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Syntheses and Properties of the Polymethylenebis(diphenylcyclopropenium) Dications[1]

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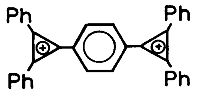
A series of polymethylenebis(diphenylcyclopropenium) dications with the polymethylene chain of one to six carbons ($\mathbf{4}_{n=1-6}$) were synthesized and characterized by spectral and analytical means. Among the dications $\mathbf{4}_{n=3-6}$ which were isolated as perchlorates, $\mathbf{4}_{n=3}$ was shown by the pK_{R^+} measurements to be destabilized by 1.3 pK units as compared with $\mathbf{4}_{n=4-6}$. The values of reduction potential exhibited the same tendency. The chromium(II) ion reduction of $\mathbf{4}_{n=6}$, a representative dication, afforded a polymeric material containing a hexylbenzene unit. The dication $\mathbf{4}_{n=2}$ was isolable only as a complex salt with $SbCl_6^-$ and Cl^-: the conventional hydride abstraction from 1,2-dicyclopropenylethane using trityl perchlorate resulted in rearrangements affording 4,9,10-triphenylphenanthrene and the unknown monocation $C_{32}H_{25}^+$ containing the tropylium ring. A possible mechanism for these rearrangements is presented. On the other hand, the dication $\mathbf{4}_{n=1}$ was observable only in a highly acidic solution due to the ready deprotonation yielding a new fully conjugated monocation **17**. This cation, characterized by remarkable stability (pK_{R^+} 8.9 in 50% aq acetonitrile), is formally represented as a triafulvene with a cyclopropenium ring substituted at the 4-position, but is shown to have a partially polarized electronic structure by ^{13}C NMR spectroscopy.

The divalent carbocations are typically classified into two groups, namely, the dipositive ions, in which the dipositive charge resides on one fully conjugated π-system, as exemplified by the cyclobutadienyl[2] and cyclooctatetraenyl[3] dipositive ions, and the carbodications, which contain two separate monocationic units in the same molecule.

In the latter class of dications, those having tertiary-alkyl cationic units are observable only in solution under stable-ion conditions,[4] but those carrying nonbenzenoid aromatic cations are generally stable enough for isolation and for further investigation on their structure and reactivity. Thus, there have already been reported as stable species a variety of polyvalent cations containing two[5] or more[6] tropylium rings. Dications composed of two diaminocyclopropenium rings connected by a cyclopentadiene ring[7a] and by various hetero-atom linkages[7b—d] have also been synthesized, together with the directly bonded bis(diaminocyclopropenium) dications;[7e] even the tetracation consisting of three diaminocyclopropenium rings bonded to the central cyclopropenium ring has been reported.[8] However, studies on the dicyclopropenylio-dications carrying no stabilizing hetero atom seem to be quite limited; the reported examples are *p*-phenylenebis(diphenylcyclopropenium) dication (**1**) synthesized by Eicher and Berneth,[9] and 1,8- (**2**) and 1,5-naphthylenebis(diphenylcyclopropenium) dication (**3**), synthesized by us.[10]



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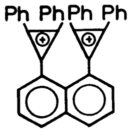

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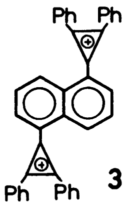

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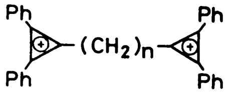
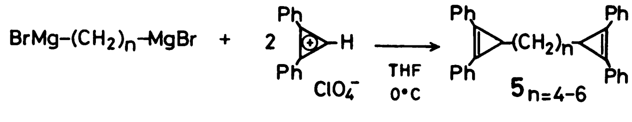
In connection with our previous work on the syntheses and both inter- and intramolecular reductive cyclization of the polymethylenebistropylium dications,[5h] we have synthesized a series of new dicyclopropenylio-dications, *i.e.* the polymethylenebis(diphenylcyclopropenium) dications ($\mathbf{4}_{n=1-6}$), and examined their stability and reducibility with reference to the polymethylene chain length. In this paper, these results will be described, together with unusual molecular rearrangements observed during the course of syntheses.[1b]



$\mathbf{4}_{n=1-6}$

Syntheses of Polymethylenebis(diphenylcyclopropenium) Dications ($\mathit{4}_{n=1-6}$). It has been reported that chlorophenylcarbene thermally generated from chlorophenyldiazirine readily adds to mono- and diphenylacetylenes to give the chlorocyclopropene derivatives, which can be converted to the cyclopropenium ions.[11] This method has been successfully applied to the synthesis of the dication **3** in our previous work.[10] Thus, we first attempted the thermal reaction of two molar equivalents of chlorophenyldiazirine with 1,8-diphenyl-1,7-octadiyne as a representative alkadiyne. The product, however, was an intractable mixture of unwanted materials, and there was observed no indication of the formation of the cyclopropenyl or cyclopropenium ring. Apparently the first formed 1-alkyl-3-chloro-2,3-diphenylcyclopropene was unstable and was subjected to further reactions; several modifications of the reaction conditions did not improve the results.

Subsequently, we examined direct coupling of the di-Grignard reagent, α,ω-(bromomagnesio)alkanes, with the diphenylcyclopropenium ion as shown in Scheme 1, and obtained the corresponding α,ω-bis(2,3-diphenyl-2-

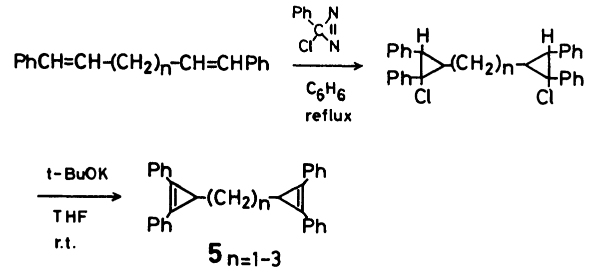


Scheme 1.

