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Enhanced Polarization of Heptafulvene and Tropone by Annelation with Three Bicyclo[2.2.2]octene Frameworks

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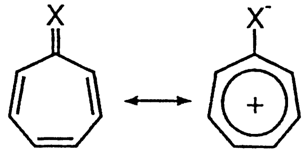
The heptafulvene and tropone annelated with three bicyclo[2.2.2]octene frameworks (**4**(X=CH_2,O)) were synthesized as stable crystals, and were found to be more polarized than the corresponding parent compounds. Accordingly, the basicity of **4**(X=O) is increased as was shown by the enhanced pK_a of the conjugate acid **3**(R=OH) by 2.1-2.5 pK units. The results of dynamic NMR as well as molecular mechanics calculations indicate that **4**(X=CH_2) exists in a boat form while **4**(X=O) is nearly planar.

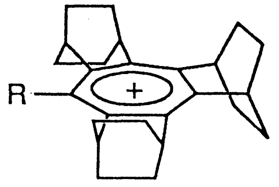
In the cross-conjugated cyclic π-systems such as heptafulvene (**1**(X=CH_2))$^{1)}$ and tropone (**1**(X=O)),$^{2)}$ it is known that contribution of the polarized form (**2**) is not as large as first expected. In the case of **1**(X=CH_2), replacement of hydrogens of the exocyclic methylene by electron withdrawing groups greatly stabilizes the polarized form,$^{3)}$ whereas no example has been reported in which the polarized form is stabilized by structural modification of the seven-membered ring.$^{4)}$

Recently, we found that tris-annelation with bicyclo[2.2.2]octene frameworks in the tropylium ion **3**(R=H) greatly increases the thermodynamic stability of the cationic ring by both the inductive and $\sigma-\pi$ conjugative effects.$^{5)}$ The similar tris-annelation of **1** is then expected to stabilize the corresponding polarized structure. Here we report the syntheses and enhanced polarization of such annelated compounds **4**(X=CH_2, O$^{6)}$).

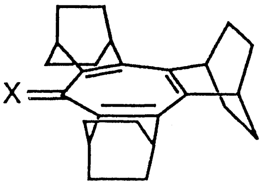
1,2:3,4:5,6-Tris(bicyclo[2.2.2]octeno)heptafulvene (**4**(X=CH_2))$^{7)}$ was obtained quantitatively as a stable yellow powder by deprotonation of the methyltropylium ion (**3**(R=CH_3))$^{5)}$ with Et_3N in CH_2Cl_2 and extraction with pentane. 2,3:4,5:6,7-Tris(bicyclo[2.2.2]octeno)tropone (**4**(X=O))$^{8)}$ was synthesized in 34% yield as stable white crystals by oxidizing the cycloheptatriene **5**$^{9)}$ with SeO_2 in 90% aqueous dioxane at 95 °C for 40 h.



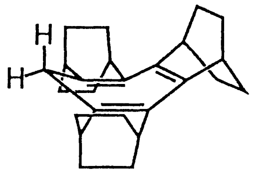
1 (X = CH_2, O) **2**



3 (R = H, CH_3, OH)



4 (X = CH_2, O)



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The ^{13}C NMR signals of sp^2 carbons carrying the bicyclo[2.2.2]octene frameworks exhibited general downfield shift in the order of **5** (δ ($CDCl_3$) 130.1, 133.0, 139.3),[9] **4**($X=CH_2$) (δ 136.7, 139.3, 140.8), and **4**(X=O) (δ 143.8, 148.0, 149.6), suggesting that the seven-membered ring acquires slight positive charge increasingly in this order. Furthermore, the signals for the carbons of the exocyclic double bond in **4**($X=CH_2$) (δ 149.3 (>C=), 107.0 ($=CH_2$)) are appreciably more separated than those of the parent heptafulvene (**1**($X=CH_2$); δ 146.6 (>C=), 111.9 ($=CH_2$)).[1c]

In good agreement with this, the IR stretching frequency for the exocyclic double bond of **4** ($X=CH_2$, ν(KBr) 1574; X=O, (CCl_4) 1558 cm^{-1}) was found to be lowered as compared with **1**($X=CH_2$, ν(CCl_4-CS_2) 1583;[1d] X=O, (CCl_4) 1597 cm^{-1} [10]), indicating larger contribution of the polarized form in **4** than in the parent compounds **1**.

