

# Formation, Properties, and Reactions of the 1,2:3,4:5,6-Tris(bicyclo[2.2.2]octeno)tropylium Ion<sup>1</sup>

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**Abstract** The titled cation **4** has been synthesized and its properties and chemical reactivities investigated in detail. The cation **4** was shown to be formed in high yields not only by hydride abstraction from but also by the action of halogenoacetic acids upon the cycloheptatriene derivative **6**. Based on the results of UV-Vis and NMR spectroscopies together with iodometric analysis, this reaction was shown to proceed via protonation of **6** followed by dehydrogenation with molecular oxygen. The cation **4** was also shown to be formed by the action of rather weak Brønsted acids such as  $H_3PO_4$ ,  $H_2CO_3$ ,  $H_3BO_3$ ,  $C_6H_5OH$ , and  $CH_3NO_2$  upon the 7-methoxycycloheptatriene **10**. These facts are in agreement with the extraordinarily high thermodynamic stability of **4** as is shown by its  $pK_R^+$  value, 13.0 (50% aqueous  $CH_3CN$ , 25 °C). The cation **4** does not show any reactivity towards the nucleophiles with the  $pK_a$  of conjugate acid smaller than 10.3 except for the case of a slow reaction with  $CN^-$  ( $pK_a(NuH)$  9.21). Also **4** does not react with the carbanions  $R^-$  with  $pK_a(RH)$  below 8.3, such as the tris(7H-dibenzo[c,g]fluorenylidene)methyl methyl anion (Kuhn's anion,  $C_{67}H_{39}^-$ ) and the 9-cyanofluorenyl anion, and a new hydrocarbon salt,  $4 C_{67}H_{39}^-$ , was isolated. In contrast, the reaction of **4** with the carbanions  $R^-$  with  $pK_a(RH)$  larger than 11, such as dicyanomethyl,  $\alpha$ -cyano-*p*-nitrobenzyl, 1,1-dicyanoethyl, and dibenzo[c,g]fluorenyl anions, afforded the covalent compounds **4-R**. Whereas the compound **4-R** (as represented by the case of  $R$ =dibenzo[c,g]fluorenyl) only regenerated the cation **4** upon treatment with the trityl cation, the 7-methylcycloheptatriene **13** afforded the fully substituted cation **14**, which was found to be rather destabilized ( $pK_R^+ 12.4$ ) as compared with the hexasubstituted cation **4**.

It is of great importance in carbocation chemistry to pursue the highest thermodynamic stability for the carbocations having no conjugatively stabilizing hetero-atoms and clarify the mode of stabilization operating therein.

For cyclopropenyl cations, the  $\sigma$ -conjugation of cyclopropyl groups has been shown to be far more stabilizing than the inductive effect of simple alkyl groups,<sup>2</sup> which in turn was known to be more stabilizing than  $\pi$ -conjugation with phenyl groups.<sup>3</sup> In the tropylium ion series, the same order of substituent effects holds, but the stabilization by cyclopropyl groups met with limitation due to the saturation effect.<sup>4</sup> Apparently, the requirement for the cyclopropyl group to assume the bisected conformation decreases as the cation becomes more stabilized by higher substitution.

These observations led us to examine the effect of annelation of the tropylium ion with a bicyclo[2.1.1]hexene unit as in the cation **2**, whose  $\sigma$ -framework is strained similarly to a cyclopropyl group and yet rigidly fixed to the cationic  $\pi$ -system. The expected  $\sigma$ - $\pi$  conjugation with the tropylium ring, however, was opposed by destabilization of the cationic ring due to the increased angle strain brought about by annelation with such a highly strained system<sup>5</sup> (Table 1).

Table 1 Comparison of  $pK_{R+}$  and Reduction Potential ( $E_{red}$ ) for Representative Disubstituted Tropylium Ions

Tropylium ion	$pK_{R+}$ (50% aq. $CH_3CN$ )	$E_{red}$ ( $CH_3CN$ ) V vs $Ag/Ag^+$	Substituent effects
Unsubstituted <sup>a</sup>	3.88	-0.51	None
1,4-(t-Bu) <sub>2</sub> - <sup>a</sup>	5.42	-0.72	Inductive
1,4-(cyclo-Pr) <sub>2</sub> - <sup>a</sup>	7.63	-0.76	$\sigma$ -Conjugative
1,2-bicyclo[2.1.1]hexeno- (2) <sup>b</sup>	5.10	-0.71	$\sigma$ -Conjugative <i>minus</i> angle strain
1,2-bicyclo[2.2.2]octeno- (3) <sup>b</sup>	7.80	-0.765	$\sigma$ -Conjugative <i>plus</i> Inductive

<sup>a</sup> Ref 4 <sup>b</sup> Ref 5

Rather, annelation with a much less strained bicyclo[2.2.2]octene unit as in the cation 3 was found to be as effective as substitution with two cyclopropyl groups in stabilizing the tropylium ion as shown in Table 1. Apparently, the stabilizing effect of a bicyclo[2.2.2]octene unit is due to both the inductive electron donation and  $\sigma$ - $\pi$  conjugation of the tropylium 2p orbitals with the  $\sigma$ -bonds which are rigidly fixed at the position nearly parallel to the vacant 2p orbitals. These facts are in agreement with the results of theoretical calculations by INDO (Table 2), which demonstrate that, for the three model cations 1, 2, and 3, the total charge density on the tropylium ring decreases while the  $\pi$ -bond order between the cationic carbon and the  $\alpha$ -carbon of the substituent increases, in this order. The charge distribution in the cationic ring of 3 does not show too much alternation such as in 2.

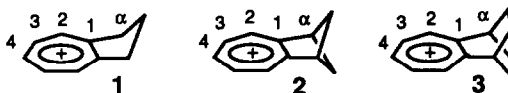


Table 2 Results of MO Calculations by INDO

Cation	$\pi$ -Bond order (C $\alpha$ -C1)	Total charge density on the tropylium ring	Charge density			
			C-1	C-2	C-3	C-4
1	0.2277	+0.6423	+0.0968	+0.0805	+0.0986	+0.0906
2	0.2359	+0.6202	+0.1089	+0.0546	+0.1135	+0.0662
3	0.2500	+0.6098	+0.0910	+0.0765	+0.0940	+0.0868

From these results, tris-annelation of the tropylium ring with bicyclo[2.2.2]octene units is expected to afford a highly stabilized new carbocation, and this was shown to be true as has been reported in a preliminary communication.<sup>6</sup> The tris-annelated cation 4 was found to exhibit the highest  $pK_{R+}$  value ever reported (13.0 in 50% aqueous acetonitrile). In the present paper are described the full accounts on the formation and properties of this highly stabilized carbocation as well as its chemical reactivity.



## RESULTS AND DISCUSSION

*Synthesis of the cation 4*

In spite of the severe steric hindrance caused by the bicyclic  $\sigma$ -frameworks, the central  $\pi$ -system of tris(bicyclo[2.2.2]octeno)benzene (**5**)<sup>7</sup> was enlarged by the CuBr-catalyzed reaction with a large excess (ca 30 equiv) of diazomethane to give the cycloheptatriene derivative **6** in 30% yield (73% based on the consumed **5**)



Conventional hydride abstraction from **6** by the use of a trityl salt afforded the objective cation **4** in high yield. The spectral data of **4** are given in Table 3 together with those of the mono-annulated cation **3** and the fully substituted cation **14** (vide infra). The definite upfield shifts observed for both the <sup>13</sup>C and <sup>1</sup>H NMR signals of the tropylium ring in **4** as compared with **3** indicate decreased charge density on the cationic ring in **4** in agreement with its enhanced thermodynamic stability.

Table 3 Spectral Properties of the Cations **3**, **4**, and **14**

Cation	<sup>1</sup> H NMR (CD <sub>3</sub> CN) $\delta$			<sup>13</sup> C NMR (CD <sub>3</sub> CN) $\delta$				IR (KBr) $\nu$			UV (CH <sub>3</sub> CN)
	-CH <sup>+</sup> -	-CH<	CH <sub>2</sub> <	-C <sup>+</sup> <	-CH <sup>+</sup> -	-CH<	CH <sub>2</sub> <	cm <sup>-1</sup>			$\lambda_{\max}$ nm (log $\epsilon$ )
<b>3</b> ClO <sub>4</sub> <sup>-</sup>	8.98	3.76	2.11	176.5	152.2	42.5	24.5	2950	2874	1636	225 (4.64)
	(5 H)	(2 H)	(4 H)		151.5			1479	1466	1450	285 (3.68)
			1.46		151.2			1319	1122	1024	297 (3.64)
			(4 H)					812	758	625	
<b>4</b> SbF <sub>6</sub> <sup>-</sup>	8.55	4.13	2.05	168.3	144.2	42.7	25.0	2951	2873	1625	256 (4.71)
	(1 H)	(2 H)	(12 H)	166.0		36.6	24.8	1458	1420	1320	308 (4.01)
		4.07	1.44	163.9		36.1	24.7	1270	1245	1173	
		(2 H)	(12 H)					1040	1025	814	
		3.56						658			
		(2 H)									
<b>14</b> SbF <sub>6</sub> <sup>-</sup>	-	3.96	2.03	164.9	-	36.6	24.8	2950	2870	1620	262 (4.73)
		(6 H)	(12 H)	162.6		36.0	24.7	1448	1322	1287	317 (3.93)
			1.43	162.4		35.8	24.5 <sub>5</sub>	1172	1137	1024	330 (3.91)
			(12 H)	162.3				818	650		
	2.82 (3 H, CH <sub>3</sub> )				24.6 (q, CH <sub>3</sub> )						

*Formation of the cation 4 by protolytic ionization (oxidation) of the hydrocarbon 6*

In the course of a preparative study of the cation **4**, it was found that the cycloheptatriene **6** can be cleanly ionized to **4** simply by dissolving in trifluoroacetic acid (TFA) in dichloromethane.

