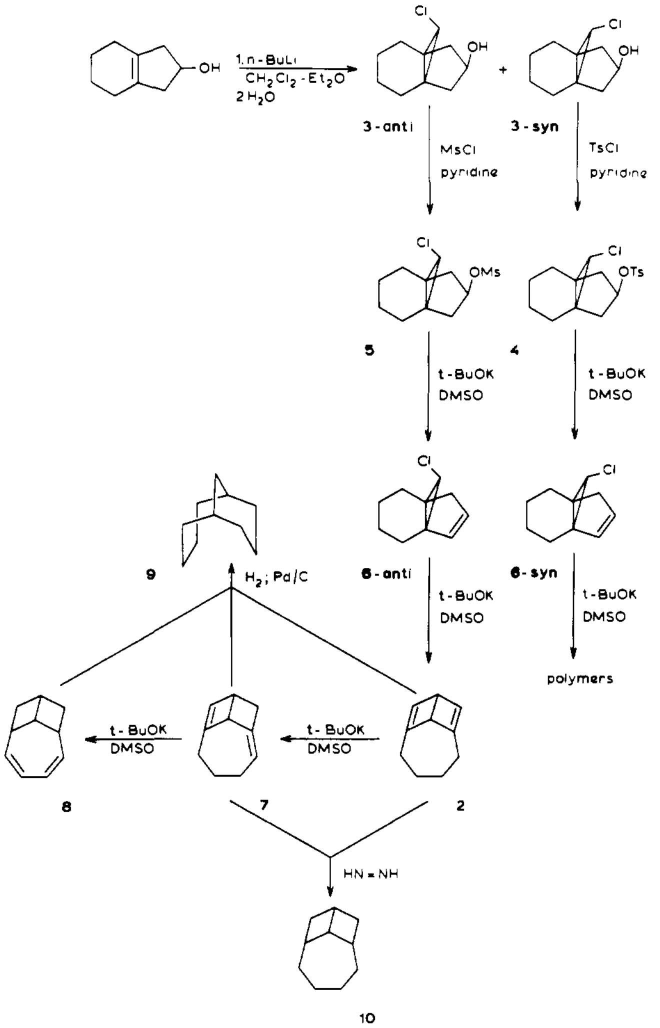
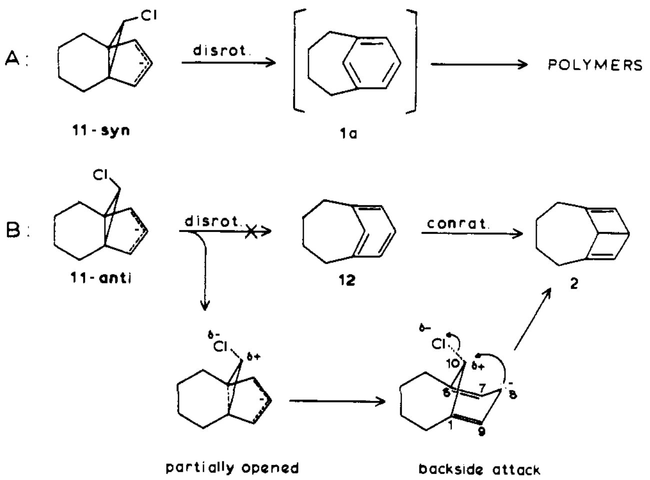
Scheme I



Scheme II



corresponding anions, **11**-syn and **11**-anti, respectively (Scheme II). **11**-syn might yield **1a** by loss of chloride ion in a symmetry-allowed disrotatory opening of the cyclopropane ring, unless strain in **1a** is prohibitive; it is feasible that either instability of **1a** or escape reactions are responsible for the observed formation of polymers. An analogous course of reaction is less probable for **11**-anti, as it would furnish the highly strained *trans*-benzene **12**; in principle, the latter could lead to **2** in a thermally allowed conrotatory process. It seems more likely that, while chloride ion is beginning to leave and the cyclopropane ring is partially opening, the developing negative charge at C(8) of the pentadienyl anion furnishes nucleophilic assistance toward C(10), while C(8) and C(10) move toward each other, thus establishing the central bond of the Dewar benzene. Alternative routes are conceivable and cannot be excluded; however, carbene formation, initiated by proton abstraction at C(10), is less likely in view of the difference in behavior between **6**-syn and **6**-anti. Isolation of **2** and **7** by preparative gas chromatography and separate treatment of both isomers with *t*-BuOK in Me_2SO proved that **2** rearranges to **7** and **7** to **8**. This may be explained by a sequence of deprotonations and reprotonations in allylic positions, leading consecutively to less strained isomers. While **7** is the result of one such sequence of reactions from **2**, it is remarkable that no further intermediates between **7** and **8** could be detected.

