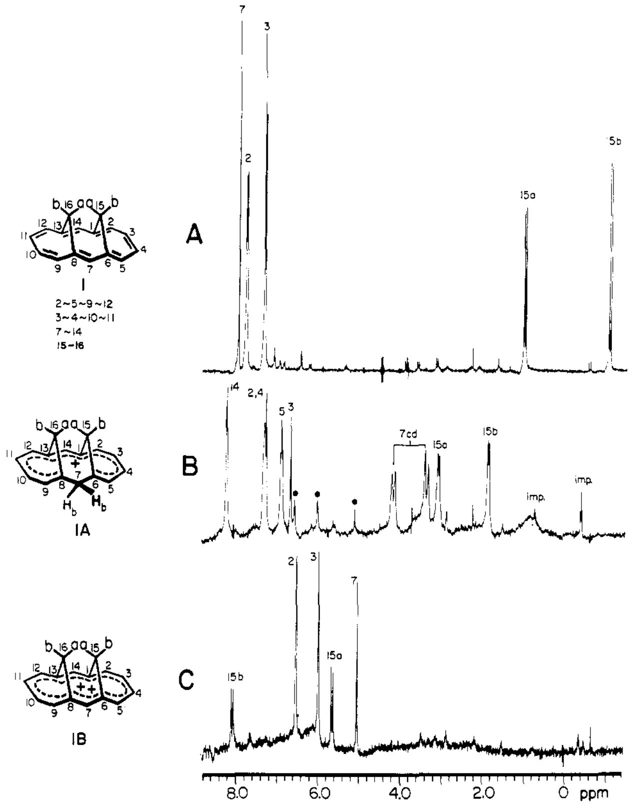

Figure 3. ^1H NMR spectra: (A) **1** in $CDCl_3$ at room temperature; (B) **1A** in superacid at −80 °C, traces of **1B** marked by black dots; (C) **2B** at room temperature.

1:6,8:13-Ethanediylidene[14]annulene (2). Figure 4A shows the spectra of the parent ethano-bridged hydrocarbon. A mixture of ions is initially produced in superacid solution at −80 °C. Over a period of 8 h the ^{13}C NMR spectrum changes until only 16 ^{13}C NMR resonances are observed (Figure 4B). An attempt to slow down the disappearance of the species responsible for the initially present additional resonances by performing the experiment at −100 °C was unsuccessful. In general, it proved to be considerably more difficult to generate high concentrations of ions from **2** than from the other annulenes. The ^1H NMR spectra for the parent and the species identified as **2A** are shown in Figure 5 (cf. Table I). The green solution of the ion **2A** turns opaque brown upon prolonged standing at low temperatures or warming to room temperature. This change is accompanied by the production of polymeric materials.

When **2** is dissolved in a mixture of CF_3COOD and $CDCl_3$ (1:1), the aromatic protons are exchanged by deuterons at different relative rates ($2 > 3 \gg 7$), but this time the ^1H NMR spectra of the aliphatic protons are affected as well and their resonances broaden dramatically. Overall, the rate of deuterium incorporation is slower than was the case for **3**. Removal of the acid causes the original sharp singlet for the bridgehead protons to reappear, showing no evidence of deuterium incorporation at the bridge positions. If the experiment is repeated with CF_3COOH, the signals of the aliphatic protons again broaden, and some changes in the aromatic region are observed as well (Figure 6). In particular, the multiplet labeled 2,3 loses