Direct conversion of hydrocarbons into carbocations by the action of strong acid such as superacids<sup>8</sup> has been of considerable interest as one of the fundamental reactions in petrochemical processes. However, the mechanism for such a reaction, as represented by direct hydride abstraction by a proton, has been a subject of controversy, except for a very clean reaction yielding a stable saturated carbocation of a rather unusual structure recently reported by McMurry.<sup>9</sup> For the formation of  $\pi$ -conjugated carbocations, it has been reported that the strong acid having oxidizing ability such as fluorosulfonic acid is effective.<sup>10</sup> The acid-catalyzed oxidation of cycloheptatriene has also been reported, but the yield of the tropylium ion based on cycloheptatriene is low with considerable polymerization.<sup>11</sup>

Compared with these results, the present observation, i.e. the highly efficient conversion of the hydrocarbon **6** to the cation **4** by the use of a simple acetic acid derivative is quite remarkable. As is shown in Table 4, the ionization rate apparently depends on the acid strength. In acetic acid, the reaction is quite slow, but after about one month, the cation **4** was formed in 65% yield.

Table 4 Ionization of **6** to **4** by the Action of Acetic Acid Derivatives in Dichloromethane under Air at 25 °C

Acid	(pK <sub>a</sub> )	Concentration, M		Time hr	<b>4</b> Yield % <sup>a</sup>
		[Acid]	[ <b>6</b> ]		
CCl <sub>3</sub> CO <sub>2</sub> H	(0.89)	1.0	1.0 × 10 <sup>-3</sup>	4	71
		3.2	3.0 × 10 <sup>-5</sup>	2	99
CHCl <sub>2</sub> CO <sub>2</sub> H	(1.30)	1.0	1.0 × 10 <sup>-3</sup>	4	64
		2.9	3.0 × 10 <sup>-5</sup>	0.3	85
CH <sub>2</sub> ClCO <sub>2</sub> H	(2.86)	1.0	1.0 × 10 <sup>-3</sup>	4	58
		2.9	3.0 × 10 <sup>-5</sup>	0.3	85
CH <sub>3</sub> CO <sub>2</sub> H	(4.76)	1.0	1.0 × 10 <sup>-3</sup>	4	~0
		15 <sup>b</sup>	3.0 × 10 <sup>-4</sup>	890	65

<sup>a</sup> Determined by UV spectroscopy. <sup>b</sup> Neat.

The mechanism of this reaction was examined by the use of UV-Vis and NMR spectroscopies. When the cycloheptatriene **6** was dissolved in TFA, yellow coloration ( $\lambda_{\max}$  452 nm) was immediately observed. As shown in Figure 1(a), this absorption gradually decreased with concomitant increase of the absorption at 308 nm corresponding to the cation **4**. In contrast to this, the first-formed yellow species was much more stable in the absence of air (Figure 1(b)). The <sup>1</sup>H NMR spectrum of this yellow solution prepared under vacuum (Figure 2(b)) exhibited three groups of signals, i.e. a group of broad singlets ( $\delta$  3.68, 3.53, 3.43, 3.31, 3.18 and 2.09) corresponding to the bridgehead protons, a group of broad multiplets ( $\delta$  2.26–1.43) of the bridging ethylene protons, and a group of multiplets which were wiped out in TFA-*d* and were therefore assigned to the exchangeable protons, H<sub>a</sub> ( $\delta$  2.98 (dd, *J* = 19.5, 19.2 Hz)), H<sub>b</sub> ( $\delta$  2.88 (dd, *J* = 19.5, 5.4 Hz)), and H<sub>c</sub> ( $\delta$  2.53 (dd, *J* = 19.2, 5.4 Hz)). These assignments were further confirmed by the use of 2D (COSY and C/H COSY) NMR technique. Since the <sup>13</sup>C NMR spectrum exhibited the signals typical for the substituted pentadienyl cation ( $\delta$  202.1, 200.7, 199.4, 150.3, 147.2), the most probable structure of this species is supposed as the cation **7** (Scheme 1). After 2 days at room temperature, the <sup>1</sup>H NMR spectrum exhibited an appreciable change, although the color and the UV-Vis spectrum of the solution stayed almost unchanged. The typical spectrum is shown in Figure 2(e) here, the original signals assigned to **7** are greatly reduced and instead is observed the growth of new signals assignable to another pentadienyl cation **8** (Scheme 1) ( $\delta_{\text{H}}$  7.27 (s, H<sub>a</sub>), 2.71 and 2.61 (d x 2, *J* = 21.4 Hz, H<sub>b</sub> and H<sub>c</sub>),  $\delta_{\text{C}}$  (sp<sup>2</sup> carbons) 212.0, 205.0, 202.1, 149.0, 131.5) as well as the signals of the final product **4**.

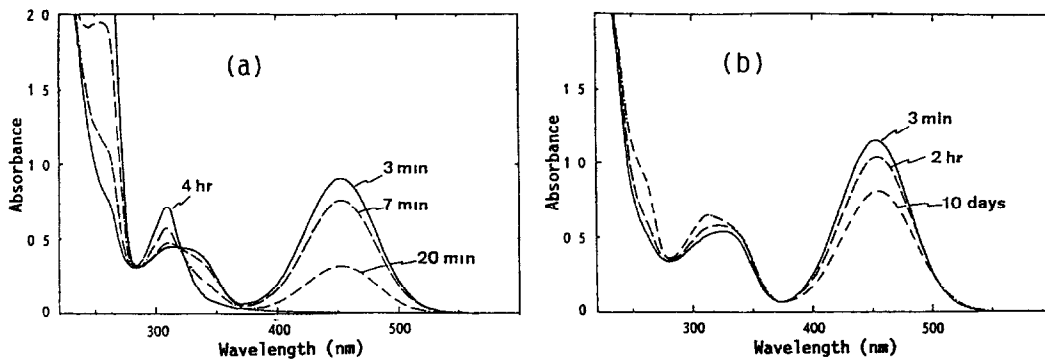


Fig 1 UV-Vis spectral change of **6** ( $1 \times 10^{-3}$  M) in a solution of TFA (1 M) in  $\text{CH}_2\text{Cl}_2$  at room temperature (a) under air; (b) under vacuum ( $<10^{-4}$  Torr)

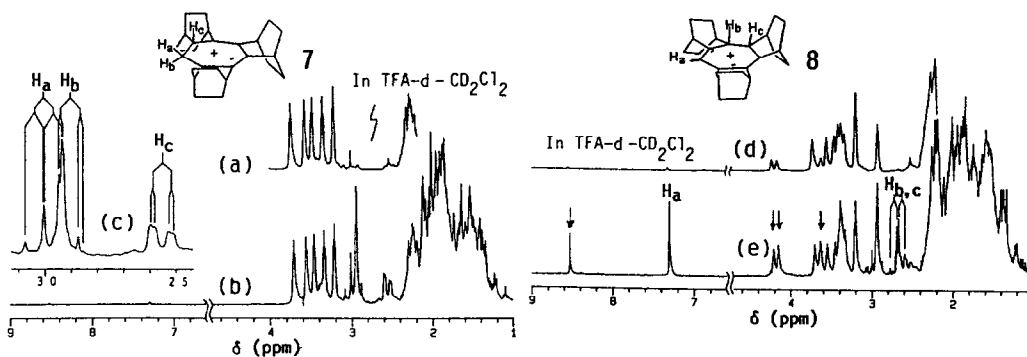


Fig 2  $^1\text{H}$  NMR spectra (270 MHz) of **6** (ca 0.05 M) in a solution of TFA or TFA- $d_4$  (ca 6 M) in  $\text{CD}_2\text{Cl}_2$  under vacuum at room temperature (a) after 0.2 hr in TFA- $d_4$ - $\text{CD}_2\text{Cl}_2$ , (b) after 0.2 hr in TFA- $\text{CD}_2\text{Cl}_2$  (an expanded spectrum is shown in (c)), (d) after 30 days in TFA- $d_4$ - $\text{CD}_2\text{Cl}_2$ , (e) after 30 days in TFA- $\text{CD}_2\text{Cl}_2$  ( $\downarrow$  denotes signals of **4**)

The time-dependent change in distribution of the cations **7**, **8**, and **4** estimated from the  $^1\text{H}$  NMR spectra is shown in Figure 3. From Figure 3(a) it is apparent that at about 2 days after preparation of the solution a quasi-equilibrium between the cations **7** and **8** is attained and is followed by very slow formation of **4** at the expense of the cation **7**.<sup>12</sup> However, when air was introduced at 2 hr after preparation of the solution, the amount of the tropylium ion **4** smoothly increased with a concomitant decrease in the cation **7** as is shown in Figure 3(b). Thus molecular oxygen must be playing an important role in the formation of **4**. In fact, formation of a peroxide (most probably  $\text{H}_2\text{O}_2$ ) in an amount corresponding to more than 60% of the product **4** was confirmed by iodometrical analysis of the final sample solution.