Acknowledgment. We thank Dr. D. Schipper for recording the ^{13}C NMR spectra and assistance in the interpretation.

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(7) Tricyclo[6.1.1.$0^{3,9}$]deca-2,8(10)-diene (**2**): ^1H NMR ($CDCl_3$, δ in ppm) 6.27 (m, 2 H), 3.82 (m, 1 H), 3.71 (m, 1 H), 2.28 (m, 4 H), 1.78 (m, 4 H); ^{13}C NMR ($CDCl_3$, δ in ppm) 164.6 (s, $C_{3,8}$), 137.9 (d, $C_{2,10}$), 56.4 (d, C_9), 44.6 (d, C_1), 31.6 (t, $C_{4,7}$), 28.3 (t, $C_{5,6}$); MS *m/z* (% fragment) 132 (22, $C_{10}H_{12}^{+}\cdot$) (found 132.0936, $C_{10}H_{12}$ calcd 132.0939), 91 (100, $C_7H_7^{+}\cdot$); UV (cyclohexane) 242 nm (sh), end absorption. Tricyclo[6.1.1.$0^{3,9}$]deca-2,7-diene (**7**): ^1H NMR ($CDCl_3$) 5.59 (d of d, $J = 2$, 1.5 Hz, 1 H), 5.49 (m, 1 H), 3.83 (m, 1 H), 3.05 (d of d of d, $J = 7.5$, 2, 1.5 Hz, 1 H), 2.9–1.9 (m, 6 H), 1.85–1.45 (m, 2 H); ^{13}C NMR ($CDCl_3$) 157.6 (s, C_3), 147.1 (s, C_8), 126.8 (d, $J = 172$ Hz, C_2), 126.0 (d, $J = 154$ Hz, C_7), 54.5 (d, $J = 156$ Hz, C_9), 35.4 (d, $J = 154$ Hz, C_1), 31.8 and 31.2 (d, $J = 124$ Hz, C_4 and C_8), 30.2 (t, $J = 136$ Hz, C_{10}), 27.3 (t, $J = 126$ Hz, C_5); MS 132 (46, $C_{10}H_{12}^{+}\cdot$) (found 132.0936, $C_{10}H_{12}$ calcd 132.0939), 117 (100, $C_9H_9^{+}\cdot$); UV (cyclohexane) 229 nm (sh), end absorption. Tricyclo[6.1.1.$0^{3,9}$]deca-4,6-diene (**8**): ^1H NMR ($CDCl_3$) 5.85 (m, 4 H), 3.41 (m, 2 H), 2.55 (m, 4 H), 2.10 (m, 2 H); ^{13}C NMR ($CDCl_3$) 137.3 (d, $C_{4,7}$), 124.6 (d, $C_{5,6}$), 46.4 (d, C_9), 38.4 (d, $C_{3,8}$), 34.2 (t, $C_{2,10}$), 28.6 (d, C_1); MS 132 (65, $C_{10}H_{12}^{+}\cdot$) (found 132.0939, $C_{10}H_{12}$ calcd 132.0939), 104 (100, $C_8H_8^{+}\cdot$); UV (cyclohexane) 265 nm.
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(9) Tricyclo[6.1.1.$0^{3,9}$]decane (**10**): ^1H NMR ($CDCl_3$) 1.3–2.1 (m, 10 H), 2.3–3.1 (m, 6 H); ^{13}C NMR ($CDCl_3$) 41.9 (d, $J = 140$ Hz, C(9) or C(1)), 36.0 (d, $J = 136$ Hz, $C_{3,8}$), 34.8 (t, $J = 133$ Hz, $C_{2,10}$), 31.4 (t, $J = 124$ Hz, $C_{4,7}$), 29.6 (d, $J = 150$ Hz, C(1) or C(9)), 26.4 (t, $J = 126$ Hz, $C_{5,6}$); MS 136 (2, $C_{10}H_{16}^{+}\cdot$) (found 136.1249, $C_{10}H_{18}$ calcd 136.1252), 95 (100, $C_7H_{11}^{+}\cdot$).