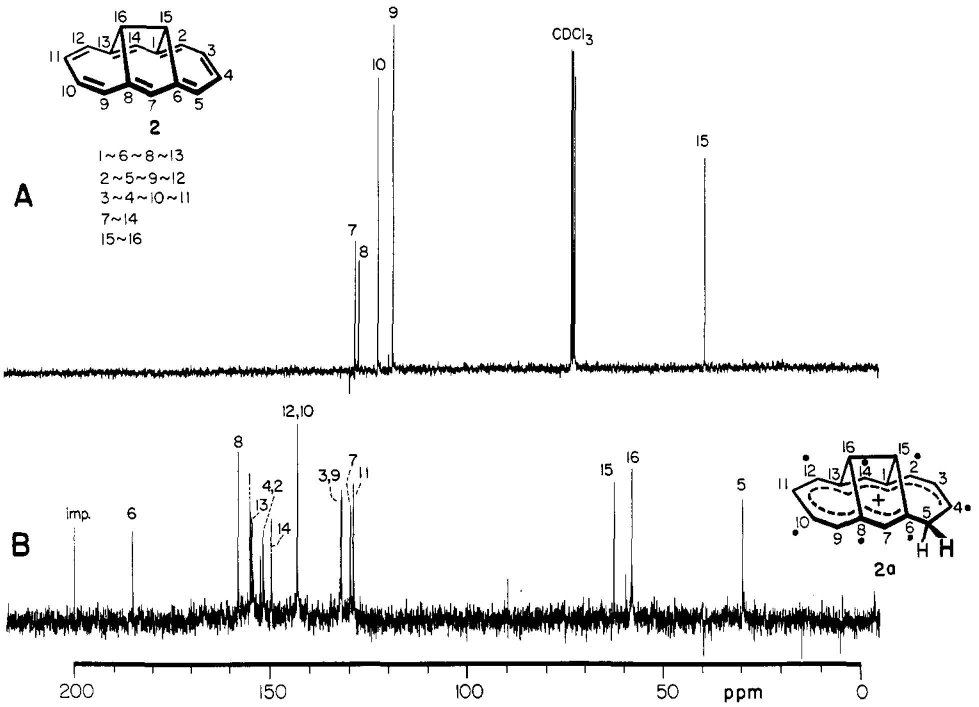

Figure 4. ^{13}C NMR spectra: (A) **2** in $CDCl_3$ at room temperature; (B) **2A** at -80 °C in superacid solution.

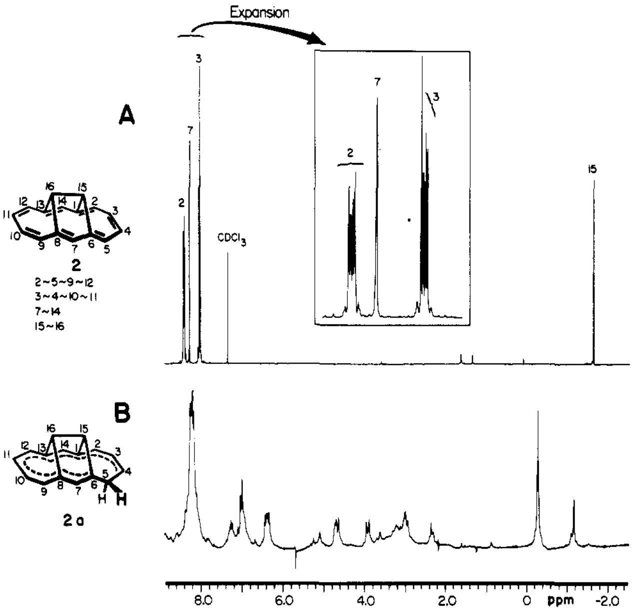

Figure 5. ^1H NMR spectra: (A) **2** in $CDCl_3$ at room temperature; (B) **2A** at -80 °C in superacid solution.

some of its structure. No changes are observed in the ^{13}C NMR spectra under these conditions, either decoupled or coupled.

Discussion

1,6:8,13-Propanediylidene[14]annulene (3). The NMR properties of this annulene have already been described.[10a] The ten ^{13}C resonances of the form **3A** present in a solution in a superacid at -80 °C appear both upfield and downfield of the signals observed in the spectrum of **3** (Figure 1A). The coupled ^{13}C spectrum (not shown) shows two singlets (6, 1) in the aromatic region, indicating two sets of quaternary carbon atoms. Two triplets for methylene carbons (16, 7) are observed in the aliphatic region. Due to limited resolution, it is not clear whether this is due to pairs of isochronous protons or to sets of protons with similar coupling constants. The other resonance in the aliphatic region in Figure 2C is a doublet from carbon 15. These results are consistent with symmetrical ion structure **3A** whose site of protonation is carbon 7 (Figure 1B). The chemical shifts of the ring carbons are quite similar to those of the anthracenium cation.[10b]

The ^1H NMR spectrum is in agreement with the structure **3A**. Note in particular the two pairs of doublets observed for the hydrogens on methylene carbons 7 and 16 (Figure 2). The chemical shifts of the bridgehead protons (16, 15) experience a substantial increase in δ relative to their positions in **3** since the diamagnetic ring current is interrupted by protonation. At the same time, the aromatic protons are not shifted very far upfield, presumably due to the positive charge on the ring. The selective decoupling experiments confirm the assignments shown in Figures 1 and 2. Given the fact that the skeleton of the annulene remains intact on protonation as shown by the quenching experiment, the only structure that is consistent with the NMR data is the symmetrical structure **3A**.