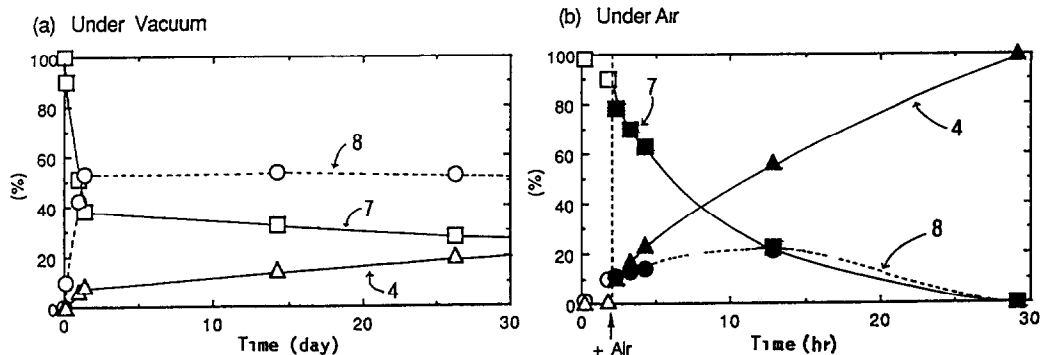
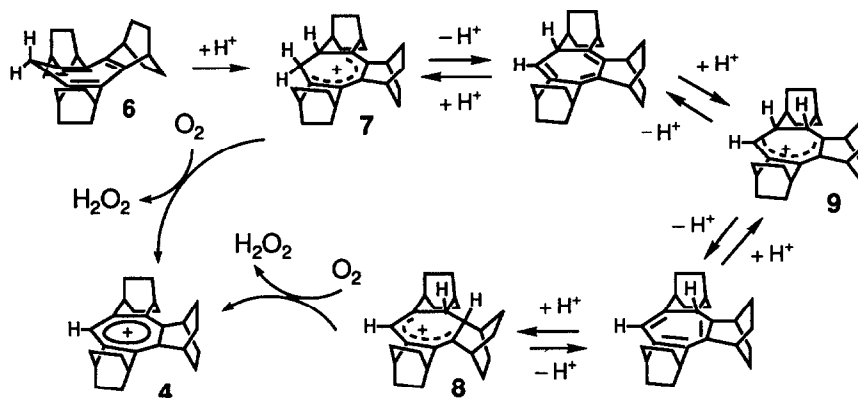


Fig 3 The time dependent change in distribution, estimated from  $^1\text{H}$  NMR spectra, of the cations 7, 8, and 4 in a solution originally prepared with 6 (ca. 0.05 M) in a solution of TFA (ca. 6 M) in  $\text{CD}_2\text{Cl}_2$ , (a) under vacuum, (b) after introduction of air, both at room temperature

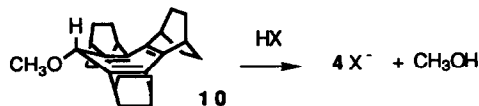
From these results, the overall reaction is supposed to proceed as shown in Scheme 1. Among the pentadienyl cations 7, 8, and 9 produced in the protonation-deprotonation equilibria, the cations 7 and 8, in which the pentadienyl's C-1, C-3, and C-5 carbons are all substituted, are supposedly more stabilized than the cation 9 and were directly observable. Abstraction of two hydrogen atoms by triplet oxygen from either 7 or 8 can afford the final tropylium ion 4. To the best of our knowledge there seems to be no precedent for such high-yield transformation of a hydrocarbon to a carbocation by the action of carboxylic acid and air. The most important factor leading to the present result appears to be the remarkably high thermodynamic stability of the product cation 4, in addition to the structural protection, by surrounding  $\sigma$ -frameworks, of the intermediate pentadienyl cations against polymerization.



Scheme 1

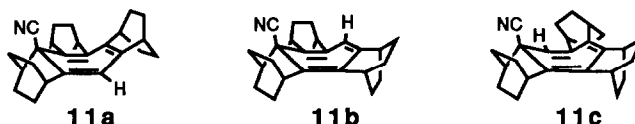
#### Reactions of the tropylium ion 4

The  $\text{pK}_{\text{R}^+}$  value of the cation 4 has been determined spectrophotometrically as 13.0 in 50% aqueous acetonitrile at 25 °C.<sup>6</sup> The spectral change was completely reversible, the cation being quantitatively regenerated upon acidification of the once neutralized solution. This implies that the cation 4 can be generated from its covalent counterparts (alcohols or ethers) upon treatment with a Brønsted acid of  $\text{pK}_{\text{a}} < 12$ . In good accordance, besides strong acids such as HBr, rather weak Brønsted acids such as  $\text{H}_3\text{PO}_4$  ( $\text{pK}_{\text{a}}^{13}$  2.15), carbonated water ( $\text{H}_2\text{CO}_3$ , 6.36),  $\text{H}_3\text{BO}_3$  (9.24),  $\text{C}_6\text{H}_5\text{OH}$  (9.99), and  $\text{CH}_3\text{NO}_2$  (10.21) were found to be able to ionize the methoxycycloheptatriene 10 into 4 (Scheme 2) when examined by  $^1\text{H}$  NMR spectroscopy in  $\text{CD}_3\text{CN}$ .



Scheme 2

These facts are also in agreement with quite low reactivity of the cation **4** towards various nucleophiles. When examined by UV spectroscopy in H<sub>2</sub>O, the cation **4** showed no reactivity toward the nucleophiles (added as Na<sup>+</sup> or K<sup>+</sup> salts) such as NCO<sup>-</sup> (cyanate ion) (pK<sub>a</sub><sup>13</sup> of the conjugate acid, 3.46), N<sub>3</sub><sup>-</sup> (4.59), CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> (4.76), CrO<sub>4</sub><sup>2-</sup> (6.50), C<sub>6</sub>H<sub>5</sub>S<sup>-</sup> (6.50), SO<sub>3</sub><sup>2-</sup> (7.21), C<sub>6</sub>H<sub>5</sub>O<sup>-</sup> (9.99), and CO<sub>3</sub><sup>2-</sup> (10.33). The only one exception was the reaction with CN<sup>-</sup> (pK<sub>a</sub><sup>13</sup> of the conjugate acid 9.21), which was very slow (t<sub>1/2</sub> 130 min at 25 °C, when [4]=1×10<sup>-5</sup> M, [CN<sup>-</sup>]=5×10<sup>-4</sup> M) but afforded a mixture of isomeric 7-cyanocycloheptatrienes **11a**, **11b**, and **11c** (in a ratio of approximately 1.0 : 0.4 : 0.2), among which the least strained isomer **11a**<sup>14</sup> was the major product. It may be inferred here that not only the basicity of the nucleophile but the bond energy of the newly formed covalent bond is playing an important role in determining the reactivity of **4**.



In addition to the extraordinarily high pK<sub>R</sub><sup>+</sup> value, the cation **4** is also characterized by a highly negative reduction potential (-1.120 V vs Ag/Ag<sup>+</sup> in acetonitrile) as compared with the unsubstituted cation (-0.510 V),<sup>4</sup> and resists any attempt for chemical one-electron reduction with metallic powder such as Zn, Mg, and Al.

#### Reactions of the tropylium ion **4** with carbanions

In order to obtain further insight into the correlation between the cation's reactivity and anion's stability, the reactions of the cation **4** with potassium salts of various carbanions were investigated next. The reactions were carried out either in dimethyl sulfoxide (DMSO) (followed with UV-Vis spectroscopy) or in tetrahydrofuran (THF) - CH<sub>3</sub>CN on a preparative scale.

As summarized in Table 5, the covalent bond formation becomes dominant as the stability of carbanion R<sup>-</sup> decreases. A borderline between carbocation-carbanion coexistence (i.e. no reaction between **4** and R<sup>-</sup>) and covalent-bond formation appears to be present between the entries 2 and 3, that is, between the reactions with the carbanions whose precursor's pK<sub>a</sub> values are 8.3 and 11.0.

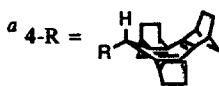
According to the Arnett's thermodynamic "master equation" for carbocation-carbanion reaction (equation 1),<sup>15</sup>

$$\Delta H_{\text{het}} = -\Delta H_{\text{rxn}} = 11.98 - 1.178\text{pK}_{\text{R}^+} + 1.176\text{pK}_{\text{a}} \quad (1)$$

the value of  $\Delta H_{\text{rxn}}$  should be negative, that is, the covalent-bond formation should be favorable between the present cation **4** (pK<sub>R</sub><sup>+</sup> 13.0) and the carbanions with precursor's pK<sub>a</sub> (= pK<sub>a</sub>(RH)) larger than 2.8. A discrepancy between this predicted value (2.8) and observed pK<sub>a</sub>(RH) value (8.3 - 11.0) may be attributed to the considerable steric hindrance between cationic carbons of **4** and the reaction center of various carbanions. In fact, a change in reactivity due to the steric hindrance is apparent from the comparison of entries 3 and 5 in Table 5. The 1,1-dicyanoethyl anion, which is a tertiary carbanion, exhibits no reactivity towards the cation **4** in DMSO in spite of its lower thermodynamic stability than the dicyanomethyl anion.

