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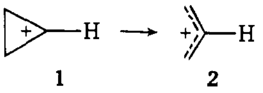
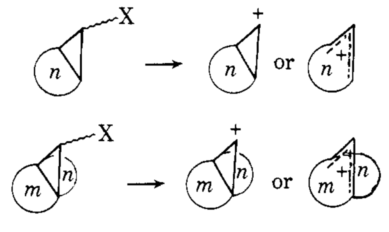
11-Methyl-11-tricyclo[4.4.1.0^{1,6}]undecyl Cation. First Long-Lived, Distinct Cyclopropyl Cation Showing Significant 2π-Homoaromatic Nature[1]

Sir:

The direct observation of the cyclopropyl cation **1** thus far has evaded all attempts owing to its facile ring opening to the energetically more favorable allyl cation **2**.[2] The former has been shown to be some 39 kcal/mol higher in energy than the latter, and the rearrangement takes place with little or no energy barrier.[3]



Evidence has been presented for the intermediacy of cyclopropyl cations under solvolytic conditions in geometrically constrained bicyclic and tricyclic systems where the cyclopropyl ring is "locked in" so that the ring-opening process is forbidden or at least is minimized.[4,5] In the solvolytic reactions, indeed, the unrearranged cyclopropyl products were obtained with retention of configuration. According to an interpretation first advanced by Schleyer and Schöllkopf, the intermediate carbocationic species in such reactions are partially opened ("half-opened" cyclopropyl cations).[3a,4] We wish to report now the direct observation under stable ion conditions of the first stable, distinct cyclopropyl cation showing significant 2π-homoaromatic nature.



The highly strained 11-methyl-11-bromotricyclo[4.4.1.0^{1,6}]undecane **3**[5,6] in surfuryl chloride fluoride (SO_2ClF) solution at −60 °C displays in the ^{1}H NMR spectrum (60 MHz, Figure 1a) a methyl singlet at δ 1.83 and methylene multiplets at 1.2–1.8. When this solution is slowly added into a well-stirred solution of antimony pentafluoride (SbF_5) in SO_2ClF at −120 °C, a light yellow solution is obtained which is stable up to −60 °C.[7] The 60-MHz ^{1}H NMR spectrum (Figure 1b) of the solution at −90 °C displays three proton resonances centered at δ 3.18 (m, 4 H), 3.03 (s, 3 H), and 1.90 (m, 4 H). The substantial deshielding of both the methyl and methylene protons points to the formation of a discrete carbocation **4**.

The ^{1}H NMR spectrum of **4** seems to indicate the symmetrical nature of the ion. The proton-decoupled ^{13}C NMR spectrum (Figure 1c) of the ion obtained at −90 °C, however, shows *seven* carbon resonances. According to the off-resonance ^{13}C NMR spectrum, the two most deshielded resonances at $\delta_{^{13}C}$ 210.0 and 168.5 (from external TMS) are singlets, which