It is noteworthy that the rate of deuterium exchange at positions 7 and 14 is quite slow relative to the other ring positions. Yet, protonation at these positions yields the apparently thermodynamically most stable ion **3A**. This can be understood if the removal of the endo proton from carbon 7 of the protonated form **3A** by a base is far slower than the removal of the exo proton.

The symmetrical ion **3B** is the dication of **3**. The ^{13}C NMR data agree with the chemical shifts of the dication generated previously in SbF_5/FSO_2Cl mixtures[4] and the five-line ^1H NMR spectrum is consistent with this structure as well. The dication is a 12-electron system; the paratropic character of **3B** and other 4N-electron [14]-

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Table I. NMR Data for Bridged Annulenes[a]

no.	^{13}C	(C–H)	mult	^1H	(H–H)
1					
1	101.3		s		
2	133.2	(157.5)	d	7.80	
3	122.8	(154.7)	d	7.35	
7	129.5	(154.3)	d	8.00	
15	21.7	(247.8)	t	0.85	(12.5)
				inner	
				−1.05	(14.6)
				outer	
1a					
1	113.6		s		
2	151.3	(167.6)	d	7.36	
3	132.0	(158.9)	d	6.74	
4	165.0	(174.3)	d	7.36	
5	127.8	(170.2)	d	7.00	
6	165.6		s		
7	51.3	(130.2)	t	3.75[g]	(23.0)[e]
14	185.5	(161.7)	d	8.32	
15	33.9	(143.6)	t	3.13	(11.0)
				inner	
				1.92	(11.0)
				outer	
1b[f]					
1	137.5		s		
2	165.5	(166.0)	d	6.76	
3	144.6	(178.6)	d	6.21	
7	159.9	(161.7)	d	5.26	
15	30.7	(147.0)	t	5.86	(15.0)
				inner	
				8.32	(15.0)
				outer	
2					
1	131.5		s		
2	122.8	(149.1)	d	8.35	
3	126.5	(152.8)	d	7.97	
7	132.4	(158.9)	d	8.17	
15	43.0	(144.2)	d	−1.72	
2A[d]					
1	154.8		s		
2	151.5	(155.2)	d		
3	131.8	(158.9)	d		
4	149.6	(153.3)	d		
5	28.8	(139.2)	t		
6	185.5		s		
7	129.5	(163.6)	d		
8	157.9		s		
9	131.8	(158.9)	d		
10	149.6	(153.3)	d		
11	128.7	(164.6)	d		
12	151.5	(155.2)	d		
13	154.4		s		
14	142.9	(154.7)	d		
15	57.3	(126.6)	d		
16	61.9	(146.3)	d		
3					
1	112.0		s		
2	127.6	(160.5)	d	7.81	
3	130.0	(156.1)	d	7.61	
7	127.1	(156.1)	d	7.94	
15	29.0	(140.6)	t	−1.10	
16	19.0	(132.2)	t	−0.55	
3A					
1	123.0		s		
2	156.2	(116.7)	d	7.34	
3	133.7	(143.7)	d	6.61	
4	170.3	(116.7)	d	7.34	
5	135.1	(126.6)	d	7.03	
6	174.4		s		
7	50.5	(119.5)	t	3.80[e]	
14	187.2		d	8.21	
15	41.1	(143.5)	d	2.01	
16	22.7	(133.5)	t	0.78[e]	
3B					
1	143.2		s		
2	175.4	(171.6)	d	6.47	
3	153.7	(173.0)	d	5.66	
7	157.4	(177.5)	d	4.70	
15	45.1	(147.7)	d	7.88	
16	35.1	(137.8)	t	4.87	
4[c]					
1	111.9				
2	135.5	7.57			
3	126.3	7.12			
7	134.6	7.86			
15	35.3	−0.96			
16	24.0	0.52			
4A					
1	124.0				
2	154.0	7.45			
3	132.2	6.84			
4	168.2	7.45			
5	136.4	7.00			
6	174.1				
7	53.5	2.70			
14	187.5	8.36			
15	49.1	1.36			
16	25.0	−0.24			
4B					
1	145.1				
2	147.5	5.12			
3	145.1	6.10			
7	167.0	6.65			
15	44.2	6.44			
16	27.3	3.78			