Table 5 Results of the Reaction of the Cation 4 with Carbanions R<sup>-</sup>

Entry	R <sup>-</sup>	pK <sub>a</sub> (RH) <sup>b</sup>	Products <sup>a</sup>	
			in DMSO <sup>c</sup>	in THF-CH <sub>3</sub> CN <sup>d</sup>
1		5.9 <sup>e</sup>	4 + R <sup>-</sup>	4 R <sup>-f</sup>
2		8.3 <sup>g</sup>	4 + R <sup>-</sup>	4 + R <sup>-</sup>
3		11.0 <sup>h</sup>	4-R (single product)	4-R (single product)
4		12.3 <sup>i</sup>	4-R (single product)	4-R (single product)
5		12.5 <sup>g</sup>	4 + R <sup>-</sup>	4-R (+ byproducts)
6		16.8 <sup>j</sup>	4-R (single product)	4-R (single product)



<sup>b</sup> Determined in DMSO

<sup>c</sup> [4]=[R<sup>-</sup>]=5×10<sup>-4</sup> M    <sup>d</sup> [4]=[R<sup>-</sup>]=5×10<sup>-2</sup> M    <sup>e</sup> Ref. 17

<sup>f</sup> The salt 4 R<sup>-</sup> was isolated (see text)

<sup>g</sup> Bordwell, F G, Hughes, D L *J Org Chem.* 1983, 48, 2206

<sup>h</sup> Bordwell, F G *Acc Chem Res*, 1988, 21, 456

<sup>i</sup> Arneti, E M, Chawla, B, Amarnath, K Witsell, Jr, L G  
*Energy and Fuels*, 1987, 1, 17

<sup>j</sup> Kuhn, R; Rewicki, D. *Liebigs Ann Chem* 1967, 704, 9

#### Preparation of a new hydrocarbon salt

We have already reported isolation and properties of a series of new "hydrocarbon salts," i.e. carbocation-carbanion salts composed of only carbon and hydrogen.<sup>16</sup> In the present work another such salt was isolated from the reaction of 4 with the highly  $\pi$ -conjugated carbanion, tris(7H-dibenzo[*c,g*]fluorenylidene)methyl anion<sup>17</sup> (Kuhn's carbanion, C<sub>64</sub>H<sub>39</sub><sup>-</sup>), carried out in THF-CH<sub>3</sub>CN (entry 1 in Table 5). The salt (4 C<sub>64</sub>H<sub>39</sub><sup>-</sup>) is a dark green powder and its structure was established based on elemental analysis and on the IR (solid sample in a KBr disk; Figure 4) and the UV-vis spectra (solution in DMSO; Figure 5), each of which consisted of the spectra of the respective cation and anion superimposed.



## 1,2,3,4,5,6-Tris(bicyclo[2.2.2]octeno)troplium ion

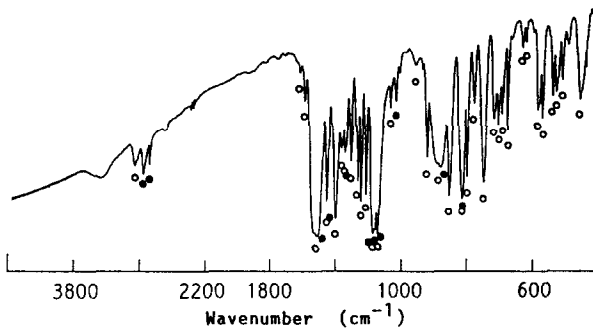


Fig 4 The IR spectrum (KBr disk) of the salt  $4\text{C}_{64}\text{H}_{39}^-$  closed circle, absorptions of  $4$ , open circle, absorptions of  $\text{C}_{64}\text{H}_{39}^-$

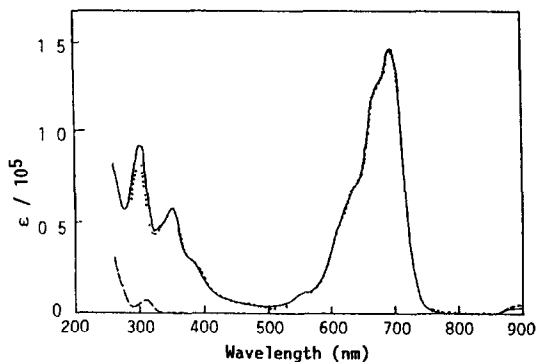
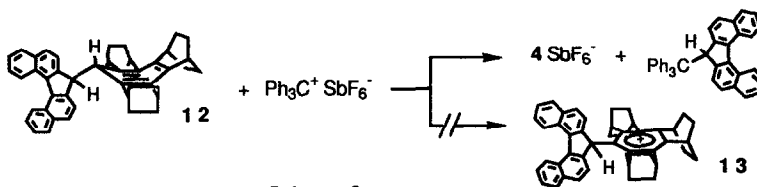


Fig 5 The UV-Vis spectrum of the salt  $4\text{C}_{64}\text{H}_{39}^-$  in DMSO solid line, an observed spectrum, broken line,  $4$ , dotted line,  $\text{C}_{64}\text{H}_{39}^-$

### Reactions of the covalent compounds 4-R

In order to prepare the 7-substituted troplium-ion derivative **13**, the cycloheptatriene **12** obtained from the reaction of entry **6** in Table 5 was treated with the trityl cation. However, the result was not the formation of **13** but only the regeneration of the cation **4**, as shown in Scheme 3. This may be ascribed to the considerable difference in thermodynamic stability between the hepta- and hexa-substituted troplium ions, the hepta-substituted troplium ion being destabilized due to severe steric constraint against the planarity of the troplium ring.<sup>18</sup> Dissolution of **12** in TFA in  $\text{CH}_2\text{Cl}_2$  (vide supra) also resulted in the formation of **4** instead of **13**. Furthermore, the cycloheptatriene **12** resisted any attempt for thermal<sup>19</sup> or photochemical<sup>20</sup> sigmatropic hydrogen migration, which is commonly observed for ordinary cycloheptatrienes.



Scheme 3

Only the 7-methylcycloheptatriene derivative, which was obtained by a reaction of **4** with methyl lithium, was converted to the corresponding cation **14** upon treatment with the trityl cation. Among the spectral

properties of **14** shown in Table 3 (*vide supra*), it is to be noted that NMR signals of all the bridgehead protons (and carbons) resonate at almost the same position indicating that they are suffering from the steric compression effect to a similar extent. Thus, the tropylium ring in **14** might be somewhat distorted from complete planarity to minimize the steric constraint. The general upfield shift observed for the  $^{13}\text{C}$  NMR signals of substituted tropylium-ring carbons of **14** relative to those of **4** is considered to be resulting from a slight change in hybridization due to this distortion of the tropylium ring.<sup>21</sup> Such steric effect seems to be reflected in a decrease in thermodynamic stability of the cation **14** as is shown by lowered values of its  $\text{pK}_{\text{R}^+}$  ( $12.4 \pm 0.5$  in 50% aqueous  $\text{CH}_3\text{CN}$ ) and reduction potential ( $-1.094$  V vs  $\text{Ag}/\text{Ag}^+$ ) compared with those of the cation **4**. These results suggest the difficulty in raising the stability of the cation **4** simply by placing an extra substituent at the C-7 position.

## EXPERIMENTAL

Melting points were determined on a Yamato MP-21 apparatus and are uncorrected. Elemental analyses were performed by Microanalytical Center, Kyoto University, Kyoto. NMR spectra were recorded on a JEOL GSX270 (270 MHz for  $^1\text{H}$  and 67.8 MHz for  $^{13}\text{C}$  NMR) or on a JEOL FX90 (90 MHz for  $^1\text{H}$  and 22.5 MHz for  $^{13}\text{C}$  NMR) spectrometer using  $\text{Me}_4\text{Si}$  as an internal standard unless otherwise noted. IR spectra were taken on a Nicolet 20DXB FT IR spectrometer or on a Hitachi 215 spectrometer. UV-Vis spectra were taken on a Hitachi 200-10 spectrometer. High resolution mass (HRMS) spectra were taken on a Hitachi M-80 spectrometer at 70 eV unless otherwise noted. Cyclic voltammograms were obtained by the method and apparatus described in a previous paper.<sup>16c</sup> A Sartorius 4503MP6 microbalance was employed for weighing samples of less than 2 mg.

THF was freshly distilled from sodium benzophenone ketyl before use. DMSO and methanol were distilled over  $\text{CaH}_2$ .  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  were distilled over  $\text{P}_2\text{O}_5$ .