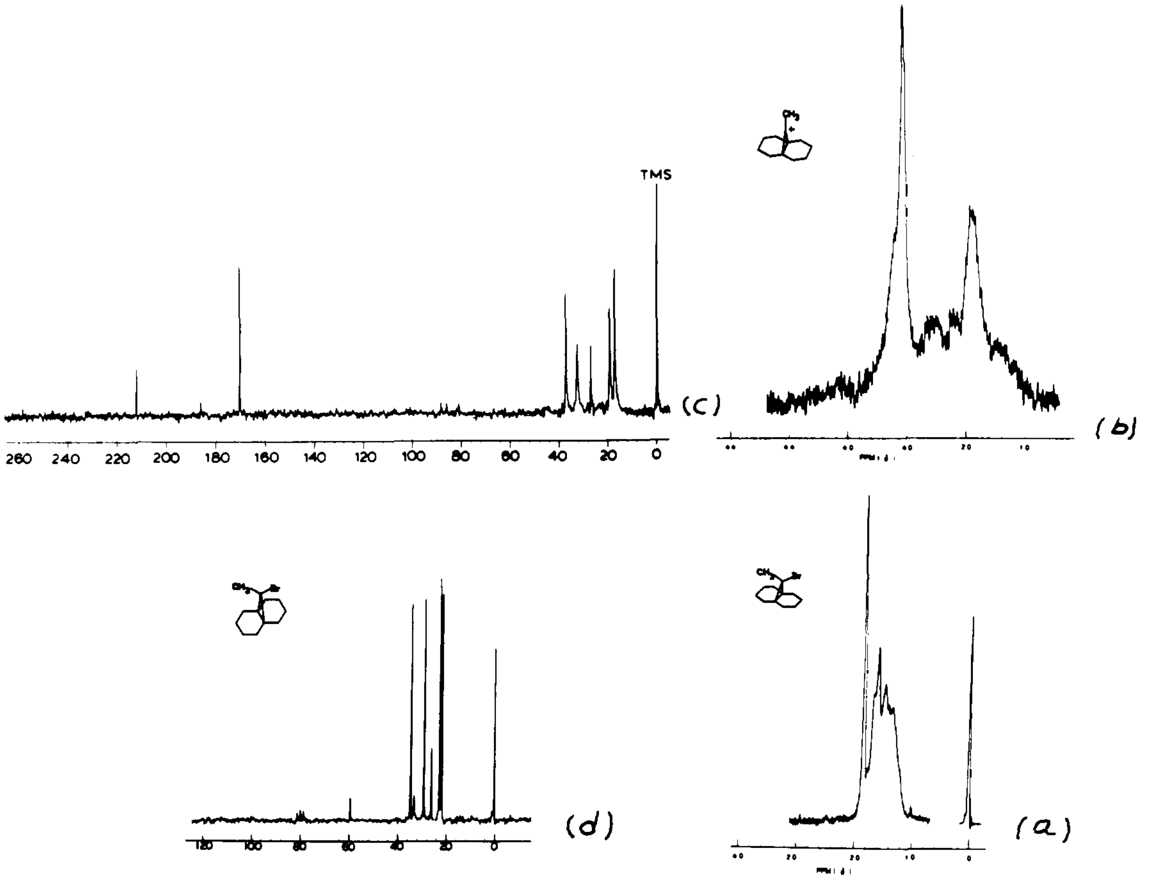
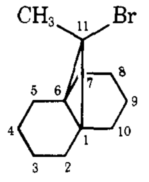
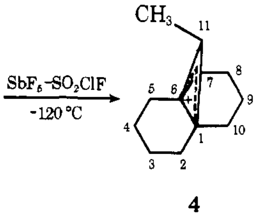


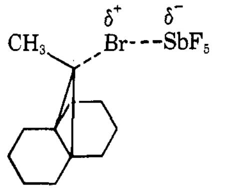
Figure 1. (a) 60-MHz ^{1}H NMR spectrum of **3** in SO_2ClF at −60 °C; (b) 60-MHz ^{1}H NMR spectrum of **4** in SbF_5-SO_2ClF at −90 °C; (c) proton decoupled ^{13}C NMR spectrum of **4**; (d) proton decoupled ^{13}C NMR spectrum of **3**.



3

Position	δ^1H	$\delta^{13}C$
1,6		32.6 (s)
2,5/7,10	1.2	28.7, 34.0
3,4/8,9	1.8	22.4, 21.5
11		58.5 (s)
CH_3	1.83	25.7 (q)