TABLE 1. SPECTRAL PROPERTIES OF α,ω-BIS(2,3-DIPHENYL-2-CYCLOPROPENYL)ALKANES ($\mathbf{5}_{n=1-6}$)

5	IR (KBr)[a] ν/cm^{-1}	UV (CHCl$_3$) λ_{max}/nm (log ε)	^{1}H NMR (CDCl$_3$) δ from Me$_4$Si
$n=1$	1815	317sh(4.66)	7.73 (m, 8H, *o*-H)
		327(4.74)	7.36 (m, 12H, *m*, *p*-H)
		344(4.61)	2.41 (t, 2H, >CH–)
			1.92 (t, 2H, –CH$_2$–)
$n=2$	1807	317sh(4.65)	7.61 (m, 8H, *o*-H)[b]
		326(4.72)	7.30 (m, 12H, *m*, *p*-H)
		344(4.57)	2.17 (m, 2H, >CH–)
			1.84 (d, 4H, –CH$_2$–)
$n=3$	1810	317sh(4.69)	7.63 (m, 8H, *o*-H)
		326(4.74)	7.33 (m, 12H, *m*, *p*-H)
		344(4.59)	2.17 (t, 2H, >CH–)
			1.72 (br s, 6H, –CH$_2$–)
$n=4$	1808	316sh(4.68)	7.64 (m, 8H, *o*-H)
		325(4.75)	7.34 (m, 12H, *m*, *p*-H)
		343(4.60)	2.14 (t, 2H, >CH–)
			1.60 (br s, 8H, –CH$_2$–)
$n=5$	1806	317sh(4.68)	7.61 (m, 8H, *o*-H)[b]
		325(4.74)	7.25 (m, 12H, *m*, *p*-H)
		344(4.59)	2.10 (t, 2H, >CH–)
			1.51 (br s, 10H, –CH$_2$–)
$n=6$	1810	316sh(4.68)	7.67 (m, 8H, *o*-H)
		325(4.74)	7.37 (m, 12H, *m*, *p*-H)
		343(4.60)	2.16 (t, 2H, >CH–)
			1.47 (br s, 12H, –CH$_2$–)

a) ν(cyclopropene). b) Taken in CCl$_4$.

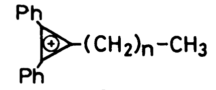


Scheme 2.

cyclopropenyl)alkanes ($\mathbf{5}_{n=4-6}$) in 37—60% yield. This method, however, is applicable only to the compounds with $n \geq 4$ due to the synthetic limitation for the di-Grignard reagent. For the syntheses of the dicyclopropenylalkanes $\mathbf{5}_{n=1-3}$, we adopted a stepwise method involving the addition of chlorophenylcarbene to the α,ω-alkadienes and the subsequent elimination of HCl, as shown in Scheme 2. The crude overall yield for $\mathbf{5}_{n=1-3}$ was 43—57%, based on the alkadienes. The dicyclopropenylalkanes $\mathbf{5}_{n=1-6}$ thus obtained were characterized by the spectral data listed in Table 1.

For the purpose of conversion to the polymethylenebiscyclopropenium dication **4**, the dicyclopropenylalkanes $\mathbf{5}_{n=1-6}$ were treated with two equivalents of trityl perchlorate. In the case with the polymethylene chain length of three to six carbons, the corresponding perchlorate salts of the dications $\mathbf{4}_{n=3-6}\cdot 2ClO_4^-$, were obtained as white powder in 70—94% yield. When the 1,2-dicyclopropenylethane $\mathbf{5}_{n=2}$ was treated with the trityl cation, an unexpected rearrangement occurred as a main reaction, as will be described later in detail. Among various other hydride-abstraction reagents examined, only antimony pentachloride[12] was effective to give a dicationic salt, which was analyzed as $\mathbf{4}_{n=2}\cdot 0.5SbCl_6^-\cdot 1.5Cl^-$, with no attendant rearrangement. On the other hand, the methylenebiscyclopropenium dication $\mathbf{4}_{n=1}$,[1b] obtained by the reaction of $\mathbf{5}_{n=1}$ with two equivalents of the trityl cation, was observable only in the highly acidic solution (*e.g.* in CF$_3$CO$_2$H–CF$_3$SO$_3$H (9 : 1)) owing to its ease in deprotonation which afforded the fully conjugated monocations, as will also be shown later.

Properties of the Polymethylenebis(diphenylcyclopropenium) Dications ($4_{n=1-6}$). The dicyclopropenylio-dications $\mathbf{4}_{n=1-6}$ are characterized by the spectral properties shown in Table 2, which also includes the data for the related monocations $\mathbf{6}_{n=0-3}$ and **17** (*vide infra*) for comparison. All the di- and monocations (except **17**) exhibit strong IR absorption due to the cyclopropenium ring stretching near 1420 cm^{-1} and characteristic UV absorptions near 247, 293, and 307 nm. In the ^{1}H NMR spectra the methylene protons of the dications **4** are generally deshielded compared with the corresponding protons of the monocations **6**. Among the dications, the signals for each methylene proton are gradually shifted downfield as the chain length decreases. This tendency in methylene chemical shifts suggests the presence of some repulsive interaction between the two cationic rings through the polymethylene chain.



$\mathbf{6}_{n=0-3}$

In order to examine the effect of such repulsive interaction, the pK_{R^+} and reduction potential of the purely isolated perchlorates of the dications $\mathbf{4}_{n=3-6}$ were determined by the use of the spectrophotometric method and cyclic voltammetry (CV), respectively. The results are shown in Table 3, together with the data for $\mathbf{6}_{n=2}$ as the representative monocation for comparison. For the dications, two pK_{R^+} values were determined, corresponding to the stepwise neutralization sequences for the two cationic units present at both ends of the polymethylene chain. The comparison of pK_{R^+} values for the first neutralization clearly shows that the dication $\mathbf{4}_{n=3}$, with the chain length of only three carbons, is destabilized by 1.3 pK units, *i.e. ca.* 1.8 kcal/mol at 25 °C, as compared with the dications with longer chain length.

The values of reduction potential also exhibit the same tendency; the dication $\mathbf{4}_{n=3}$ is most susceptible towards the electrochemical one-electron reduction. Notice here that the reduction wave observed at the potential listed in Table 3 is irreversible, and only corresponds to the first one-electron transfer to the dicationic species; this was determined from the comparison of the peak current with that of ferrocene determined under the identical conditions. The second reduction wave was not clearly observed in the sweep range of 0 to −2.0 V *vs.* Ag/Ag$^+$. This is presumably

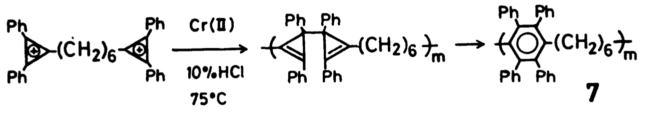
TABLE 2. SPECTRAL PROPERTIES OF THE SALTS OF POLYMETHYLENEBIS(DIPHENYLCYCLOPROPENIUM) DICATIONS ($\mathbf{4}_{n=1-6}$) AND 1-ALKYL-2,3-DIPHENYLCYCLOPROPENIUM ($\mathbf{6}_{n=0-3}$) AND 1,2-DIPHENYL-3-(1,2-DIPHENYLTRIAFULVEN-4-YL)CYCLOPROPENIUM (**17**) MONOCATIONS