[a] Ions **1A**–**4A** in superacid solution at −80 °C; ions **1B**–**4B** at room temperature. Chemical shifts in ppm relative to external TMS. 1–4 in $CDCl_3$ at room temperature, internal TMS. All coupling constants in hertz. [b] Due to the small amount of material on hand, it was not possible to obtain a coupled spectrum. [c] Values taken from Günther, H.; Schmickler, H. *Pure Appl. Chem.* **1975**, *44*, 807; and ref 4. [d] Proton spectrum unassigned. [e] Doublet of doublets. [f] The difference in chemical shift between **1B** and **3B** and those of ref 4 are attributed to temperature and solvent effects. [g] Center of doublets.

annulene derivatives is discussed by the authors of ref 4.

1,6:8,13-Butanediylidene[14]annulene (4). Comparison of the decoupled ^{13}C NMR spectra of **3A** and **4A** (Table I) shows that the chemical shifts for the two sets of ten resonances are nearly identical. A similar correspondence is seen in the ^1H NMR spectra with appreciable differences found only for the methylene protons on the bridge (16) and the protonated ring carbon (7). The spectral data for **3B** and **4B** are also very similar. Thus it appears that the site of protonation for the butano-bridged annulene is also the central carbon (7) and that the stable symmetrical cation produced (Figure 4B) is slowly oxidized at low temperatures to a dication in which the original skeleton of the annulene remains intact.

Bismethano[14]annulene (1). Structurally and spectroscopically 1 is very similar to **3**.[11] Thus it might be anticipated at first sight that it too would protonate at carbon 7 to give a symmetrical cation. This is indeed the case.

The ^{13}C NMR spectrum of **1A** is not as straightforward as that of **3A** due to the accidental equivalence of some of the resonances. The ^1H NMR spectrum is more obvious with the familiar AB quartet for the methylene ring protons and the upfield pair of doublets from the inner and outer bridge protons assigned as they were for 1. Ion **1B**

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[11] Vogel, E. *Isr. J. Chem.* **1980**, *20*, 215.

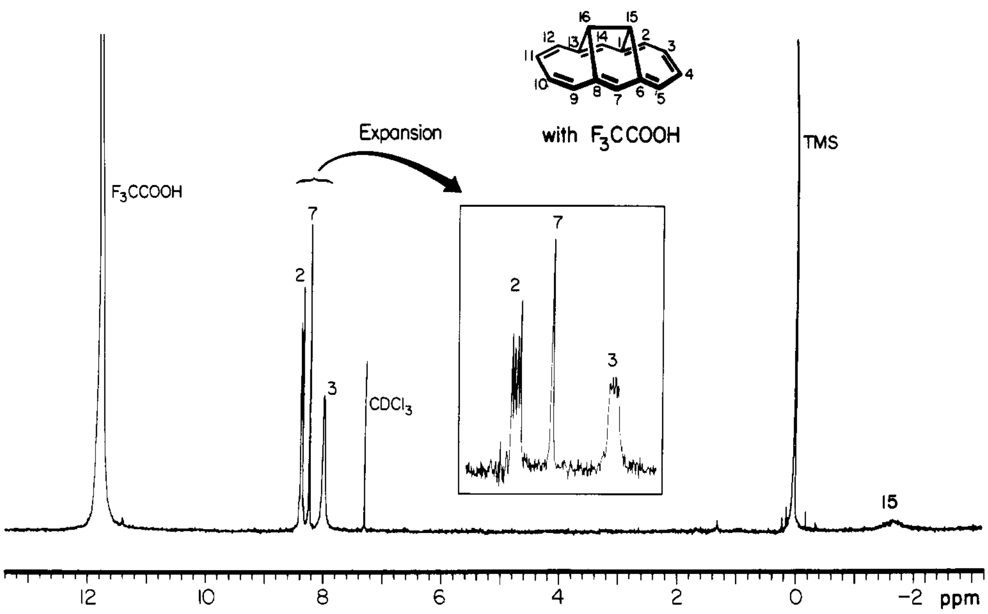

Figure 6. ^{1}H NMR spectrum of **2** in CF_3COOH–$CDCl_3$ 1:1 at room temperature.

gives the simple ^{13}C and ^{1}H NMR spectra expected of the dication. The ^{1}H NMR spectrum is particularly easy to assign, since the two sets of bridge protons still show geminal coupling (Figure 3C).