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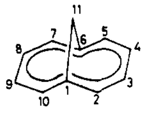
Aromatic Protonation. 5.[1]
Diprotonated 1,6-Methano[10]annulene. NMR Evidence for a Cyclopropyldicarbinyl Dication Moiety

Sir:

Recently we reported on the high reactivity of the 1,6-methano[10]annulene system (**1**)[2] toward sulfonation.[3] For a better understanding of the electrophilic aromatic substitution of **1**[4] and in relation to our recent interest in arenium ions,[5] we were inspired to investigate the protonation of **1**. Winstein et al., already a decade ago, described the monoprotonation of **1** by FSO_3H yielding the stable cation **2**, the structure of



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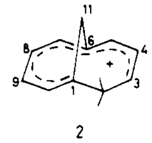

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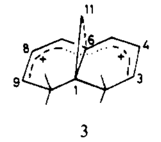

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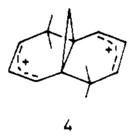
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Table I. ^1H and ^{13}C NMR Parameters of **3**[a]

	δ						
	1	**2** (= **10**)	**3** (= **9**)	**4** (= **8**)	**5** (= **7**)	**6**	**11**
^1H		2.78 and 3.79 (AB pattern, 23)	8.36 (m)	7.65 (t, ≈6)	8.84 (d, 6)		4.02 (s)
^{13}C	29.6 (s)	37.2 (t, 133)	172.6 (d, 173)	133.7 (d, 174.5)	176.4 (d, 167)	140.2 (s)	72.4 (t, 159)

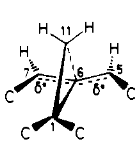
[a] ^1H and ^{13}C chemical shifts are in parts per million from external Me_4Si (capillary). Multiplicities and coupling constants (J_{HH} and J_{CH} in hertz) are in parentheses. Multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet.

which was soundly characterized by ^1H NMR.[6] We now report on the diprotonation of **1** in "magic acid" with formation of the stable dication **3** containing the so far unknown cyclopropyldicarbinyl dicationic type of moiety (**5**), which has the two allyl cations bound to the same carbon of the cyclopropane ring.

Addition of **1** in SO_2ClF to a solution of FSO_3H-SbF_5 (1:1 molar ratio) in SO_2ClF (1:1 v/v) at ca. −120 °C in an NMR tube and subsequent heating to −60 °C resulted in a dark red solution of **3**.[7,9] Quenching of the ion solution by pouring it into sodium bicarbonate buffered methanol at −78 °C resulted in the recovery of **1** (70–75%), demonstrating that the annulene skeleton remains intact and that no rearrangement has occurred.

The ^1H and ^{13}C NMR spectra of ion **3** are shown in Figure 1 and the chemical shifts and coupling constants with the assignments are compiled in Table I. The equal intensities of the singlet absorption of the two bridge hydrogens (δ 4.02) and the three "aromatic" absorptions in the ^1H NMR spectrum are in agreement with both the structures **3** and **4**;[10] the presence of a total of seven ^{13}C absorptions confirms the C_s symmetry of **3** and rules out structure **4**.[10] Evidence for the dicationic nature of **3** comes further from a comparison of the sum of the ^{13}C chemical shifts of all of the carbons of species **3** (1282.0 ppm) and of the hydrocarbon obtained by addition of two hydride ions to **3** at the positions 5 and 7 (678.3 ppm[12]). According to Schleyer et al., the per charge effects are very characteristic and for carbomonocations the difference is ~350 ppm.[13] The present difference of 603.7 ppm then suggests[13] a dicationic species.

Remarkable is the large spread in the C(1), C(6), and C(11) chemical shifts of **3**, e.g., $\delta_{C(6)} - \delta_{C(1)} = 110.6$ ppm.[14] The high field resonance of C(1) at 29.6 ppm infers that (ring) contraction between C(1) and C(6) has taken place upon forming **3** from **1**. To explain the very low field absorption of C(6), and also of C(11), a recent theoretical study by Hehre et al.[15] on the cyclopropylcarbinyl cation[16] is instructive. They showed that there is a second minimum on the potential energy surface, only 0.5 kcal mol^{-1} higher in energy than the bisected ion. The geometry of that minimum (shown as **6**) is defined by (i) all



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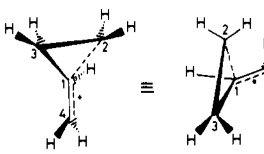


6

of the six atoms C(4) H_2, C(1) H, and C(3) are in one plane, (ii) the C(1)–C(2) bond is weakened, (iii) the C(1)–C(3) linkage is strengthened, and (iv) the C(1)–C(4) linkage possesses double-bond character.[15]