Cation salt	IR (KBr) ν/cm^{-1}	UV (MeCN) λ_{max}/nm (log ε)	^{1}H NMR (CF$_3$CO$_2$H) δ from Me$_4$Si
$\mathbf{4}_{n=1}$	—	298(4.77)[a] 313(4.78)	8.41 (m, 8H, *o*-H)[a] 7.90 (m, 12H, *m*, *p*-H) 6.19 (s, 2H, -CH$_2$-)
$\mathbf{4}_{n=2}\cdot 0.5SbCl_6^-\cdot 1.5Cl^-$	1420[b]	247(4.53) 292(4.66) 308(4.63)	—[c]
$\mathbf{4}_{n=3}\cdot 2ClO_4^-$	1420[b] 1090[d]	247(4.53) 292(4.80) 306(4.81)	8.42 (m, 8H, *o*-H) 7.90 (m, 12H, *m*, *p*-H) 4.10 (t, 4H, α-CH$_2$-) 3.27 (quint, 2H, β-CH$_2$-)
$\mathbf{4}_{n=4}\cdot 2ClO_4^-$	1420[b] 1090[d]	247(4.38) 293(4.80) 306(4.82)	8.38 (m, 8H, *o*-H) 7.90 (m, 12H, *m*, *p*-H) 3.87 (br t, 4H, α-CH$_2$-) 2.62 (br m, 4H, β-CH$_2$-)
$\mathbf{4}_{n=5}\cdot 2ClO_4^-$	1420[b] 1090[b]	247(4.43) 294(4.80) 307(4.80)	8.39 (m, 8H, *o*-H) 7.92 (m, 12H, *m*, *p*-H) 3.77 (t, 4H, α-CH$_2$-) 2.49 (m, 4H, β-CH$_2$-) 2.10 (m, 2H, γ-CH$_2$-)
$\mathbf{4}_{n=6}\cdot 2ClO_4^-$	1420[b] 1090[d]	246(4.53) 293(4.78) 306(4.79)	8.36 (m, 8H, *o*-H) 7.91 (m, 12H, *m*, *p*-H) 3.72 (t, 4H, α-CH$_2$-) 2.37 (m, 4H, β-CH$_2$-) 1.90 (br m, 4H, γ-CH$_2$-)
$\mathbf{6}_{n=0}\cdot BF_4^-$[e]	1425[b] 1060[g]	243(4.16) 290(4.53) 304(4.55)	8.37 (m, 4H, *o*-H)[f] 7.87 (m, 6H, *m*, *p*-H) 3.20 (s, 3H, -CH$_3$)
$\mathbf{6}_{n=1}\cdot BF_4^-$	1420[b] 1055[g]	244(4.20) 290(4.53) 304(4.55)	8.37 (m, 4H, *o*-H) 7.92 (m, 6H, *m*, *p*-H) 3.63 (q, 2H, -CH$_2$-) 1.80 (t, 3H, -CH$_3$)
$\mathbf{6}_{n=2}\cdot BF_4^-$[h]	1420[b] 1055[g]	244(4.20) 290(4.50) 304(4.52)	8.27 (m, 4H, *o*-H) 7.93 (m, 6H, *m*, *p*-H) 3.52 (t, 2H, α-CH$_2$-) 2.25 (sext, 2H, β-CH$_2$-) 1.27 (t. 3H, -CH$_3$)
$\mathbf{6}_{n=3}\cdot BF_4^-$[e]	1418[b] 1055[g]	244(4.23) 290(4.54) 304(4.55)	8.39 (m, 4H, *o*-H)[f] 7.91 (m, 6H, *m*, *p*-H) 3.62 (t, 2H, α-CH$_2$-) 2.14 (quint, 2H, β-CH$_2$-) 1.57 (sext, 2H, γ-CH$_2$-) 1.04 (t, 3H, -CH$_3$)
$\mathbf{17}\cdot ClO_4^-$	1435[b] 1090[d]	243(4.45) 269(4.51) 353(4.77)	8.17 (m, 8H, *o*-H) 7.73 (m, 12H, *m*, *p*-H)

a) Observed in CF$_3$CO$_2$H–CF$_3$SO$_3$H (9 : 1). b) ν(cyclopropenium ring). c) Not measured due to poor solubility in the common solvents. d) ν(ClO$_4^-$). e) K. Komatsu, T. Niwa, and K. Okamoto; unpublished results. f) Taken in CD$_3$CN. g) ν(BF$_4^-$). h) Ref. 13.

due to the rapid coupling of the first formed cation-radical to give the dimeric dication, which upon further reduction and repeated coupling gives some polymeric material which accumulates at the electrode surface. Actually, this polymerization, which supposedly results in the coating of the working electrode, caused marked depression of the reduction wave (to less than one third of the peak height of each previous scan) at the second and subsequent scans.

Chromium(II) Ion Reduction of the Hexamethylenebis-(diphenylcyclopropenium) Dication ($4_{n=6}$). The above-mentioned result of the electrochemical reduction led us to investigate the chemical reduction of the dicyclopropenylio-dication. In our previous kinetic and product study, the 1,2-diphenyl-3-propylcyclopropenium ion was found to be reduced by the chromium(II) ion in 10% HCl at 75 °C smoothly to give the dimer of the corresponding cyclopropenyl radical in good yield (82.1%).[13] Thus, the chromium(II) ion reduction was carried out under similar reaction conditions on $\mathbf{4}_{n=6}$ as the representative dication. The product, obtained as a yellowish solid in 81% yield, exhibited the IR absorptions only for the polymethylene chain and the benzene nuclei, but no absorption for the cyclopropene structure near 1800 cm^{-1}; the ^{1}H NMR spectrum showed only two broad signals, one centered at δ 7.2 and the other ranging from δ 2.5 to 0.9, with an integrated ratio of 5 : 3. This product was developed on a TLC plate (SiO$_2$) as a streak with benzene–hexane (1 : 1) as a solvent but not as spots, as are commonly observed for polymeric hydrocarbons. Based on these findings, the product is supposed to be an oligomer or a polymer of the structure such as **7**, formed by repeated coupling of the cyclopropenyl radicals generated at both ends of the polymethylene chain, followed by the subsequent "bicyclopropenyl→benzene" rearrangement,[14] as shown in Scheme 3.