### 1,2,3,4,5,6-Tris(bicyclo[2.2.2]octeno)cycloheptatriene (**6**)

To a heated and stirred suspension of  $\text{CuBr}$  (0.10 g, 0.70 mmol) and tris(bicyclo[2.2.2]octeno)benzene (**5**)<sup>7</sup> (1.282 g, 4.03 mmol) in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (12 ml) was added dropwise a solution of diazomethane (120 mmol) in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (200 ml), prepared from *N*-methyl-*N*-nitrosourea<sup>22</sup> and 50%  $\text{KOH}$ , at  $80^\circ\text{C}$  over 30 min. After refluxing for 10 min, the mixture was filtered and evaporated to give 1.52 g of a crude product, which was chromatographed over silica gel (90 g) impregnated with  $\text{AgNO}_3$  (7% by weight). Elution with hexane afforded the unchanged benzene **5** (0.752 g, 58.6%). The following fraction eluted with hexane-ether (20:1 by volume) gave the cycloheptatriene **6** as white crystals (0.402 g, 30.0%). mp  $175.8\text{--}177^\circ\text{C}$  (recrystallized from  $\text{CH}_2\text{Cl}_2$ ),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  2.89 (br s, 2 H, CH), 2.82 (br s, 2 H, CH), 2.49 (br s, 2 H, CH), 2.38 (s, 2 H,  $\text{CH}_2$ (cycloheptatriene)), 1.66–1.01 (m, 24 H,  $\text{CH}_2$ ),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.8 MHz)  $\delta$  139.3 (s), 133.5 (s), 130.1 (s), 37.4 (t), 36.8 (d), 32.1 (d), 31.0 (d), 27.0 (t), 26.2 (t), 26.1 (t), IR (KBr) 2935, 2855, 1600, 1450, 1318, 1248, 1178, 1144, 1126, 1020, 862,  $812\text{ cm}^{-1}$ , UV (EtOH)  $\lambda_{\text{max}}$  276 nm ( $\log \epsilon$  3.75). HRMS ( $\text{M}^+$ ,  $\text{C}_{25}\text{H}_{32}$ ) calcd 332.2502, found 332.2495.

### 1,2,3,4,5,6-Tris(bicyclo[2.2.2]octeno)tropylium hexafluoroantimonate (**4 SbF<sub>6</sub>**)

To a stirred solution of **6** (0.306 g, 0.922 mmol) in  $\text{CH}_2\text{Cl}_2$  (9 ml) was added  $\text{Ph}_3\text{C}^+\text{SbF}_6^-$ <sup>23</sup> (0.400 g, 0.835 mmol) in one portion. After stirring for 30 min at room temperature, the solution was concentrated to ca. 3 ml. To this solution was added ether (50 ml) to cause the formation of white precipitates, which were collected by filtration and dried under vacuum to give **4 SbF<sub>6</sub>** as a yellowish powder (0.431 g, 82.6%). Colorless crystals were obtained by recrystallization from  $\text{CCl}_4\text{--CH}_3\text{CN}$  (2:1) mp  $289.5\text{--}292^\circ\text{C}$  (dec). The spectral data are shown in Table 3. Anal. Calcd for  $\text{C}_{25}\text{H}_{31}\text{F}_6\text{Sb}$ : C, 52.93, H, 5.51. Found: C, 52.72, H, 5.51.

### 7-Methyl-1,2,3,4,5,6-tris(bicyclo[2.2.2]octeno)tropylium hexafluoroantimonate (**14 SbF<sub>6</sub>**)

To a stirred suspension of **4 SbF<sub>6</sub>** (0.0831 g, 0.147 mmol) in THF (10 ml) was added dropwise a solution of 1.86 M methyl lithium (0.3 ml, 0.56 mmol) in ether under argon atmosphere. After stirring for 30

min at room temperature, the mixture was treated with H<sub>2</sub>O (10 ml) and extracted with ether (20 ml x 4). The ethereal solution was washed with 10% NaCl, dried (MgSO<sub>4</sub>), and evaporated to give 0.0664 g of a viscous oil, which was shown to contain 0.0372 g (0.103 mmol, 70.1%) of 7-methyl-1,2,3,4,5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene by <sup>1</sup>H NMR analysis. (In a separate experiment, the 7-methylcycloheptatriene derivative was isolated by chromatography over a short silica gel column, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ 2.85 (br s, 6 H, CH), 1.41 (br s, 24 H, CH<sub>2</sub>), 1.26 (s, 3 H, CH<sub>3</sub>), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 22.5 MHz) δ 139.1 (s), 132.7 (s), 128.6 (s), 32.1 (d), 31.3 (d), 31.2 (d), 27.1 (t), 26.5 (q), 26.2 (t), 25.8 (t).) The crude product from the above reaction was dissolved in 0.8 ml of CH<sub>3</sub>CN-CH<sub>2</sub>Cl<sub>2</sub> (4:1 by volume), and to this solution was added dropwise a solution of Ph<sub>3</sub>C<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (0.0498 g, 0.104 mmol) in 0.6 ml of CH<sub>3</sub>CN-CH<sub>2</sub>Cl<sub>2</sub> (4:1) with magnetic stirring and heating at 60 °C under argon. After stirring for 1 hr at 60 °C, the resulting brownish solution was evaporated and the residue redissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 ml). To the stirred CH<sub>2</sub>Cl<sub>2</sub> solution which was cooled with a dry-ice/methanol bath was added ether (15 ml) under nitrogen to cause formation of white precipitates. After stirring for 30 min with cooling, the supernatant solution was removed by the use of a syringe leaving **14** SbF<sub>6</sub><sup>-</sup> as a beige-colored powder (0.0339 g, 56.6%) after drying under vacuum. The salt **14** SbF<sub>6</sub><sup>-</sup> was found to gradually decompose either in a solution (CH<sub>2</sub>Cl<sub>2</sub>) or as a solid and therefore satisfactory analytical data could not be obtained mp >300 °C (charring at >200 °C). The spectral data are shown in Table 3. Anal. Calcd for C<sub>26</sub>H<sub>33</sub>F<sub>6</sub>Sb: C, 53.72, H, 5.72. Found: C, 55.21, H, 5.86.

#### 7-Methoxy-1,2,3,4,5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene (**10**)

To a stirred suspension of **4** SbF<sub>6</sub><sup>-</sup> (0.0941 g, 0.166 mmol) in dry methanol (10 ml) was added dropwise a 0.303 M solution of NaOCH<sub>3</sub> in methanol (3.5 ml, 1.1 mmol). After stirring for 15 min the mixture was evaporated and the residue extracted with pentane (10 ml x 6). Evaporation of pentane afforded **10** as a pale yellow oil (0.0543 g, 90.2%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz, 25 °C) δ ~3.6 (v br s, 1 H, CH(cycloheptatriene)), 3.21 (br s, 3 H, OCH<sub>3</sub>), 2.97 (br s, 2 H, CH), 2.91 (br s, 2 H, CH), 2.80 (br s, 2 H, CH), 1.67-1.22 (br m, 24 H, CH<sub>2</sub>), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.8 MHz, 25 °C, considerable line broadening was observed resulting from partly frozen ring-inversion of the cycloheptatriene system) δ 139.1, 132.9 (br), 132.6, 81.6 (br), 56.2, 32.1, 31.1, 27.1, 27.0, 26.9, 26.4, 25.8, <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.8 MHz, -55 °C, two sets of signals were observed corresponding to two isomers having the OCH<sub>3</sub> group at an equatorial position (**10**(eq-OCH<sub>3</sub>)) and at an axial position (**10**(ax-OCH<sub>3</sub>)) in a ratio of ca. 2:1, the assignment was made based on the data of frozen <sup>1</sup>H NMR spectra exhibiting H-7 of **10**(eq-OCH<sub>3</sub>), which is known to resonate at the higher field, at δ 2.97 and that of **10**(ax-OCH<sub>3</sub>) at δ 4.58) δ (**10**(eq-OCH<sub>3</sub>)) 139.4 (s), 132.0 (s), 131.3 (s), 79.9 (d), 57.8 (q), 31.8 (d), 30.3 (d), 27.3 (t), 27.0 (d), 26.4 (t), 26.1 (t), 25.9 (t), 25.5 (t), 25.3 (t), δ (**10**(ax-OCH<sub>3</sub>)) 137.9 (s), 134.8 (s), 131.6 (s), 83.4 (d), 53.7 (q), 36.3 (d), 31.3 (d), 31.1 (d), 27.6 (t), 26.4 (t), 26.3 (t), 25.6 (t), 25.3 (t). HRMS (20 eV) (M<sup>+</sup>, C<sub>26</sub>H<sub>34</sub>O) calcd 362.2608, found 362.2610.

#### Protolytic oxidation (ionization) of the cycloheptatriene **6**

(a) *Experiment on a preparative scale* Into a glass tube containing **6** (0.0225 g, 0.0677 mmol) was vacuum-distilled 0.5 ml of CF<sub>3</sub>CO<sub>2</sub>H (0.739 g, 6.48 mmol) to give a deep yellow-orange solution. The tube was opened under air, diluted with 3 ml of CH<sub>2</sub>Cl<sub>2</sub>, and let stand for 2 hr. Evaporation of the solvent and acid afforded a highly viscous oil, which exhibited a <sup>1</sup>H NMR spectrum identical to that for the cation **4**.