That **1** behaves in a fashion quite identical with that of **3** and **4** is actually more surprising than might appear at first sight. It is known that **1** reacts with electrophiles, such as Br_2, to give addition rather than substitution products.[12] Furthermore, it might be anticipated that the absence of connectivity between the bridging carbons would make the cation prone to rearrangements similar to those observed for methano[10]annulene where warming to temperatures above −60 °C results in the formation of protonated dications and cyclopropylcarbinyl cations.[13] This is not observed for **1** and monoprotonation cleanly gives the ion **1A**, which at higher temperatures converts into the dication **1B**.

1,6:8,13-Ethanediylidene[14]annulene (2). The behavior of this annulene in superacid media contrasts markedly with those of **1**, **3**, and **4**. Rather than cleanly producing a single symmetrical monoprotonated ion as anticipated, protonation yields a mixture of relatively short-lived species. All of these species except **2A** disappear in a matter of hours at −80 °C (Figure 4B). In view of the large downfield shifts of some of the resonances, it may be that some of these species are doubly protonated dications. Unfortunately, it was difficult to generate sufficient concentrations of these cations for ^{13}C NMR spectroscopy. The concentration of **2A** was never as large as the concentrations of the cations **1A**, **3A**, and **4A**, even after the resonances from the other species disappeared. This may be due to the fact that the unstable ions yield polymeric decomposition products and do not rearrange to the ion **2A**.

There are 14 ^{13}C NMR resonances for **2A** (Figure 4B). In the upfield region three signals are observed, one that is a triplet and two that are doublets in the C–H coupled spectrum. The ^{13}C NMR data are consistent with an unsymmetrical ion structure in which the site of protonation is either carbon 2 or 3. The two missing resonances then would be due to the accidental equivalence of two pairs of aromatic carbons. This spectrum is tentatively assigned in Table I.

The ^{1}H NMR spectrum is considerably more complicated than those of the other annulenes. One feature that stands out clearly is a pair of doublets at 4.2 ppm, apparently due to the protonated ring carbon. As before, the bridgehead resonances are shifted downfield when compared to the parent, but they no longer appear as a sharp singlet. This is consistent with an unsymmetrical structure.

It is not apparent whether the site of protonation is at the 2 or 3 position. On the basis of the relative rates of deuterium exchange, protonation at 2 seems more likely.

The behavior of **2** is also different in that it does not convert cleanly into the dication but rather decomposes at higher temperatures (above −20 °C) into uncharacterized mixtures. No evidence for a stable dication was obtained.

The reasons for the difference in behavior between **2** and the other annulenes can be rationalized in terms of different degrees of transannular interactions.

(i) Site of Protonation. Geometrically the perimeter of **2** is the least disturbed (the most planar)[5] of the compounds studied, with the π-type p AO's at the bridgehead carbons overlapping the least in transannular fashion. Its electronic spectra also show the smallest contribution from transannular interactions between the bridgehead carbons.[3a]

In an ideal [14]annulene of D_{14h} symmetry, the HOMO would be degenerate. Introduction of transannular interaction in the bridged annulenes stabilizes the member of the degenerate pair of MO's that has a node through atoms 7 and 14 and has little effect on the other, which has large coefficients there. The inductive effect of the bridge is just the opposite and destabilizes the orbital with a node through atoms 7 and 14. The ESR spectrum of the radical cation of **3** indeed shows high spin density in these positions,[2a] as does the radical cation of anthracene. Clearly, the effect of transannular interaction is strong and dictates the orbital ordering. To the contrary, the ESR spectrum of the radical cation of **2** shows that the HOMO of **2** has a node at carbons 7 and 14.[2a] Now, transannular interaction is weaker and the ordering of the orbitals is dictated by other factors such as the inductive effect.

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[12] Vogel, E.; Böhm, S.; Hedwig, A.; Hergarten, B. O.; Lex, J.; Uschmann, J.; Glieter, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1000.

[13] Kelly, D. P.; Leslie, D. R.; Smith, B. D. *J. Am. Chem. Soc.* **1984**, *106*, 687. Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 4528.