Scheme 3.

The same type of polymerization has already been observed upon the chromium(II) ion reduction of polymethylenebistropylium dications under similar reaction conditions.[5h)]

Reaction of 1,2-Bis(2,3-diphenyl-2-cyclopropenyl)ethane ($5_{n=2}$) with the Trityl Cation Accompanied by Molecular Rearrangements. As has been mentioned, unexpected rearrangements were observed upon hydride abstraction from the dicyclopropenylethane $\mathbf{5}_{n=2}$. When two equivalents of trityl perchlorate were allowed to react with $\mathbf{5}_{n=2}$ in dichloromethane at room temperature, a mild exothermic reaction took place, as shown by the immediate darkening of the reaction mixture. However, no dicationic salt was obtained but rather some unknown monocationic salt with the molecular formula $C_{32}H_{25}ClO_4$† (40.7% yield based on $\mathbf{5}_{n=2}$) upon precipitation with ether. After hydrolysis of the filtrate and the usual work-up, the rest of the products were separated and identified as a hydrocarbon with the molecular formula $C_{32}H_{22}$ (46.3% yield based on $\mathbf{5}_{n=2}$), triphenylmethane (50.9% yield based on Ph$_3$C$^+$), and triphenylmethanol (32.9% yield based on Ph$_3$C$^+$). The product distribution was not affected greatly, the variation in the yield being less than 15% of the above values, upon changes in reaction temperature (0 to 60 °C), in mode of addition (*i.e.* inverse addition), and in the solvent to more polar acetonitrile and even to trifluoroacetic acid. Triphenylmethanol is apparently derived from the unchanged trityl cation, since the product distribution was not changed when the reaction was carried out with only one equivalent of the trityl salt. These results suggest that some rearrangement of the dicyclopropenylethane structure took place immediately after abstraction of one equivalent of the hydride ion from $\mathbf{5}_{n=2}$.

The hydrocarbon $C_{32}H_{22}$, which exhibits the parent peak at *m/e* 406 in the mass spectrum, does not react with bromine, and no longer retains any cyclopropene ring, as is also shown by the absence of specific IR absorption near 1800 cm^{-1}; rather, the absorptions at 820 and 727 cm^{-1} suggest the presence of a phenanthrene framework. In the ^{1}H NMR spectrum taken in CCl$_4$, which exhibits signals for only the aromatic protons mainly at δ 7.47—7.10, two rather broad singlets are prominent at δ 7.42 (5H) and 7.15 (10H), together with a small doublet at δ 7.78 (1H, *J*=8.5 Hz). The two broad singlets seem to represent two types of phenyl groups, both of which are in a conformation that prevents effective conjugation with the other aromatic nucleus, and are thus reasonably correlated with the phenyl signals in 4-phenylphenanthrene (δ 7.36)[15] and in 9,10-diphenylphenanthrene (δ 7.20),[16] respectively. The doublet at δ 7.78, on the other hand, seems to correspond to 4-phenylphenanthrene's H-5 (δ 7.60),[15] which is markedly shielded by the oposing phenyl group as compared with H-4,5 (δ 8.55)[15] in phenanthrene itself. Based on these facts, together with other similarities in the UV spectrum (λ_{max} (cyclohexane) 264 nm (log ε, 4.59), 271 sh (4.57), 304 sh (4.18)) with that for 9,10-diphenylphenanthrene (λ_{max} (cyclohexane) 260 nm (log ε, 4.52), 271 (4.20), 302 (4.00)),[16,17] the hydrocarbon $C_{32}H_{22}$ is assigned to 4,9,10-triphenylphenanthrene (**15**) as the most probable structure.

TABLE 3. THE pK_{R^+} AND REDUCTION POTENTIAL OF THE DICATIONS $\mathbf{4}_{n=3-6}$ AND THE MONOCATION $\mathbf{6}_{n=2}$

Cation	pK_{R^+} a)	Red'n potential b) V *vs.* Ag/Ag$^+$
$\mathbf{4}_{n=3}$	2.06 (4.50)	−0.95
$\mathbf{4}_{n=4}$	3.38 (4.75)	−1.16
$\mathbf{4}_{n=5}$	3.35 (4.80)	−1.26
$\mathbf{4}_{n=6}$	3.35 (4.67)	−1.28
$\mathbf{6}_{n=2}$	3.52	−1.31

a) Measured in 50% aq MeCN at 25°C. The values for the second neutralization are given in the parentheses.
b) The peak potential observed by CV in MeCN with Bu$_4$N$^+$ClO$_4$$^-$ as a supporting electrolyte.

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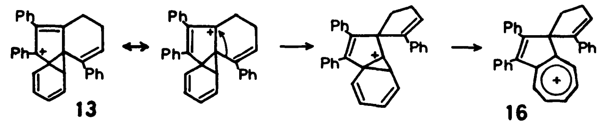
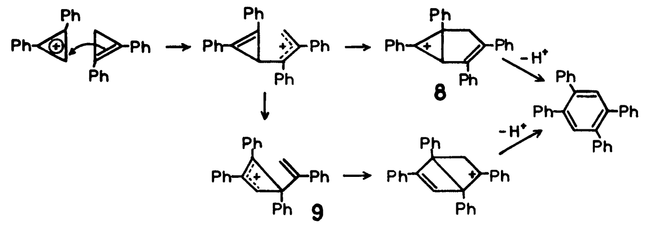
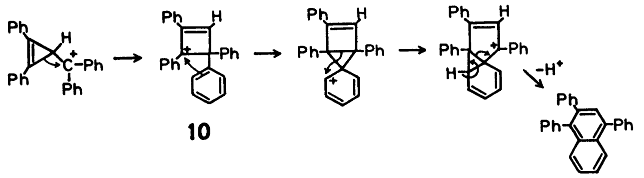
† This cation salt is yellow and exhibits no IR absorption for the cyclopropenium ring. From the ^{1}H and ^{13}C NMR data (see Experimental), the long-wave UV-Vis absorption (λ_{max} (MeCN) 433 nm), high stability (pK_{R^+} 6.89 in 23% EtOH),and the facile NaBH$_4$ reduction to the cycloheptatriene derivative, this cation is supposed to have a structure composed of the tropylium ring with a conjugative substituent. Assuming that this cation is derived as shown below from the same reaction intermediate (**13** in Scheme 6) as the one leading to the phenanthrene **15**, the structure **16** may be tentatively assigned to this cation.

