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THE TROPYLIUM ION ANNELATED WITH BICYCLO[2.1.1]HEX-2-ENE: STABILIZATION DUE TO σ-π CONJUGATION VERSUS DESTABILIZATION DUE TO MILLS-NIXON TYPE π-BOND LOCALIZATION

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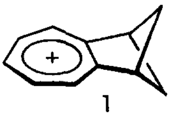
Summary: In the tropylium ion annelated with bicyclo[2.1.1]hex-2-ene, stabilization due to the σ-π conjugation of tropylium p-orbitals with the highly strained bicyclic σ-framework was shown to be more effective than destabilization due to the Mills-Nixon type π-bond localization.

It is generally accepted that the carbocation is stabilized by σ-conjugation with highly strained substituents having large p-character. Thus, the highly strained bicyclo[2.1.1]hex-2-ene unit[1] is expected to stabilize the tropylium ring in the title cation **1** by effective σ-π conjugation. At the same time, this bicyclic system may bring about severe angular strain and the resultant partial π-bond localization, known as the Mills-Nixon effect,[2] into the annelated aromatic ring. In order to clarify which of these opposing effects is dominant, we have synthesized the cation **1** and examined its properties in comparison with the structurally related cations, **2**,[3] **3**,[4] **4**,[3] and **5**.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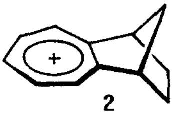
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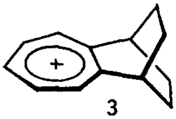
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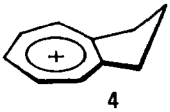
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5

The precursors for **1** and **5**, i.e. benzobicyclo[2.1.1]hex-2-ene (**6**) and 3-phenylcyclobutene (**7**), were prepared by the reaction of bicyclobutane with benzyne,[5] and were separated by HPLC (hexane/μ-porasil). In a Cu(I) catalyzed reaction of **6** with CH_2N_2, the bicyclo[2.1.1]hexene unit was found to remain intact, and only the benzene moiety was enlarged to the cycloheptatriene. The crude product was then treated with $Ph_3C^+SbF_6^-$ to give $\mathbf{1}\cdot SbF_6^-$ [6] (83% yield based on consumed **6**). Similarly, $\mathbf{5}\cdot SbF_6^-$ [7] was synthesized from **7** after catalytic hydrogenation.

As is shown schematically in Figure, the ^{13}C NMR signals for C-1 and C-3 are shifted upfield while those for C-2 and C-4 are shifted downfield as the ring strain in the bicyclic system increases in the order **3**, **2**, and **1**. Although the chemical shift behaviors observed for C-3 and C-4 may be partly ascribed to the Streitwieser-Finnegan rehybridization effect,[3] the chemical shifts for C-1 and C-2, which are remote from the annelated carbons, are supposed to reflect directly the differences in charge densities caused by the Mills-Nixon type bond alternation. This is also supported by the results of INDO MO calculations for the cation **1** (charge density for C-1, +0.0662; C-2, +0.1135; C-3, +0.0546; C-4, +0.1089).

On the other hand, the value of the bridgehead ^{13}C-H coupling constant, known to be proportional to the s-character, increases in the order **3** (141.6 Hz), **2** (151.6 Hz), and **1** (164.5 Hz), suggesting that the p-character in the bicyclic σ-framework correspondingly increases to make the σ-π conjugation quite effective in the cation **1**.