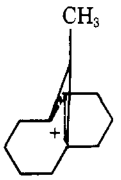


4 **5**

δ^1H	$\delta^{13}C$
	168.5 (s)
3.18	36.9, 32.4
1.90	19.2, 17.1
	210.0 (s)
3.03	26.8 (q)

are assigned to C_{11}, and C_1 and C_6, respectively. The methyl quartet is found at $\delta_{^{13}C}$ 26.8. The additional four carbon resonances are all triplets corresponding to four sets of methylene carbons. The precursor bromide **3** also shows seven carbon resonances in its ^{13}C NMR spectrum (Figure 1d). The ^{13}C NMR spectra of **3** in SO_2ClF and its ion **4** in SbF_5-SO_2ClF solution closely resemble each other except that both cyclopropane ring carbons of the latter are substantially deshielded, 150 ppm for C_{11} and 135 ppm for both C_1 and C_6. These deshieldings are too large for a polarized donor-accepter complex **5**,[8] and thus further indicate ionization of the bromide precursor. Both the ^1H and ^{13}C NMR spectra of **3** in SbF_5-SO_2ClF solution are in accord with development of a carbocationic center at C_{11} and substantial charged nature of C_1 and C_6.

Although the observed ^1H NMR spectrum of ion **4** could be in accord with a symmetrical ion, the ^{13}C NMR spectra, nevertheless, clearly show the ion to be unsymmetrical. Owing to the rigidity of the molecular framework, an open symmetrical allylic cation such as **6** is highly unlikely since it must have the central C_1-C_6 bent cyclopropane σ bond perpendicular to the developing p orbital at the electron-deficient C_{11}. Neither is the carbon deshielding pattern compatible with that of a typical allylic cation.[9] A "perpendicular" allyl cation **7** is also ruled out by the ^{13}C NMR data. The unsymmetrical nature of the NMR spectra also eliminates the possibility of a planar, symmetrical cyclopropyl cation **8** in which the methyl group lies in the plane of the cyclopropane ring; both **6** and **8** should only give *five*, instead of *seven* carbon resonances. The unchanged methyl quartet in the off-resonance ^{13}C NMR spectrum of the ion also excludes a cyclopropylcarbinyl type cation **9**, which could arise from a hydrogen shift, i.e., of **8** → **9**. A "bent" cyclopropyl cation **4** is the only structure which reasonably accounts for all the experimental data.



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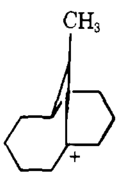

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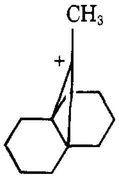

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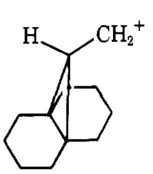
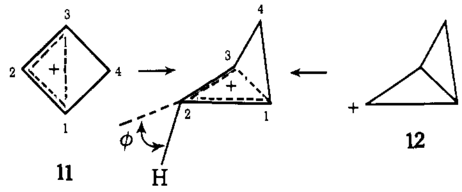


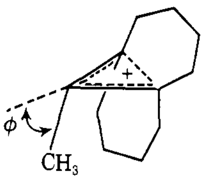
9

The direct observation of ion **4** is of particular interest in that it clearly does not involve a significantly opened cyclopropane ring which could lead to the formation of an allytic cation. Thus it must be considered as a bent, distinct cyclopropyl cation.[3a,4] It is, however, clear that the C_1-C_6 σ bond must have somewhat mixed itself into the "empty" p orbital at C_{11} that "homoconjugation" between them becomes the important factor in stabilizing such a "bent" cyclopropyl species.