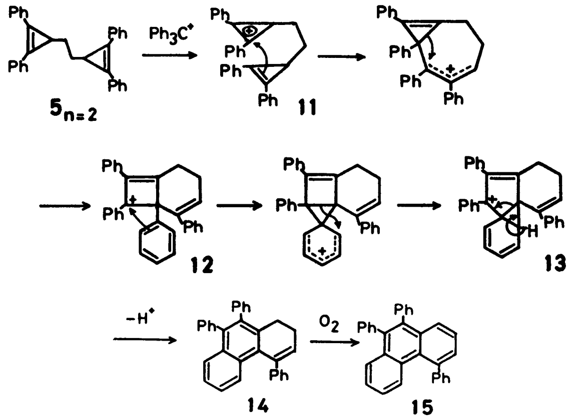




Scheme 4.



Scheme 5.

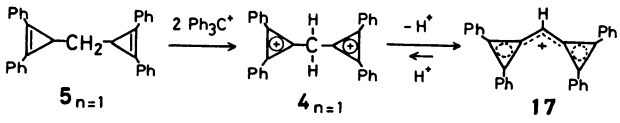


Scheme 6.

1,2-Diphenylcyclopropene is known to react with the diphenylcyclopropenium ion to give 1,2,4,5-tetraphenylbenzene according to Scheme 4.[18] The mechanism proceeding through the cation **9** seems more likely than the originally reported one involving the cation **8**, as judged from the results of later work by Moerck and Battiste[19] and by Weiss and Andrae.[14b] On the other hand, a unique rearrangement of the cyclobutenyl cation **10** giving the naphthalene derivative (Scheme 5) has also been reported by Breslow and Battiste.[20] Considering the mutual accessibility of the two three-membered rings connected by an ethylene linkage in $\mathbf{5}_{n=2}$, it seems reasonable to interpret the observed transformation of $\mathbf{5}_{n=2}$ to **15** in analogy with these two reported rearrangements, as shown in Scheme 6: the intramolecular cyclization of the first formed monocation **11**, followed by the subsequent rearrangement to the cyclobutenyl cation **12**, and the ring expansion of **12** to **14** through **13** are formally analogous to the rearrangements shown in Schemes 4 and 5, respectively. Since in the ^{1}H NMR spectrum of the crude product the presence of the ethylenic linkage was indicated by two rather broad multiplets at δ 2.45 and 2.15, the aromatization of **14** to the phenanthrene **15** is supposed to have occurred by air oxidation during the course of isolation procedures involving the repeated preparative TLC, in which exposure to air was inevitable.

The reaction of $\mathbf{5}_{n=2}$ with various other hydride abstraction reagents was surveyed to see if the rearrangement of **11** can be suppressed to allow the formation of the dication $\mathbf{4}_{n=2}$. However, the course of the reaction was not changed by the use of such reagents as: diphenylmethyl cation,[12] which is less stable and supposed to have stronger hydride abstracting ability than the trityl cation; 2,3-dichloro-5,6-dicyano-*p*-benzoquinone[21] with high complexing ability with the produced cation; and the Lewis acids, *e.g.* phosphorus pentachloride and boron trifluoride etherate.

Reaction of Bis(2,3-diphenyl-2-cyclopropenyl)methane ($5_{n=1}$) with the Trityl Cation——The Formation of the 1,2-Diphenyl-3-(1,2-diphenyltriafulven-4-yl)cyclopropenium Ion (17).[1b] As has already been described briefly, when the dicyclopropenylmethane $\mathbf{5}_{n=1}$ was treated with two equivalents of trityl perchlorate, the perchlorate of the expected dication was not obtained but rather that of the monocation, which was yellow and analyzed as $C_{31}H_{21}ClO_4$. The spectral data are included in Table 2. While the presence of the cyclopropenium ring is clearly exhibited by the broad and strong IR absorption at 1435 cm^{-1}, in the ^{1}H NMR spectrum taken in CD_3CN (Fig. 1a) the signal for the proton of the central carbon appears as a singlet at the olefinic range (δ 6.52), and the signals for the phenyl protons are somewhat shifted upfield compared with those for the dications $\mathbf{4}_{n=3-6}$ implying an appreciable decrease of positive charge in the three-membered rings. The multiplicity of the phenyl signals also indicates the restricted rotation of the three-membered ring with respect to the bond



Scheme 7.

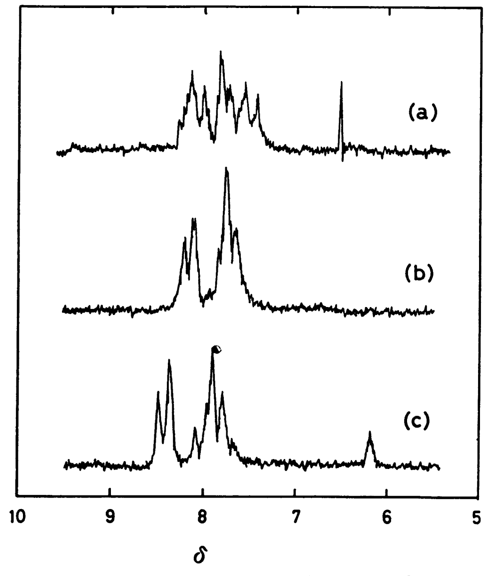


Fig. 1. The ^{1}H NMR spectra of the triafulvenylcyclopropenium ion **17** (a) in CD_3CN, (b) in CF_3CO_2H, and (c) in CF_3CO_2H-CF_3SO_3H (9 : 1).