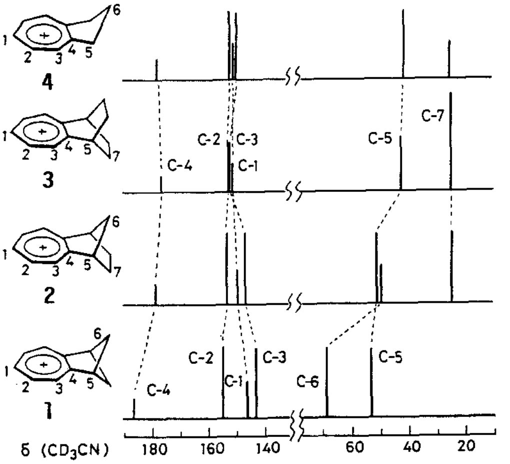

Figure ^{13}C NMR data for the cations **1**~**4**

Table pK_{R^+} and Reduction Potential Data

Cation	pK_{R^+} a) 50% aq. MeCN	Reduction Pot'l b) V vs Ag/Ag^+
1	5.10	-0.710
2	7.80 (4.08) c)	-0.762
3	7.80 (8.82) d)	-0.765
4	3.9-4.7e) (4.15) c)	-0.707
5	4.43	-0.603

a) Determined spectrophotometrically at 25°C; accuracy, ±0.05. b) CV peak potential in MeCN with 0.1M TBAP; scan rate, 0.1V/s. c) In H_2O; Ref. 3. d) In 20%MeCN; Ref. 4. e) Low accuracy due to poor reversibility upon neutralization.

As for the thermodynamic stability, the values of pK_{R^+}[8] and reduction potential (Table) reveal that, although the cation **1** is less stable than the cations **2** and **3**, it is slightly more stabilized than the cation **4**, which can be regarded as the lower homologue of **1** with one of the methylene bridges removed and the severe strain energy released to effect the good positive-charge delocalization. Thus, the cationic destabilization in **1** due to the π-bond localization is actually surmounted by the stabilization gained by the σ-π conjugation between the tropylium 2p orbitals and the bicyclo[2.1.1]hex-2-ene σ-framework.

In an earlier mechanistic study directed to the quantitative estimation of the σ-π conjugation in the bicyclo[2.1.1]hex-2-yl cation, it was shown that the S_N1 acetolysis rate for 5,5-dimethylbicyclo[2.1.1]hexyl-2β tosylate is enhanced by an anchimeric assistance and is comparable to that for cyclopentyl tosylate despite the severe angle strain.[9] It is noteworthy that the similar results are obtained for these two totally different cationic systems, i.e. a stable Hückeloid system and a solvolytic intermediate.

Finally, the cyclobutyltropylium ion (**5**) exhibits the pK_{R^+} and reduction potential data (Table) typical for a monoalkyl-substituted tropylium ion (for example, compare with t-butyltropylium ion; pK_{R^+} 4.57; E_{red} -0.61 V vs Ag/Ag^+).[10] No σ-conjugative stabilization such as observed for the cyclopropyltropylium ion (5.76; -0.64 V)[10] seems to be present in the cation **5**.

References and Notes:

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4. T. Nakazawa, Y. Niimoto, K. Kubo, and I. Murata, *Angew. Chem.*, 92, 566 (1980).
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6. Mp 147-148°C (dec); satisfactory C,H analyses; λ_{max} (MeCN) 239 nm (log ε 4.49), 281 (3.49), 296 (3.42), 323 (3.37); δ_H (CD_3CN) (300MHz) 8.88 (d, 2H), 8.80 (t, 2H), 8.68 (t, 1H), 3.79 (t, 2H), 3.23 (m, 2H), 3.06 (dd, 2H); δ_C (CD_3CN) 186.8 (s), 154.8 (d), 146.6 (d), 143.5 (d), 69.0 (t), 53.7 (d).
7. Mp 93-96°C (dec); satisfactory C,H analyses; λ_{max} (MeCN) 224 nm (log ε 4.20), 304 (3.60); δ_H (CD_3CN) (300MHz) 9.02 (s, 6H), 4.30 (m, 1H), 2.67 (m, 2H), 2.41 (m, 2H), 2.21 (m, 2H); δ_C (CD_3CN) 180.2 (s), 153.9 (d), 153.7 (d, 2 peaks), 46.1 (d), 30.9 (t), 18.5 (t).
8. The pK_{R^+} data for **2** and **4** differ from the reported values determined by potentiometric titration (Ref. 3). The data obtained by the spectrophotometric method in the present study seem to be more reliable since the actual equilibrium can be directly observed by this method.
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