Next, it seemed of interest to evaluate quantitatively the extent of this polarization, and the basicity measurement was carried out on **4**(X=O) for comparison with the parent compound (**1**(X=O)). Since the ^1H NMR spectrum of **4**(X=O) taken in CF_3CO_2D exhibited the signals (δ 1.56 (d, 12H), 2.16 (d, 12H), 4.06 (br. s, 4H), 4.17 (br. s, 2H)) with the chemical shifts comparable to those for the cation **3** (R=H; δ 1.44 (12H), 2.05 (12H), 3.56 (2H), 4.07 (2H), 4.13 (2H)),[5] and no spectral change was observed by further acidification with addition of CF_3SO_2H, **4**(X=O) is considered to be completely protonated to form the hydroxytropylium ion **3**(R=OH) in CF_3CO_2D. Similarly, the UV spectrum of **3**(R=OH) generated in CF_3CO_2H was essentially identical to the spectrum taken in 97% H_2SO_4, and is shown in Fig. 1 together with that of **4**(X=O) taken in EtOH. The UV spectral change from **4**(X=O) to **3**(R=OH) was followed by changing the acidity of the solvent according to the literature method,[11] and the pK_a of **3**(R=OH) was determined as 1.50(±0.2). This value is 2.1-2.5 pK units larger than that reported for the conjugate acid of **1**(X=O) (-0.60(±0.3),[12a] -1.02[12b]), clearly indicating the enhanced basicity of **4**(X=O).

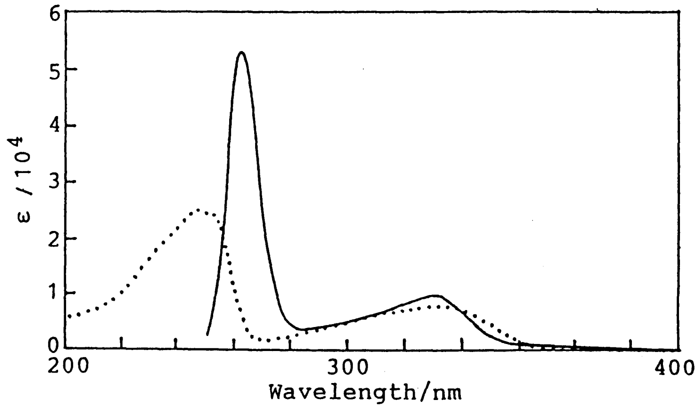

Fig. 1. UV spectra of **3**(R=O) in CF_3CO_2H (solid line) and **4**(X=O) in EtOH (dotted line).

The structure of **1**($X=CH_2$, O) has already been demonstrated to be planar by microwave spectroscopy on **1**($X=CH_2$)[13] or by X-ray crystallography on **1**(X=O).[14] In order to examine the planarity of the π-system in **4**($X=CH_2$, O), their ^{13}C NMR spectra were taken at low temperatures. The spectrum of **4**(X=O) exhibited no appreciable line broadening at the temperatures ranging from +20 °C down to -110 °C, supporting the presence of an essentially planar π-system. In contrast, signals for methylene carbons of bicyclo[2.2.2]octene frameworks in **4**($X=CH_2$) were found to split into three sets of doublet at a low temperature as shown in Fig. 2, indicating that **4**($X=CH_2$) exists in rapidly interconverting boat forms (Scheme 1). The activation energy for the ring inversion was determined by line shape analysis as 8.5 kcal·mol^{-1},[15] which coincides with the value previously determined for the cycloheptatriene **5** (8.5 kcal·mol^{-1})$^{9)}$ in spite of the steric hindrance by an exocyclic methylene group. The effect of such hindrance might have been canceled out by electronic stabilization of the essentially planar transition-state structure due to increased polarization.

Finally, molecular mechanics calculations (MMP2$^{16)}$) were carried out. The energy for the planar form of **4**(X=CH_2) was calculated to be 16.0 kcal·mol^{-1} higher than that for the boat form$^{17)}$ due to the increase in both the steric repulsion between the exocyclic methylene and bridgehead hydrogens and angle strain. In contrast, the optimized structure for **4**(X=O) was calculated as the boat form but its energy was only slightly (4.1 kcal·mol^{-1}) below that for the planar form.

In conclusion, the tris-annelation of **1**(X=CH_2, O) with bicyclo[2.2.2]octene units was shown to stabilize the polarized structure as expected, in spite of the steric disadvantage toward the planarity of the conjugated π-system.