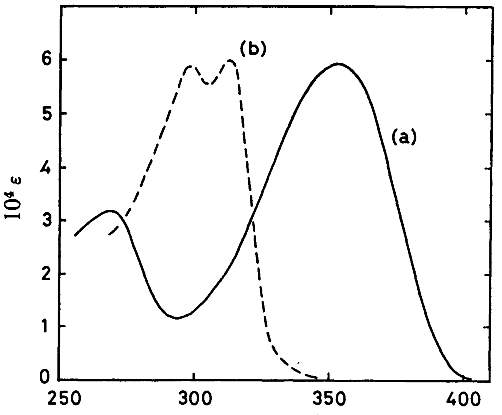
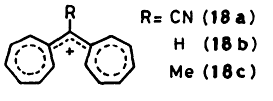


Fig. 2. The UV spectra of the triafulvenylcyclopropenium ion **17** (a) in MeCN and (b) in CF_3CO_2H-CF_3SO_3H (95:5).

connecting the central carbon and the three-membered ring. These data are most compatible with the assignment of the fully conjugated structure **17**, formed by deprotonation of the first formed dication $\mathbf{4}_{n=1}$ (Scheme 7), to this new monocation. In the ^1H NMR spectrum taken in trifluoroacetic acid (Fig. 1b), the olefinic proton signal disappears, presumably owing to the rapid proton exchange process occurring in the equilibrium between **17** and $\mathbf{4}_{n=1}$. When the stronger acid, CF_3SO_3H, is added (*ca.* 10%), the equilibrium is shifted towards the dication $\mathbf{4}_{n=1}$, as shown by the appearance of a methylene singlet at δ 6.19 (2H) and the downfield shift of the phenyl protons (Fig. 1c). Similarly, the long-wavelength absorption of **17** at 353 nm in acetonitrile, reflecting the fully conjugated structure, is shifted upon addition of CF_3SO_3H to 313 nm (log ε, 4.78) and 298 nm (4.77), which is a characteristic absorption pattern for the cyclopropenium ion, as shown in Fig. 2.

The stable monocations having a similar type of cross-conjugated structure, such as **18**[22] and **19**,[23] have been synthesized by Kitahara *et al*, and the analogous anion **20** by Jutz and Amschler.[24] The monocation **17** is thus regarded as the smallest-ring member in the family of these cross-conjugated ionic systems, and its stability is of much interest. The preliminary measurement of its pK_{R^+} value was carried out spectrophotometrically in 23% ethanol. In this solvent a considerable decomposition of the cation was observed after partial hydrolysis commenced at pH 7.1. Based on the plot of absorbance of the cation at 350 nm recorded at 15 min after preparation of the sample solution against the pH value, the pK_{R^+} was determined to be 7.23; however, this value should be considered as somewhat smaller than the true value, when the partial decomposition is taken into account. In 50% aq acetonitrile, the cation was found to be more stable, not being neutralized appreciably until the pH of the solution reached 8.0. In the solution with the pH near 10, almost all of the cation was neutralized, but about 90% of the cation was regenerated upon acidification. From the absorbance-pH plot, the most probable value for pK_{R^+} was determined to be surprisingly high, *i.e.* 8.9±0.2, for such a strained molecule. This remarkable increase in stability, as compared with the cation **18b** (pK_{R^+} 7.49 in 10% ethanol),[22b)] may have arisen from the increased aromatic character in **17** with four stabilizing phenyl substituents. This result is in good agreement with the ^{13}C NMR data shown below.



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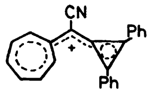

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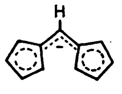

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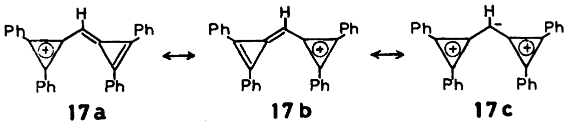
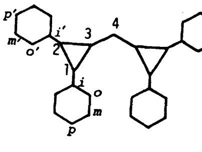
The ^{13}C NMR spectrum of **17** measured in CD_3CN exhibited the following signals (in the parentheses are given the peak multiplicity in the off-resonance spectrum, assignments,[††] and the charge density calculated by simple HMO method using the following parameters; $\beta_{1,3}=\beta_{2,3}=0.9$, $\beta_{C-Ph}=0.8$): δ (ppm from Me_4Si) 144.0 (s), 145.0 (s) (C-1, C-2; charge density +0.1833); 148.4 (s) (C-3; +0.1955); 68.6 (d) (C-4; −0.2632); 122.6 (s), 123.0 (s) (C-*i*, C-*i*′; −0.0106); 133.4 (d), 134.4 (d) (C-*o*, C-*o*′; +0.0166); 130.5 (d), 131.0 (d) (C-*m*, C-*m*′; −0.0007); and 135.7 (d), 136.4 (d) (C-*p*, C-*p*′; +0.0134). The planarity of the whole π-system in **17** is clearly demonstrated by the appearance of C-1, C-2, and phenyl carbons in sets of pairs of signals. It should be noted here that the central carbon, C-4, is resonating at an unusually high field at δ 68.6. This marked upfield shift is attributable to the considerable amount of negative charge residing on this carbon, which is in agreement with the calculated result. This spectral feature thus demonstrates the significant contribution of the dipolar structure, **17c**, with both of the three-membered rings positively charged, to the resonance hybrid of **17** (Scheme 8). A similar type of polarization seems to be present also in cation **18**, as shown by the charge density (−0.1972) calculated by the same method for the central carbon of **18b** and the ^{13}C chemical shift (δ 100.1) observed for **18a**.[25] However, comparison of these values with those for the cation **17** indicates that the contribution of such a polar structure is greater in **17** than in **18**. Thus, it is supposed that this greater polarization in **17**, which forms the two Hückeloid aromatic rings, has caused a considerable



Scheme 8.

[††] The numbering system is as follows:



17

increase in the aromatic stabilization of the cation **17**, as has already been noted from its $\mathrm{p}K_{\mathrm{R}^+}$ value.

Experimental

Melting and boiling points are uncorrected. Elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. IR and UV-Vis spectra were recorded with a Hitachi 215 and a Hitachi 200-10 spectrometers, respectively. ^{1}H NMR spectra were taken on a Hitachi R-24 (60 MHz) and on a Varian HA-100 (100 MHz) spectrometers, with Me_4Si as an internal standard. ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer (25 MHz) operated in the pulse Fourier transform mode. Mass spectra were recorded with a JEOL JMS-01SG spectrometer.

All reagents were of reagent-grade quality unless otherwise noted. MeCN and CH_2Cl_2 were refluxed and distilled over P_2O_5, and THF was distilled over $LiAlH_4$. Merck SiO_2 type GF_{254} and type PF_{254} were used for analytical and preparative TLC, respectively.