(b) *Spectral investigation* The UV-Vis (Figure 1(a)) and NMR measurements under air were carried out by the use of an ordinary quartz cell (1.00 mm) and an NMR tube (o.d. 5 mm). The UV-Vis measurements under vacuum were conducted by the use of a vacuum quartz cell (1.00 mm) described in a previous paper.<sup>16c</sup> A precisely weighed amount of **6** was placed in a side arm, and known amounts of CH<sub>2</sub>Cl<sub>2</sub> and CF<sub>3</sub>CO<sub>2</sub>H were vacuum-distilled into the bottom part. The whole apparatus was sealed under vacuum, and after thorough mixing of the solution the spectrum was recorded to give the result shown in Figure 1(b). Sample solutions for NMR measurements under vacuum were similarly prepared using a similar apparatus equipped with an NMR sample tube. The <sup>1</sup>H NMR spectra are shown in Figure 2. (The chemical shifts were read with reference to the signal of

trace amount of  $\text{CH}_2\text{Cl}_2$  taken as  $\delta$  5 32 ) The  $^{13}\text{C}$  NMR data are as follows (the chemical shifts were read with reference to the signal of  $\text{CD}_2\text{Cl}_2$  taken as  $\delta$  53 80) the cation **7**,  $\delta$  202.1 (s), 200 7 (s), 199 4 (s), 150 3 (s), 147 2 (s), 45 4 (d,  $\text{CH}_\text{C}$ ), 44 8 (d), 40 9 (d), 39 1 (t,  $\text{CH}_\text{a}\text{H}_\text{b}$ ), 37 2 (d), 34 4 (d), 34 3 (d), 33.0 (d), 28.0 (t), 27 8 (t), 27 5 (t), 25.9 (t), 25 6 (t), 25 5 (t), 25 4 (t), 25.1 (t), 24 6 (t), 24 5 (t), 24 2 (t), 21 2 (t), the cation **8**,  $\delta$  212 0 (s), 205 0 (s), 202.1 (s), 149 0 (s), 131.5 (d,  $\text{CH}_\text{a}$ ), 47 4 (d), 45 7 (d,  $\text{CH}_\text{b}$  or  $\text{CH}_\text{C}$ ), 44 9 (d,  $\text{CH}_\text{C}$  or  $\text{CH}_\text{b}$ ), 43 4 (d), 37 5 (d), 33 4 (d), 30 3 (d), 30 0 (d), 29 5 (t), 28 2 (t), 27 7 (t), 25 6 (t), 25 5 (t), 25 3 (t), 24 9 (t), 24.6 (t), 24 3 (t), 23 9 (t), 21 5 (t), 21 3 (t)

#### *Ionization of the methoxycycloheptatriene 10 by Brønsted acids*

To a 0.6-ml aliquot of a solution of **10** (0 0035 g, 0 0097 mmol) in  $\text{CD}_3\text{CN}$  (3 5 ml) was added each of the following acids with vigorous mixing 75%  $\text{H}_3\text{PO}_4$  (0 031 g, 0 24 mmol), saturated carbonated water (0 1 ml, calculated to contain 0 003 mmol of  $\text{H}_2\text{CO}_3$ ),  $\text{H}_3\text{BO}_3$  (0 041 g, 0 66 mmol), and phenol (0 120 g, 1 28 mmol) Each solution exhibited  $^1\text{H}$  NMR (270 MHz) signals of the cation **4** in place of those of **10**

In the case of HBr, the gaseous acid was bubbled into a solution of **10** (0 0092 g, 0 0254 mmol) in ether (5 ml) Evaporation of the solvent afforded a brownish powder (0 0123 g, 98 4% as **4** Br<sup>-</sup> HBr), which exhibited  $^1\text{H}$  NMR (270 MHz) and  $^{13}\text{C}$  NMR (67 8 MHz) spectra identical to those of **4**, in  $\text{CD}_3\text{CN}$

A solution of **10** (0 001 g, 0 002 mmol) in  $\text{CD}_3\text{NO}_2$  (0 8 ml) also showed the  $^1\text{H}$  NMR (270 MHz) signals of the cation **4**

#### *Reactions of the cation 4 with nucleophiles*

To 3.00 ml of a  $5.73 \times 10^{-5}$  M aqueous solution of  $4 \text{ SbF}_6^-$  was added 0 50 ml each of  $6 \times 10^{-4}$  M aqueous solution of the following nucleophiles  $\text{NaOCN}$ ,  $\text{NaN}_3$ ,  $\text{CH}_3\text{CO}_2\text{Na}$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{C}_6\text{H}_5\text{SNa}$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{C}_6\text{H}_5\text{ONa}$ , and  $\text{Na}_2\text{CO}_3$  In each case, no spectral change was observed for the specific absorption of **4** at 308 nm over 1 hr at room temperature

When 3 ml of an aqueous solution of KCN ( $6.59 \times 10^{-4}$  M) was added to 1 ml of an aqueous solution of  $4 \text{ SbF}_6^-$  ( $4.58 \times 10^{-5}$  M), an appreciable decrease in the UV absorption of **4** was observed (see text) For a preparative purpose, an aqueous solution (10 ml) of KCN (0 0091 g, 0 140 mmol) was added to a stirred suspension of  $4 \text{ SbF}_6^-$  (0 0386 g, 0 0679 mmol) in  $\text{H}_2\text{O}$  (15 ml) and the stirring continued for 2 hr at room temperature Then the solution was extracted with ether (20 ml x 3), and the ethereal solution washed with 10% NaCl, dried ( $\text{MgSO}_4$ ), and evaporated to give 0 0197 g of a pale yellow viscous oil, which was shown to be a mixture of 7-cyano-1,2,3,4,6,7-tris(bicyclo[2.2.2]octeno)cycloheptatriene (**11a**), 7-cyano-1,2,4,5,6,7-tris(bicyclo[2.2.2]octeno)cycloheptatriene (**11b**), and 7-cyano-2,3,4,5,6,7-tris(bicyclo[2.2.2]octeno)cycloheptatriene (**11c**) (total yield, 81 1%) based on the following findings The  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz) spectrum of the crude product exhibited three singlets of =CH- at  $\delta$  6 29, 6.02, and 5 11 with the integrated ratio of 0 4 1 0 0 2, together with broad singlets of -CH< at  $\delta$  3.1-2 3 and broad multiplets of -CH<sub>2</sub>- at  $\delta$  1 2-0 8 In the  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.8 MHz) were observed three singlets of CN groups at  $\delta$  121 8, 121 6, and 121 2, together with ca. 20 signals at the range of  $\delta$  147 3-123.3 and ca. 55 signals at the range of  $\delta$  44 2-20 8 By the reaction of the crude product (0 0031 g, 0.0087 mmol) with  $\text{Ph}_3\text{C}^+\text{SbF}_6^-$  (0.0048 g, 0 010 mmol) in  $\text{CH}_2\text{Cl}_2$  (0 5 ml) for 3 hr at room temperature followed by addition of ether (30 ml), there was obtained  $4 \cdot \text{SbF}_6^-$  (0.0045 g, 91%), which was identified by  $^1\text{H}$  NMR (270 MHz) and IR spectroscopies From ca. 0 020 g of the crude product mixture from the same reaction was isolated **11a** as a colorless viscous oil (0 0078 g) by HPLC using a microporasil column (Waters) eluted with hexane-ether (98 2 by volume), though isolation of either **11b** or **11c** in a pure state was not successful: **11a**,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  6 02 (s, 1 H, =CH-), 3 01 (br s, 1 H, CH), 2 95 (br s, 1 H, CH), 2 91 (br s, 1 H, CH), 2 61 (br s, 1 H, CH), 2 40-2 37 (br m, 2 H, CH x 2), 2 17-1 27 (m, 24 H,  $\text{CH}_2$ ),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.8 MHz)  $\delta$  142.0 (s), 141 9 (s), 139.7 (s), 138.5 (s), 131 8 (s), 123 3 (d), 121.8 (s), 43.4 (s), 35 9 (d), 35 3 (d), 32.6 (d), 32.5 (d), 32.4 (d), 32 3 (d), 27.7 (t), 27.5 (t), 26.5 (t), 26 4 (t), 26.2 (t), 26 1 (t), 25 8 (t), 25 7 (t), 25 4 (t), 25 2 (t), 23 9 (t), 22 2 (t), IR ( $\text{CCl}_4$ ) 2942, 2864,

2221, 1469, 1456, 1360, 1264, 1218, 1147, 1089, 866  $\text{cm}^{-1}$ . HRMS ( $\text{M}^+$ ,  $\text{C}_{26}\text{H}_{31}\text{N}$ ) calcd 357 2454, found 357.2450.

#### Reactions of 4 $\text{SbF}_6^-$ with carbanions

(a) *A general procedure for the reaction in DMSO* The carbanions were generated by the reaction of 0.00570 M DMSO solution of *t*-BuOK (0.40 ml,  $2.3 \times 10^{-3}$  mmol) with the corresponding carbon acids ( $2.5 \times 10^{-3}$  mmol) in DMSO (5.0 ml) either under argon or under vacuum in a vacuum quartz cell described previously.<sup>16c</sup> After thorough mixing of the carbanion with 4  $\text{SbF}_6^-$  ( $2.5 \times 10^{-3}$  mmol), which had been placed in a side arm of the cell, the UV-Vis spectrum was recorded.