The substantial deshielding at both C_1, C_6, and C_{11} undoubtly shows that the positive charge has been delocalized in some manner over all these three positions. The previously reported significant 1,3 interaction in the cyclobutenyl cation causes it to bend out of plane and become a stable 2π-aromatic system, the "nonplanar" homocyclopropenyl cation **10**.[10] Ion **10** can be characterized as an energy minimum between the two extreme cases, i.e., the *planar* cyclobutenyl cation **11** and the bent bicyclo[1.1.0]butyl cation **12**.[11] In the calculations by hehre and Devaquet[12] and Jorgensen[13] on the homocyclopropenyl cation **10**, the hydrogen at C_2 is found to be below and bent out of the plane by 5.2-8.7°. The 1,3 overlap, which significantly stabilizes the nonplanar cyclobutenyl cation **10**, could be the cause for the asymmetry of the ion **4** as the two terminal cyclohexyl ring must be both twisted out of the plane in a disrotatory manner. C_2 and C_5 (α carbons) are thus becoming stereochemically different from C_7 and C_{10}, and C_3 and C_4 (β carbons) are different from C_8 and C_9. Furthermore, the methyl group at C_{11} in ion **4** is probably also bent out of the plane of cyclopropane ring, thus accounting for the unsymmetrical nature of **4**.[3,4] The great propensity for overlap between the electron-deficient center C_{11} and the C_1-C_6 σ bond in **4** can similarly be significant and result in the 2π-homoaromatic nature of **4**. In **10** both the C_1 and C_3 atoms are less deshielded than C_2 owing to significant 1,3 overlap. In **4**, C_{11} is more deshielded than C_1 and C_6, but, when corrected for the methyl substituent effect and the obviously more strained nature of the tricyclic system, the difference may be small. The ring-flipping process of **10** has been found to involve a barrier of 8.4 kcal/mol, and that for **4** could be considerably higher owing to its geometrical rigidity, accounting for the observed unsymmetrical nature of the ion.[14] Nevertheless, charge delocalization into the cyclopropane ring makes ion **4** of a 2π-homoaromatic nature.



11 **10** **12**



4

In conclusion, we feel that ion **4** is best described as a distinct, "bent" cyclopropyl cation. This conclusion is further supported by Ledlie's recent observation that silver assisted methanolysis of the corresponding tertiary bromide gave no ring opened products.[14]

Acknowledgment. Support of our work by the National Science Foundation and the University of Vermont is gratefully acknowledged, as are stimulating discussions with Professors Colin Reese and Paul v. R. Schleyer.

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(6) The tertiary bromide **3** was prepared from the corresponding dibromide and *n*-butyllithium in the presence of methyl iodide at low temperature.

(7) Above −60 °C, the ion slowly rearranged into a unidentified species which shows the following NMR spectrum: ^{1}H, δ 3.06, 2.12, 1.91, 1.82; ^{13}C, $\delta_{^{13}C}$ 257.3 (s), 89.4, 86.5, 81.8, 45.7, 39.9, 25.0, 24.0, 22.2, 18.1. The structure of this ion is under further investigation.

(8) The possibility of complex **5** seems to be small since we were not able to observe any fluorine resonance corresponding to the structure.

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(14) Evidence for a distinct cyclopropyl cation has also been given by D. B. Ledlie, W. Barber, and F. Switzer, *Tetrahedron Lett.*, 607 (1977), in the solvolysis of epimeric 11-methyltricyclo[4.4.1.0^{1,6}]undecen-3-yl 11-bromides. The bent conformation for the cyclopropyl cation in the presently studied system seems to be due not only to the highly energetic ring opening but also to the stability gained by introducing the methyl substituent at C_{11}.[2,3]

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Equilibrium Isotope Effects on the Proton Transfer Reactions of Methylbenzenes

Sir:

It has recently been reported[1] that the proton transfer equilibrium between an alkylbenzene and its analogue for which the side chain is deuterated

$$C_6H_n(R_D)_{(6\text{-}n)}H^+ + C_6H_n(R_H)_{(6\text{-}n)} \rightleftarrows C_6H_n(R_D)_{(6\text{-}n)} + C_6H_n(R_H)_{(6\text{-}n)}H^+ \quad (1)$$

favors the formation of the nondeuterated protonated alkylbenzene. Values of $\Delta G°$ at 300 K ranging from −0.175 ± 0.053 kcal/mol for

$$1,3,5\text{-}C_6H_3(CD_3)_3H^+ + 1,3,5\text{-}C_6H_3(CH_3)_3 \rightleftarrows 1,3,5\text{-}C_6H_3(CD_3)_3 + 1,3,5\text{-}C_6H_3(CH_3)_3H^+ \quad (2)$$

to −0.328 ± 0.040 kcal/mol for

$$CD_3C_6H_5H^+ + CH_3C_6H_5 \rightleftarrows CD_3C_6H_5 + CH_3C_6H_5H^+ \quad (3)$$

were derived from the equilibrium constants

$$-RT \ln K_{eq} = \Delta G°$$

observed in isotopic analogue mixtures of toluenes, xylenes, and mesitylene in a pulsed ion cyclotron resonance spectrometer. The existence of such large isotope effects on the heats of formation of protonated alkylbenzenes was interpreted as evidence for hyperconjugative stabilization of the protonated alkylbenzenes.[1]