Diphenylcyclopropenium Perchlorate. To a stirred solution of bis(2,3-diphenyl-2-cyclopropenyl) ether[11] (3.32 g; 8.33 mmol) in THF (10 ml) and ether (90 ml) was added dropwise 70% $HClO_4$ (3.62 g) at 0 °C. The resulting white precipitates were filtered, washed with ether, and dried under reduced pressure to give diphenylcyclopropenium perchlorate (4.01 g; 82.8%) as white powder: mp 148.5—150.0 °C (decomp) (lit, mp 149.5—150.5 °C (decomp)).[26]

Bis(2,3-diphenyl-2-cyclopropenyl)methane ($\mathit{5}_{n=1}$). 1,5-Diphenyl-1,4-pentadiene was prepared by dehydration of 1,5-diphenyl-1,5-pentanediol, which had been obtained by Grignard reaction of phenylmagnesium bromide with pentanedial, by the use of $KHSO_4$[27] in 63.3% yield: bp 132—138 °C/0.2 Torr (1 Torr = 133.322 Pa) (lit, bp 205—211 °C/12 Torr);[28] ^{1}H NMR (CCl_4) δ 7.17 (s, 10H, Ph), 6.41 (d, J = 15.5 Hz, 2H, =C<u>H</u>Ph), 6.07 (dt, 2H, =CH–), 3.03 (t, 2H, –CH_2–). A solution of 1,5-diphenyl-1,4-pentadiene (3.03 g; 13.7 mmol) and chlorophenyldiazirine[11] (6.75 g; 44.2 mmol) in dry C_6H_6 (180 ml) was heated to reflux with magnetic stirring for 4 h. After removal of the solvent *in vacuo*, the crude product was separated by the use of preparative TLC (R_f 0.34; C_6H_6–n-C_6H_{14}(1 : 4)/SiO_2) to give bis(2-chloro-2,3-diphenylcyclopropyl)methane (3.79 g; 58.9%) as a pale yellow solid: ^{1}H NMR (CCl_4) δ 7.30, 7.07 (br s×2, 20H, Ph), 2.9—1.5 (br m, 6H, ⟩CH– + –CH_2–).

To a stirred solution of the bis(chlorocyclopropyl)methane (3.60 g; 7.68 mmol) in THF (250 ml) was added t-BuOK (17.2 g; 0.153 mol) in portions during 5 min under nitrogen. After stirring for 18 h at room temp, the mixture was poured into 1 dm^3 of cold water and extracted with ether. The ethereal extract was washed with 10% NaCl, dried ($MgSO_4$), and evaporated to give the crude dicyclopropenylmethane $\mathbf{5}_{n=1}$ (2.93 g; 96.2%) as a yellow solid. Recrystallization from C_6H_6–n-C_6H_{14} afforded white needles: mp 118.0—118.6 °C. Found: C, 94.17; H, 6.06%. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10%.

1,2-Bis(2,3-diphenyl-2-cyclopropenyl)ethane ($\mathit{5}_{n=2}$). 1,6-Diphenyl-1,5-hexadiene was prepared by dehydration of 1,6-diphenyl-1,6-hexanediol, derived from hexanedial, in 83.9% yield: bp 154—157 °C/0.5 Torr, mp 77.4—77.8 °C (lit, bp 115 °C/0.005 Torr, mp 80.5—81 °C);[29] ^{1}H NMR (CCl_4) δ 7.18 (s, 10H, Ph), 6.41 (d, J = 15.5 Hz, 2H, =C<u>H</u>Ph), 6.08 (dt, 2H, =CH–), 2.31 (d, 4H, –CH_2–). The reaction of 1,6-diphenyl-1,5-hexadiene (3.27 g; 14.0 mmol) with chlorophenyldiazirine (4.94 g; 32.4 mmol) in dry C_6H_6 (100 ml) afforded 1,2-bis(2-chloro-2,3-diphenylcyclopropyl)ethane (2.87 g; 42.5%) as a pale yellow viscous oil: ^{1}H NMR ($CDCl_3$) δ 7.3—6.9 (m, 20H, Ph), 2.7—1.6 (br m, 8H, ⟩CH– + –CH_2–). The reaction of the 1,2-bis(chlorocyclopropyl)ethane (4.61 g; 9.53 mmol) with t-BuOK (17.93 g; 0.160 mol) in THF (300 ml) gave the crude 1,2-dicyclopropenylethane $\mathbf{5}_{n=2}$ (3.95 g; 100.9%) as a yellow solid. Recrystallization from MeCN afforded white needles: mp 120.1—120.9 °C. Found: C, 93.32; H, 6.46%. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38%.

1,3-Bis(2,3-diphenyl-2-cyclopropenyl)propane ($\mathit{5}_{n=3}$). 1,7-Diphenyl-1,6-heptadiene was prepared by dehydration of 1,7-diphenyl-1,7-heptanediol, obtained from heptanedial, in 51.7% yield: bp 177—180 °C/0.6 Torr; ^{1}H NMR (CCl_4) δ 7.15 (s, 10H, Ph), 6.36 (d, J = 15.5 Hz, 2H, =C<u>H</u>Ph), 6.03 (dt, 2H, =CH–), 2.20 (dt, 4H, –CH_2–), 1.26 (quint, 2H, ⟩CH_2–). The reaction of 1,7-diphenyl-1,6-heptadiene (1.16 g; 4.67 mmol) with chlorophenyldiazirine (2.14 g; 14.0 mmol) in dry C_6H_6 (65 ml) yielded 1,3-bis(2-chloro-2,3-diphenylcyclopropyl)propane (1.21 g; 52.0%) as a pale yellow viscous oil: ^{1}H NMR ($CDCl_3$) δ 7.3—6.9 (m, 20H, Ph), 2.6—1.4 (br m, 10H, ⟩CH– + –CH_2–). The dehydrochlorination of the 1,3-bis(chlorocyclopropyl)propane (0.989 g; 1.99 mmol) with t-BuOK (4.63 g; 41.3 mmol) in THF (80 ml) gave the crude 1,3-dicyclopropenylpropane $\mathbf{5}_{n=3}$ (0.774 g; 91.6%) as a yellow-brown solid. Recrystallization from MeCN afforded white needles: mp 94.8—95.6 °C. Found: C, 93.65; H, 6.56%. Calcd for $C_{33}H_{28}$: C, 93.35; H, 6.65%.