(b) *Reaction on a preparative scale* As a representative case for the reactions of entries 3-6 in Table 5, a procedure for the entry 3 is described below. To a stirred solution of 4  $\text{SbF}_6^-$  (0.0565 g, 0.100 mmol) in  $\text{CH}_3\text{CN}$  (1.0 ml) was added under argon a suspension of  $\text{K}^+\text{CH}(\text{CN})_2^-$  (0.10 mmol) in THF, prepared from  $\text{CH}_2(\text{CN})_2$  and 0.578 M THF solution of *t*-BuOK. After stirring for 10 min,  $\text{H}_2\text{O}$  (4 ml) was added and the mixture extracted with ether (5 ml  $\times$  3). The ethereal solution was washed with 10% NaCl, dried ( $\text{MgSO}_4$ ), and evaporated to give 7-dicyanomethyl-1,2,3,4,5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene as white crystals (0.0327 g, 82.4%); mp 172.5-174.0  $^\circ\text{C}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  3.89 (d,  $J = 10.6$  Hz, 1 H,  $\text{CH}(\text{CN})_2$ ), 3.41 (d,  $J = 10.6$  Hz, 1 H,  $\text{CH}(\text{cycloheptatriene})$ ), 3.05 (br s, 2 H, CH), 2.99 (br s, 2 H, CH), 2.59 (br s, 2 H, CH), 1.83-0.71 (m, 24 H,  $\text{CH}_2$ ),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.8 MHz)  $\delta$  139.9 (s), 136.0 (s), 130.1 (s), 113.4 (s), 53.2 (d), 37.8 (d), 31.9 (d, two signals), 27.7 (t), 26.1 (t), 25.8 (t), 25.5 (t), 25.3 (t), 25.25 (t), 17.9 (d), IR (KBr) 2938, 2862, 2250, 1470, 1455, 1319, 1192, 1148, 1019, 862, 810  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  ( $\text{C}_6\text{H}_{12}$ ) 228 nm (log  $\epsilon$  4.23), 277 (4.11). Anal. Calcd for  $\text{C}_{28}\text{H}_{32}\text{N}_2$ : C, 84.80, H, 8.13. Found: C, 84.95, H, 8.27.

The products from the entries 4-6 in Table 5 were as follows

7-( $\alpha$ -Cyano-*p*-nitrobenzyl)-1,2,3,4,5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene. white powder; mp 217.5-219  $^\circ\text{C}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  8.17 (d,  $J = 8.8$  Hz, 2 H, Ar-H), 7.27 (d,  $J = 8.8$  Hz, 2 H, Ar-H), 3.62 (d,  $J = 10.9$  Hz, 1 H,  $\text{CHCN}$ ), 3.43 (d,  $J = 10.9$  Hz, 1 H,  $\text{CH}(\text{cycloheptatriene})$ ), 3.12 (br s, 2 H, CH), 3.02 (br s, 1 H, CH), 2.91 (br s, 1 H, CH), 2.66 (br s, 1 H, CH), 2.05 (br s, 1 H, CH), 1.80-0.79 (m, 24 H,  $\text{CH}_2$ ),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.8 MHz)  $\delta$  147.5 (s), 143.2 (s), 138.7 (s), 135.3 (s), 132.5 (s), 129.5 (d), 123.6 (d), 120.8 (s), 58.3 (d), 38.36 (d), 38.31 (d), 32.06 (d), 31.99 (d), 31.95 (d), 31.59 (d), 27.90 (t), 27.80 (t), 26.61 (t), 26.10 (t), 25.95 (t), 25.72 (t), 25.51 (t), 25.46 (t), 25.20 (t), 24.38 (t); IR (KBr) 2930, 2855, 2240, 1600, 1531, 1465, 1450, 1340, 1270, 1120, 1070, 850, 750, 690  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  ( $\text{C}_6\text{H}_{12}$ ) 226 nm (log  $\epsilon$  4.21), 261 (4.00). HRMS (20 eV) ( $\text{M}^+$ ,  $\text{C}_{33}\text{H}_{36}\text{N}_2\text{O}_2$ ) calcd 492 2774, found 492 2766.

7-(1,1-Dicyanoethyl)-1,2,3,4,5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene. white crystals, mp 152.7-154.0  $^\circ\text{C}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  3.85 (s, 1 H,  $\text{CH}(\text{cycloheptatriene})$ ), 2.98 (br s, 4 H, CH), 2.47 (br s, 2 H, CH), 1.79-0.80 (m, 24 H,  $\text{CH}_2$ ), 1.58 (s, 3 H,  $\text{CH}_3$ ),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.8 MHz)  $\delta$  140.35 (s), 139.40 (s), 129.74 (s), 117.10 (s), 61.03 (d), 40.30 (d), 35.23 (s), 32.61 (d), 32.14 (d), 27.82 (t), 26.51 (t), 25.51 (t), 25.47 (t), 24.87 (t), 24.79 (t), 22.99 (q). HRMS ( $\text{M}^+$ ,  $\text{C}_{29}\text{H}_{34}\text{N}_2$ ) calcd 410 2719, found 410 2715.

7-(Dibenzo[*c,g*]fluoren-9-yl)-1,2,3,4,5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene. white crystals, mp 249.5-251  $^\circ\text{C}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  8.70 (d,  $J = 7.7$  Hz, 2 H, H-6,7(dibenzofluorene)), 7.94 (d,  $J = 7.3$  Hz, 2 H, H-3,10(dibenzofluorene)), 7.72, 7.68 (d  $\times$  2,  $J = 8.1$  Hz, 4 H, H-1,2,11,12(dibenzofluorene)), 7.50 (quint, 4 H, H-4,5,8,9(dibenzofluorene)), 3.74 (d,  $J = 10.6$  Hz, 1 H,  $\text{CH}(\text{dibenzofluorene})$ ), 3.23 (br s, 2 H, CH), 3.11 (br s, 2 H, CH), 2.76 (d,  $J = 10.6$  Hz, 1 H,  $\text{CH}(\text{cycloheptatriene})$ ), 2.05 (br s, 2 H, CH), 1.83-0.72 (m, 24 H,  $\text{CH}_2$ ),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.8 MHz)  $\delta$  148.37 (s), 139.53 (s), 137.39 (s), 137.35 (s), 133.86 (s), 133.16 (s), 133.11 (s), 128.45 (d), 128.33 (d), 126.81 (d), 125.61 (d), 124.33 (d), 124.04 (d), 58.13 (d), 44.06 (d), 37.44 (d), 32.22 (d), 32.08 (d), 28.89 (t), 26.82 (t), 26.15 (t), 25.92 (t, two signals), 25.37 (t), IR (KBr) 2950, 2875, 1580, 1460, 1428, 1368, 1328, 1180, 1132, 1013, 820, 750  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  (cyclohexane) 218

nm (log  $\epsilon$  4.89), 245 (4.64), (263 sh (4.38)), 352 (4.13), 370 (4.10). Anal Calcd for C<sub>46</sub>H<sub>44</sub> C, 92.57; H, 7.43 Found C, 92.70, H, 7.43.

A reaction of 4 SbF<sub>6</sub><sup>-</sup> (0.0168 g, 0.0296 mmol) with the 9-cyanofluorenyl anion (Table 5, entry 2) was carried out in the same way. However, upon treatment with H<sub>2</sub>O were formed a large amount of white precipitates, which were collected by filtration, dried under vacuum, and identified as the unchanged 4 SbF<sub>6</sub><sup>-</sup> (0.0090 g, 54%) by NMR analysis. From the ethereal extract was recovered 9-cyanofluorene (0.0082 g, 140%).

For reaction of the entry 1 in Table 5, see the next section

*Isolation of the hydrocarbon salt 4 C<sub>67</sub>H<sub>39</sub><sup>-</sup> (1,2,3,4,5,6-tris(bicyclo[2.2.2]octeno)tropylium tris(7H-dibenzo[c,g]fluorenylidene)methyl)methide)*

To a stirred solution of tris(7H-dibenzo[c,g]fluorenylidene)methyl)methane, C<sub>67</sub>H<sub>40</sub><sup>16c</sup> (0.0223 g, 0.0264 mmol) in THF (1.3 ml) was added a 0.100 M solution of *t*-BuOK in THF (0.245 ml, 0.0245 mmol) under argon. After stirring for 5 min, a solution of 4 SbF<sub>6</sub><sup>-</sup> (0.0150 g, 0.0264 mmol) in THF (1.5 ml) and CH<sub>3</sub>CN (0.2 ml) was added to the resulting deep green solution. After stirring for 5 min in the dark, pentane (30 ml) was added to cause the formation of dark green precipitates, which were collected by filtration under argon. To the precipitates was again added THF (1.5 ml) under argon, and the mixture was centrifuged. The supernatant solution was filtered by a membrane filter (0.45  $\mu$ m), the filtrate being directly dropped into pentane (30 ml) with stirring. The immediately formed dark green precipitates were collected by filtration and dried under vacuum to give a dark green powder analyzed as 4 C<sub>67</sub>H<sub>39</sub><sup>-</sup>·2H<sub>2</sub>O in spite of severe precautions taken against moisture (0.0133 g, 41.6%). mp 192 °C(dec). For the IR and UV-Vis spectral data, see Figures 5 and 6. Anal Calcd for C<sub>92</sub>H<sub>74</sub>O<sub>2</sub> C, 91.20, H, 6.16, F, 0.00 Found: C, 91.29, H, 6.40, F, 0.00

The incorporation of the cation 4 and the anion C<sub>67</sub>H<sub>39</sub><sup>-</sup> was further confirmed as follows. The salt 4 C<sub>67</sub>H<sub>39</sub><sup>-</sup>·2H<sub>2</sub>O (0.00664 g, 5.48 × 10<sup>-4</sup> mmol) was dissolved in DMSO (0.5 ml) under argon, and was shaken with 10% HCl (10 ml) and CCl<sub>4</sub> (1 ml). From the specific absorption of the cation 4 at  $\lambda_{\max}$  308 nm in the UV spectrum of the separated aqueous solution, the amount of 4 was calculated as 5.37 × 10<sup>-4</sup> mmol (97.9%). The TLC analysis (hexane-benzene(1:1)/silica gel) of the CCl<sub>4</sub> solution indicated the presence of C<sub>67</sub>H<sub>40</sub> as a single component.