Extrapolation to **3** seems justified, since the eight atoms HC C(5), HC C(7), C(6), and C(1) of **5** are more or less in one plane, although now two allyl cationic centers are substituted at C(6). This would infer that (i) the C(6)–C(11) linkage is considerably lengthened, (ii) the C(1)–C(6) bond is shortened, and (iii) the C(5)–C(6) and C(7)–C(6) linkages have some double-bond character, illustrating homoconjugation between the two allyl cationic moieties via the cyclopropane. Evidence

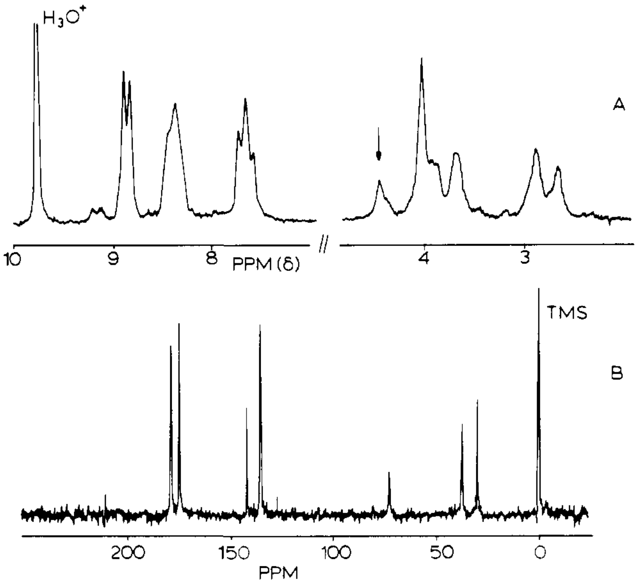
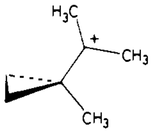


Figure 1. (A) ^1H NMR (100 MHz) spectrum of **3** in FSO_3H-SbF_5-SO_2ClF at −60 °C. The arrow indicates an impurity; see note 14. (B) ^{13}C proton noise decoupled NMR spectrum of ion **3** in the same solvent system.

in favor of this interpretation are the very deshielded resonances of C(6) and C(11) at 140.2 and 72.4 ppm, respectively. Further evidence supporting the proposed structure of moiety **5** comes from the $J_{^{13}CH}$ of the bridge methano group $H_2C(11)$. This coupling constant for **3** (159 Hz) is significantly larger than that for **2** (148 Hz[6]), indicating an enhanced cyclopropyl character in **3**. The value is smaller than that of the cyclopropyl CH_2 groups of, e.g., the bisected ions **7** (174.9 Hz[17]) and **8** (174.3 Hz[18]), indicating that one of the cyclopropyl bonds in **3** is relatively weakened.



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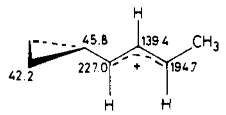

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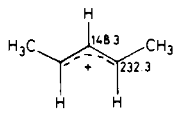
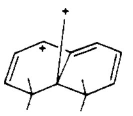


9

The C(3), C(5), C(7), and C(9) absorptions of **3** are strongly shielded relative to the corresponding carbons of the cations **8**[18] and **9**.[19] This is taken to indicate that the cyclopropyl ring participates in stabilizing the positive charge. This view is supported by the very low field ^1H NMR absorption of the bridge hydrogens (δ 4.02) which are deshielded relative to the two nonequivalent bridge hydrogens of **2** by 1.80 and 2.44 ppm. The difference in chemical shift between the two methylene hydrogens at C(2) of **3** (AB pattern, Δδ = 102 Hz) is very large and significantly greater than that found for **2** (Δδ = 56 Hz[6]); furthermore, these hydrogens are more shielded in **3** than **2**. These phenomena may be related to the anisotropy of the cyclopropyl ring.[20]

The preference for the formation of **3** rather than **4** may be explained in terms of the cyclopropane enhanced homoconjugation between the two allyl cationic centers in **3**. The conjugation between the allyl cations in **4** will be very poor, since the transmission of conjugation between two substituents via a cyclopropane bond is known to be very small.[21] The greater stability of **3** compared with **4** also follows from a comparison of the extreme resonance structures **10** and **11** in which the



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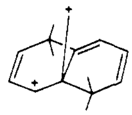

11

C(6)–C(11) bond is broken. The stabilizing contribution of **11** to **4** will be far less than that of **10** to **3** in view of the stronger inductive repulsion between the two charges with **11** (via two σ bonds) than **10** (via three σ bonds), the direct field effect in both structures being the same.