In the course of an investigation in this laboratory of proton transfer equilibria, results have been obtained which indicate that, contrary to the result reported by Hehre et al.,[1] the proton affinity of $C_6H_5CD_3$ is, within experimental error, the same as that of $C_6H_5CH_3$. This conclusion was derived from experiments performed in the NBS pulsed ion cyclotron resonance spectrometer[2] in which the equilibrium constants were measured[3] for the proton transfer equilibria between propionaldehyde and the two toluenes

$$C_2H_5CHOH^+ + CH_3C_6H_5 \rightleftarrows C_2H_5CHO + CH_3C_6H_5H^+ \qquad \Delta G°_{300} = -0.43 \pm 0.05 \text{ kcal/mol} \quad (4)$$

$$C_2H_5CHOH^+ + CD_3C_6H_5 \rightleftarrows C_2H_5CHO + CD_3C_6H_5H^+ \qquad \Delta G°_{300} = -0.44 \pm 0.05 \text{ kcal/mol} \quad (5)$$

as well as the corresponding equilibria involving methyl formate

$$CH_3OCHOH^+ + CH_3C_6H_5 \rightleftarrows CH_3OCHO + CH_3C_6H_5H^+ \qquad \Delta G°_{300} = -0.77 \pm 0.05 \text{ kcal/mol} \quad (6)$$

$$CH_3OCHOH^+ + CD_3C_6H_5 \rightleftarrows CH_3OCHO + CD_3C_6H_5H^+ \qquad \Delta G°_{300} = -0.79 \pm 0.05 \text{ kcal/mol} \quad (7)$$

(where 1 kcal/mol = 4.18 kJ = 0.043 eV). These results imply that the value of $\Delta G°_{300}$ for reaction 3 is 0.00 ± 0.05 kcal/mol. (In calculating these equilibrium constants, the abundances of the two protonated toluene ions were corrected for the presence of ^{13}C-labeled parent toluene ions, but the abundance of $CD_3C_6H_5H^+$ was not corrected for the estimated 1 at. % insufficient deuteration of the $CD_3C_6H_5$.[4]) In the earlier investigation,[1] equilibrium 3 was observed in a mixture of $CD_3C_6H_5$ with $CH_3C_6H_5$ using AsH_4^+ as a proton donor in the system. This experiment could not be duplicated to give a meaningful result because the $C_7H_5D_2^+$ ion which is formed in $C_7H_5D_3$ has the same mass as $CH_3C_6H_5H^+$.

Because of the discrepancy between the results reported by Hehre et al.[1] and those implied by the measured free energy changes for equilibria 4 through 7, a careful determination was made of the equilibrium constant for the proton transfer between p-xylene and p-xylene-d_6

$$p\text{-}(CD_3)_2C_6H_4H^+ + p\text{-}(CH_3)_2C_6H_4 \rightleftarrows p\text{-}(CD_3)_2C_6H_4 + p\text{-}(CH_3)_2C_6H_4H^+ \quad (8)$$

where K_{eq} in the discussion which follows is defined as

$$K_{eq} = \frac{[p\text{-}(CH_3)_2C_6H_4H^+]}{[p\text{-}(CD_3)_2C_6H_4H^+]}\ \frac{[p\text{-}(CD_3)_2C_6H_4]}{[p\text{-}(CH_3)_2C_6H_4]}$$

In order to accurately determine this equilibrium constant, three different p-$(CD_3)_2C_6H_4$-p-$(CH_3)_2C_6H_4$ mixtures of