*Reactions of 7-(dibenzo[c,g]fluoren-9-yl)-1,2,3,4,5,6-tris(bicyclo[2.2.2]octeno)cycloheptatriene (12)*

(a) *With trityl hexafluoroantimonate.* To a solution of 12 (0.0061 g, 0.010 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.5 ml) in an NMR tube (o.d. 5 mm) was added Ph<sub>3</sub>C<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (0.01 g, 0.02 mmol) in one portion under nitrogen. After mixing with vibration for 5 min, the resulting brownish solution was subjected to NMR analyses. The <sup>1</sup>H NMR (270 MHz) showed the signals of 4 together with multiplets at  $\delta$  8.3-7.2 and a singlet at  $\delta$  6.10. The <sup>13</sup>C NMR (67.8 MHz) exhibited the following signals besides those of 4:  $\delta$  144.7, 143.9, 143.2, 131.0, 130.3, 128.4, 128.2, 127.6, 127.0, 126.7, 126.2, 125.4, 124.7, 124.6, 63.6, 53.0

(b) *With CF<sub>3</sub>CO<sub>2</sub>H in CH<sub>2</sub>Cl<sub>2</sub>* A solution of 12 (0.0279 g, 0.0468 mmol) in CF<sub>3</sub>CO<sub>2</sub>H (0.36 ml, 4.7 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (3 ml) was stirred at room temperature for 2 days. Evaporation of the acid and solvent and washing of the residue with ether afforded a brown viscous oil, which exhibited the <sup>1</sup>H (270 MHz) and <sup>13</sup>C NMR (67.8 MHz) signals completely identical to those of 4.

*The pK<sub>R</sub><sup>+</sup> determination*

A buffer solution of pH 10 was prepared by mixing a 0.2 M solution of glycine and a 0.2 M solution of NaOH both in CH<sub>3</sub>CN-H<sub>2</sub>O (1:1). For the preparation of a sample solution, each 1-ml portion of the stock solution, prepared by dissolving 3-4 mg of the cation salt in CH<sub>3</sub>CN (10 ml), was pipetted out and made up to 10 ml by adding H<sub>2</sub>O (1 ml) and the buffer solution. The sample solutions with higher basicity were made by addition of 1-3 drops of 20% or 50% NaOH, or by mixing the sample solutions of appropriately different basicities. The UV-Vis spectrum of the sample solution was recorded using a 1-cm cell thermostated at 25 °C.

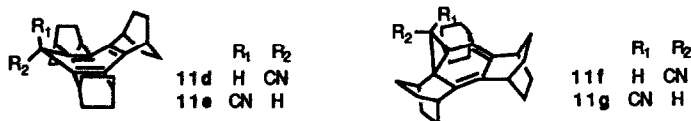
Immediately after recording the spectrum, the pH of each sample solution was determined on a Hitachi-Horiba M-8S pH meter. After complete neutralization of the cation, the reversibility was confirmed by quantitative regeneration of the cation spectrum upon acidification of the sample solution with a few drops of concd H<sub>2</sub>SO<sub>4</sub>. The observed absorbance at the specific absorption wavelength of the cation was plotted against pH to give a classical titration curve, whose midpoint was taken as the pK<sub>R</sub><sup>+</sup>. For the cation **4**, triplicated runs gave the values, 13.15, 12.95, and 12.88, while duplicated runs gave the values 12.70 and 12.00 for the cation **14**.

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### REFERENCES AND NOTES

- According to the IUPAC systematic nomenclature, this cation should be named the 1,2,3,4,5,6-tri(1,4-cyclohexylene)cycloheptatrienylum ion or the 1,2,3,4,5,6-tris(3',4',5',6'-tetrahydro-3',6'-ethanobenzo)-cycloheptatrienylum ion. However, the present naming is used throughout this and related papers because of its advantage in visualizing the molecular structure.
- (a) Kerber, R. C.; Hsu, C.-M. *J Am Chem Soc* **1973**, *95*, 3239-3245. (b) Komatsu, K.; Tomioka, I.; Okamoto, K. *Tetrahedron Lett* **1980**, *21*, 947-950. (c) Moss, R. A.; Munjal, R. C. *Ibid* **1980**, *21*, 1221-1224. (d) Moss, R. A.; Shen, S.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J.; Munjar, R. C. *J Am Chem Soc* **1986**, *108*, 134-140.
- Breslow, R.; Hover, H.; Chang, H. W. *J Am Chem Soc* **1962**, *84*, 3168-3174.
- Komatsu, K.; Takeuchi, K.; Arima, M.; Waki, Y.; Shirai, S.; Okamoto, K. *Bull Chem Soc Jpn* **1982**, *55*, 3257-3261.
- Komatsu, K.; Akamatsu, H.; Okamoto, K. *Tetrahedron Lett* **1987**, *28*, 5889-5890.
- Komatsu, K.; Akamatsu, H.; Jinbu, Y.; Okamoto, K. *J Am Chem Soc* **1988**, *110*, 633-634.
- Komatsu, K.; Jinbu, Y.; Gillette, G. R.; West, R. *Chem Lett* **1988**, 2029-2032. Komatsu, K.; Aonuma, S.; Jinbu, Y.; Tsuji, R.; Hirose, C.; Takeuchi, K. *J Org Chem* **1991**, *56*, 195-203.
- For example, see Olah, G.; Halpern, Y.; Shen, J.; Mo, Y. K. *J Am Chem Soc* **1973**, *95*, 4960-4970. See also the literatures cited in Ref. 9.
- McMurry, J. E.; Lectka, T. *J Am Chem Soc* **1990**, *112*, 869-870.
- Larsen, J. W.; Bouis, P. A.; Watson, C. R., Jr.; Pagni, R. M. *J Am Chem Soc* **1974**, *96*, 2284-2285.
- ter Borg, A. P.; van Helden, R.; Bickel, A. F. *Rec Trav Chim* **1962**, *81*, 164-176.
- This process is interpreted either by (i) spontaneous elimination of hydrogen from **7** to give **4** or by (ii) hydride abstraction by the cation **7** from the starting cycloheptatriene **6** which is supposed to be present, though in a minute amount, in this equilibrated system. The process (i) does not appear likely since the generation of hydrogen could not be detected beyond the experimental error by mass spectrometry.
- All the pK<sub>a</sub> data are taken from *Lange's Handbook of Chemistry*, 13th edition, ed. Dean, J. A. **1985**, McGraw-Hill, New York.
- The values of steric energy (SE) calculated by MMP2 for **11a**, **11b**, and **11c** are 51.9, 54.6, and 53.5 kcal/mol, respectively. The apparently more favorable isomers **11d** and **11e**, whose SE's were calculated as 49.3 and 47.2 kcal/mol respectively, were not found in the product. The reason for this is not clear at present, but might be attributed to the electronic assistance of the cyano group to shifting the cycloheptatriene-norcaradiene equilibrium toward the latter. The norcaradiene forms **11f** and **11g** containing the cyclopropane ring are apparently more strained than **11a-c**, and consequently the formation of **11d** and **11e** would be thermodynamically unfavorable.



- 15 Arnett, E M , Chawla, B , Molter, K , Amarnath, K , Healy, M *J Am Chem Soc* **1985**, *107*, 5288-5289
- 16 (a) Okamoto, K , Kitagawa, T , Takeuchi, K , Komatsu, K , Takahashi, K *J Chem Soc , Chem Commun* **1985**, 173-174 (b) Okamoto, K , Kitagawa, T , Takeuchi, K , Komatsu, K , Miyabo, A *Ibid* **1988**, 923-924 (c) Okamoto, K., Kitagawa, T.; Takeuchi, K , Komatsu, K , Kinoshita, T , Aonuma, S ; Nagai, M., Miyabo, A *J Org Chem* **1990**, *55*, 996-1002
- 17 Kuhn, R.; Rewicki, D. *Angew Chem.* **1967**, *79*, 648-649
- 18 For example, the  $pK_{R^+}$  value of the heptamethyltropylium ion (4 86 in  $CH_3CN-H_2O$  (1.1)) was found to be considerably lower than that of the hexamethyl derivative (6 60) Okamoto, K.; Takeuchi, K , Komatsu, K , Kubota, Y , Ohara, R., Arima, M , Takahashi, K , Waki, Y , Shirai, S *Tetrahedron* **1983**, *39*, 4011-4024
- 19 For example, see ter Borg, A P , Kloostertiel, H *Rec Trav. Chim.* **1969**, *88*, 266-274
20. For example, see ter Borg, A P., Razenberg, E ;Kloostertiel, H. *Chem Commun* **1967**, 1210-1210
- 21 The similar tendency in the  $^{13}C$  NMR chemical shifts of the tropylium ring carbons is observed when  $^{13}C$  NMR data of the heptamethyltropylium ion ( $^{13}C$  NMR ( $CD_3CN$ ) 160.3) is compared with those of the hexamethyltropylium ion ( for the substituted carbons 164.4, 162 1, 160 6) Takeuchi, K , Yokomichi, Y , Okamoto, K *Tetrahedron* **1980**, *36*, 2945-2953
- 22 Arndt, F. *Org Synth* **1943**, *Coll Vol 2*, 461-464.
- 23 Thummel, R P., Chayangkoon, P. *J Org Chem* **1983**, *48*, 596-601