Carbodications were reported very recently, but only as transient intermediates, e.g., the Wheland intermediates for the H–D exchange of an aromatic cyclopropenium ion[22] and monoprotonated 3-hydroxyphenalenone[23] or as species containing conjugative stabilizing electron-donating oxygen substituents, like the protonated 2,2′,2″,6,6′,6″-hexamethoxytrityl cation[23] and diprotonated 3-hydroxyphenalenone.[24] The present dication **3** is the first reported stable dication which is devoid of this type of electron-donating heteroatom substituents.

In conclusion evidence is presented that the 1,1-diallylcyclopropane moiety of the dication **3** has the allylcyclopropane elements in fixed geometries comparable with that calculated for conformation **6** of the cyclopropylcarbinyl monocation. Further and more detailed work on the protonation of annulenes is currently in progress.

Acknowledgment. We thank Professor E. Vogel (Cologne) for stimulating our present investigations, Professor J. W. Verhoeven for stimulating discussions, and Mr. C. Kruk for assistence in obtaining the NMR spectra.

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(8) The ^{13}C NMR data of **2** will be reported in the full paper.
(9) At temperatures >−60 °C an additional monocation is observed, owing to a rearrangement of **2** (see also ref 6). This rearrangement will be the subject of a forthcoming report.
(10) These four ^{1}H NMR absorptions are also in accordance with the C_2 symmetry of **4,** the structure of which would compare with the structures of the dications of hexa- and octamethylnaphthalene.[11] However, for that ion the ^{13}C NMR spectrum should display six instead of the observed seven absorptions.
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(14) For comparison the ^{13}C chemical shifts of C(1), C(6), and C(11) of the monocation **2** are 148.3, 127.8, and 40.8 ppm, respectively.
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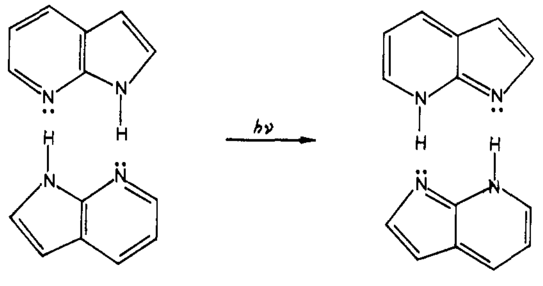
Lack of Tunneling in the Excited-State Double Proton Transfer of 7-Azaindole Dimer?

Sir:

Hydrogen-bonded dimers of 7-azaindole (7-AI) undergo a photoinduced double proton transfer. The tautomeric form (T), stable in the excited state only, exhibits green, excimer-like fluorescence (F_2), red shifted by 10 000 cm^{-1} relative to the normal violet fluorescence (F_1). The dynamics of the cooperative two-proton transfer have been intensively studied.[1-5] Two mechanisms have been proposed. The first one is a thermal process where the two protons move over the energy barrier from high vibrational levels, populated according to a Boltzmann distribution. The second, a tunneling mechanism, has been postulated in order to explain the cooperative proton transfer (green fluorescence) observed at low temperatures, down to 4 K. Our results show that a tunneling mechanism is not necessary to account for the observed experimental effects.



D T

Few data have been published concerning the triplet-state spectroscopy of 7-AI.[1] It is well known that the reactivities, especially acid-base properties, of molecules in the triplet state differ from those in the excited singlet state.[6] Moreover, the geometry of the triplet excimer formed from naphthalene was shown to be completely different from that in the fluorescent state.[7] The main task of our work was to find evidence for the existence of a tautomeric form of the dimer in the triplet state. By studying the phosphorescence and triplet ESR spectra we hoped to provide additional information on the mechanism for the cooperative two-proton transfer.

The procedure for measuring of luminescence and triplet ESR spectra were described elsewhere.[8] In the ESR measurements the triplet state was populated by continuous irradiation with a HBO-200 high pressure Hg lamp filtered through 5 cm of H_2O and a UG 11 Iena glass filter, containing mainly 313- and 302-nm Hg line groups. Concentrated solutions (10^{-3}–10^{-2}M) of 7-AI have been used. Relatively strong ESR signals were observed in alcohols and in aqueous-alcoholic solutions where the dimerization does not occur. In 3-methylpentane (3-MP) solutions where the dimerization is very efficient[3] the $\Delta m = \pm 1$ signals were extremely weak; only "$\Delta m = \pm 2$" transitions could be measured. The zero-field splitting (ZFS) parameters remained constant upon changing solvents and concentrations (see Table I). Our attempt to find