Clearly species **2** is the least "homoaromatic" or "anthracene-like" and the most "annulene-like".

The fact that carbon 7 is the thermodynamically favored protonation site in **3** but not in **2** follows the same pattern and agrees with simple frontier MO theory considerations. Most likely, in **2** the increased strain in the central ring caused by protonation at positions 7 or 14 is not compensated by transannular stabilization as it is in the case of cation **3**. Thus in superacid media the most stable species from **2** is the unsymmetrical ion protonated at carbon 2.

Although these considerations are consistent with the observation that overall **3** is deuteriated somewhat faster than **2** in weaker acids (CF_3COOD) and that position 7 in **2** is more resistant to deuterium exchange than the corresponding position in **3**, the fact that carbon 7 is kinetically the least reactive site for exchange in both **2** and **3** makes it clear that an interpretation of the exchange rates is impossible without a consideration of the relative kinetic acidities of the exo and the endo protons, in the protonated form.

(ii) Failure To Form a Dication. In the series of dianions generated from **2**, **3**, and **4**, the paratropism is observed to decrease[4] as the annulene rings become less planar and the transannular interaction increases. As these 4N-electron species are gradually transformed from "annulene-like" to "homoaromatic", or "anthracene-like", their antiaromaticity decreases. In keeping with the preceding discussion, the more strongly antiaromatic dication of **2** would be expected to be less stable and more strongly paratropic than the dications of **3** and **4**. It is tempting to attribute the failure of the ion **2B** to form to its more annulene-like nature, although the explanation may also simply be that a facile rearrangement route is available to the monocation **2A** but not to **1A**, **3A**, and **4A**, preempting the oxidation to the dication.

(iii) Broadening of the Aliphatic ^{1}H NMR Signals in CF_3COOH. Both **2** and **3** show exchange broadening in the aromatic region of the ^{1}H NMR spectrum in CF_3COOH, attributed to the reversible protonation of the ring. The mechanism of the protonation and the small effects it has on the line widths of the aromatic proton signals are not understood in detail.

The aliphatic protons of **3** are unaffected by this exchange process while the bridgehead protons of **2** broaden dramatically (compare Figures 5a and 6) in spite of the fact that the net exchange is proceeding at comparable rates for both. The ^{13}C NMR spectra show no change in either system. This rules out electron exchange of the type seen for octamethylbiphenylene in the same solvent system.[14] It is known[2a] that the hyperfine coupling of the bridgehead protons in the radical cation of **2** is much larger than in that of **3**. This is understood in terms of the better overlap of the bridgehead π-p AO's with the aliphatic C–H bond in the former. A similar hyperconjugative interaction in our diamagnetic protonated cations **2A** and **3A** would account for a chemical shift perturbation of hydrogen 15 in **2**, not seen in **3**. An analogous change in chemical shift should result from the interruption of the ring current by protonation. This, however, would be expected to occur in both **2** and **3**, and this is not observed.

In summary, the factors responsible for the differences in the spectral properties of **1**, the bridged annulenes **1A**–**4A**, and dications **1B**, **3B**, and **4B**, primarily varying degrees of transannular interaction, can also be invoked to rationalize the thermodynamics of the protonation behavior of **1**–**4**. However, additional factors, such as steric hindrance to deprotonation, dictate the deuterium exchange rates in these annulenes.

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Synthesis of *exo*-Bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic Anhydrides by Thermal Isomerization of *trans*-Diacids

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Bicyclo[2.2.2]oct-5-ene-*trans*-1,2-dicarboxylic acid and substituted analogues afford mixtures of the corresponding *exo*- and *endo*-anhydrides upon heating at 250–300 °C. This isomerization provides a practical pathway to substituted and deuterium-labeled *exo*-anhydrides which are otherwise difficult to obtain. A mechanistic study shows that retro-diene fragmentation is not involved in the isomerization.

Introduction

The Diels-Alder addition shows normally a great preference for the formation of adducts with an endo configuration.[1] In numerous cases the endo adducts are the exclusive products of the reaction. Alternative routes have to be developed in order to prepare the exo isomers.[2-5]

In the case of the adducts of cyclopentadiene and maleic anhydride **1**, the exo isomer is easily obtained by heating the original *endo*-anhydride at 190 °C.[6] Careful thermodynamic and isotope labeling studies[7,8] have shown that

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