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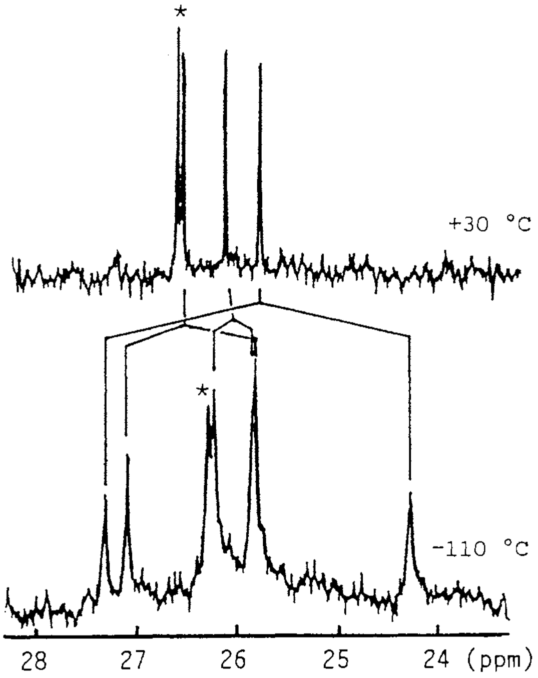
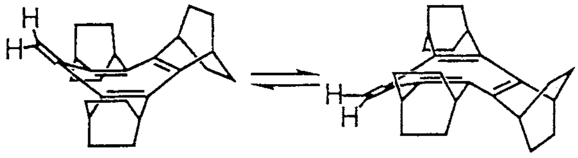


Fig. 2. ^{13}C NMR spectra (68 MHz) for methylene carbons of bicyclo[2.2.2]-octene frameworks of **4**(X=CH_2) in CD_2Cl_2:CS_2 = 1:1 (peaks marked with asterisks are of tris(bicyclo[2.2.2]-octeno)benzene as an impurity).



Scheme 1.

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7) **4**(X=CH_2): mp 129-131 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.33 (m, 12H), 1.58 (m, 12H), 2.76 (br. t, 2H), 2.89 (br. t, 4H), 4.67 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.6 (t), 26.0 (t), 26.5 (t), 31.7 (d), 31.8 (d), 37.4 (d), 107.0 (t, J_{CH} 156.3 Hz), 136.7 (s), 139.3 (s), 140.8 (s), 149.3 (s); IR (KBr) ν 3078, 2940, 2856, 1727, 1619, 1574, 1456, 1446, 1266, 1145, 847, 812, 749, 699 cm^{-1}; UV (cyclohexane) λ_{max} 224 (log ε 4.11), 250 (3.91, sh), 310 (3.74), 322 (3.67, sh); (MeCN) 224 (4.10), 249 (3.95, sh), 313 (3.75), 323 (3.70, sh) nm; HRMS (M^+, $C_{26}H_{32}$) calcd 344.2501, found 344.2483.

8) **4**(X=O): mp 253-255 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.35 (br. d, 12H), 1.72 (br. d, 12H), 3.40 (br. s, 2H), 3.41 (br. s, 2H), 3.84 (br. s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.17 (t), 25.20 (t), 25.4 (t), 30.8 (d), 32.3 (d), 32.8 (d), 143.8 (s), 148.0 (s), 149.6 (s), 183.1 (s); IR (KBr) ν 2940, 2860, 1584, 1556, 1450, 1350, 1148, 1025, 862, 817; (CCl_4) 2943, 2864, 1583, 1558, 1449, 1349, 1152, 1025 cm^{-1}; UV (MeCN) λ_{max} 247 (log ε 4.40), 253 (4.38, sh), 331 (3.91), 344(3.81); (EtOH) 248 (4.43), 254 (4.42, sh), 335 (4.00), 345 (3.98, sh); (CF_3CO_2H) 262 (4.72), 330 (4.00), (97% H_2SO_4) 262 (4.67), 317 (3.93, sh), 330 nm (3.97); HRMS (M^+, $C_{25}H_{30}O$) calcd 346.2295, found 346.2318.

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11) Ref. 12b. In order to increase the solubility, 10% EtOH (by vol.) was added. Acidity was measured by the use of a pH meter.

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15) Obtained by the method similar to that in Ref. 9. $\Delta G^{\ddagger}_{298K}$ = 10.1±0.2 kcal·mol^{-1}, $\Delta S^{\ddagger}$ = -7.5±3 cal·$mol^{-1}K^{-1}$. 1 cal = 4.184 J.

16) The MM2(87) program was obtained from QCPE, Indiana University.

17) The transition-state structure for the ring inversion of **4**(X=CH_2) was examined by changing two dihedral angles in the cycloheptatriene ring stepwise. The energy barrier for the ring inversion was calculated to be 14.8 kcal·mol^{-1}, which is 7.3 kcal·mol^{-1} larger than the experimentally obtained value. This discrepancy may be partly attributed to the tendency of the MMP2 calculations to underestimate the aromatic stability of the polarized form in the present system. Since the electronic effects of the σ-frameworks are not taken into account in the MMP2 calculations, the stabilization of the polarized form by the inductive and σ-π conjugative effects of the bicyclo[2.2.2]octene units might not be correctly evaluated.

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