1,4-Bis(2,3-diphenyl-2-cyclopropenyl)butane ($\mathit{5}_{n=4}$). A solution of the di-Grignard reagent, 1,4-bis(bromomagnesio)butane, was prepared from 1,4-dibromobutane (1.74 g; 8.06 mmol) and Mg (0.371 g; 15.3 mmol) in THF (40 ml). To the stirred solution of the di-Grignard reagent cooled at 0 °C was added diphenylcyclopropenium perchlorate (3.97 g; 13.7 mmol) slowly, at a rate such that the temperature did not exceed 5 °C, in portions under nitrogen during 15 min. After stirring for 15 h at 0 °C, the mixture was hydrolyzed with 10% HCl and extracted with C_6H_6. The extract was washed with 10% NaCl, dried ($MgSO_4$), and evaporated to give 3.19 g of the crude product, which afforded the 1,4-dicyclopropenylbutane $\mathbf{5}_{n=4}$ (1.52 g; 51.0%) as white needles after recrystallization from C_6H_6–n-C_6H_{14}: mp 122.1—123.1 °C. Found: C, 93.40; H, 7.00%. Calcd for $C_{34}H_{30}$: C, 93.11; H, 6.89%.

1,5-Bis(2,3-diphenyl-2-cyclopropenyl)pentane ($\mathit{5}_{n=5}$). Similarly, the reaction of diphenylcyclopropenium perchlorate (2.01 g; 6.88 mmol) with 1,5-bis(bromomagnesio)pentane, prepared from 1,5-dibromopentane (0.960 g; 4.17 mmol) and Mg (0.188 g; 7.75 mmol) in THF (20 ml), gave 1.81 g of the crude product, which afforded, by the use of preparative TLC (R_f 0.47, C_6H_6–n-C_6H_{14} (1 : 9)/SiO_2), the 1,5-dicyclopropenylpentane $\mathbf{5}_{n=5}$ (0.574 g; 36.9%) as a colorless viscous oil. Found: C, 92.12; H, 7.12%. Calcd for $C_{35}H_{32}$: C, 92.88; H, 7.12%.

1,6-Bis(2,3-diphenyl-2-cyclopropenyl)hexane ($\mathit{5}_{n=6}$). The reaction of diphenylcyclopropenium perchlorate (3.97 g; 13.8 mmol) with 1,6-bis(bromomagnesio)hexane, prepared from 1,6-dibromohexane (1.96 g; 8.03 mmol) and Mg (0.368 g; 15.2 mmol) in THF (40 ml), gave 5.00 g of the crude product, which afforded the 1,6-dicyclopropenylhexane $\mathbf{5}_{n=6}$ (1.89 g; 59.8%) as white needles after recrystallization from C_6H_6–n-C_6H_{14}: mp 126.0—126.9 °C. Found: C, 92.42; H, 7.61%. Calcd for $C_{36}H_{34}$: C, 92.66; H, 7.34%.

The Hydride Abstraction from $\mathit{5}_{n=1}$——Formation of 1,2-diphenyl-3-(1,2-diphenyltriafulven-4-yl)cyclopropenium Perchlorate ($\mathit{17}\cdot ClO_4^-$). A solution of trityl perchlorate ($Ph_3C^+ClO_4^-$)[30] (0.417 g; 1.22 mmol) in MeCN (7 ml) was slowly added to a stirred solution of the dicyclopropenylmethane $\mathbf{5}_{n=1}$ (0.234 g; 0.589 mmol) in dry C_6H_6 (2 ml) at room temp during 1 h under nitrogen, and the resulting dark red solution was heated at 65 °C for 10 min. To this solution was added, with stirring and ice-bath cooling, dry AcOEt (2 ml) and dry ether (100 ml) to cause the formation of orange-colored precipitates. These were filtered, washed with dry ether, and dried *in vacuo* to give the triafulvenylcyclopropenium perchlorate **17**·ClO_4^- (0.220 g; 75.8%) as yellow powder: mp 227.0—228.0 °C (decomp) after recrystallization from MeCN. Found: C, 75.52; H, 4.14%. Calcd for $C_{31}H_{21}ClO_4$: C, 75.53; H, 4.29%.

The Methylenebis(diphenylcyclopropenium) Dication (**$4_{n=1}$**). The dication **$4_{n=1}$** was observed by the use of ^{1}H NMR and UV spectra on the CF_3CO_2H solution of the triafulvenylcyclopropenium ion **17** with CF_3SO_3H added (*ca.* 10%) (see Figs. 1 and 2).

The Hydride Abstraction from **$5_{n=2}$** *with the Trityl Cation——Rearrangements to* **15** *and the Cation* $C_{32}H_{25}^+$. A solution of the dicyclopropenylethane **$5_{n=2}$** (0.201 g; 0.489 mmol) in CH_2Cl_2 (3 ml) was slowly added during 10 min to a stirred solution of $Ph_3C^+ClO_4^-$ (0.339 g; 0.988 mmol) in CH_2Cl_2 (7 ml) at room temp. During the addition the color of the solution changed from orange to dark red with an increase of the temperature from 23.0 to 26.5 °C. After stirring the mixture for 30 min at room temp and for 10 min at 40 °C, dry ether (100 ml) was added to the stirred and ice-cooled mixture to cause the formation of yellow precipitates, which were then filtered, washed with dry ether, and dried *in vacuo* to give the yellow powder (0.101 g; 40.7% based on **$5_{n=2}$**) tentatively assigned as **16**·ClO_4^-: mp 215.5—218.0 °C (decomp) after recrystallization from MeCN; IR (KBr) 3070, 2930, 2860, 1600, 1500, 1483, 1450, 1440, 1358, 1250, 1148, 1090, 840, 763, 740, 700 cm^{-1}; UV-Vis (MeCN) λ_{max} 256 nm (log ε, 4.46), 280 sh (4.19), 433 (4.15); ^{1}H NMR (100 MHz) (CF_3CO_2H) δ 8.90—8.52 (br m centered at 8.66, 5H, $\cdots CH \cdots ^+$), 7.58—7.06 (m, 15H, Ph), 7.02 (t, 1H, =CH–), 3.13—2.85 (m, 2H, $-CH_2-$), 2.73—2.54 (m, 2H, $-CH_2-$); ^{13}C NMR (CD_3CN) δ 177.4 (s), 170.0 (s), 168.9 (s), 152.2 (d), 149.7 (d), 149.2 (d), 144.6 (d), 144.3 (s), 144.1 (d), 140.7 (s), 140.0 (d), 135.3 (s), 133.7 (s), 133.0 (s), 131.4 (d), 130.6×2 (d), 130.5 (d), 130.3 (d), 129.8 (d), 129.5 (d), 129.3 (d), 126.4 (d), 75.4 (s), 36.6 (t), 33.1 (t). Found: C, 75.23; H, 4.91%. Calcd for $C_{32}H_{25}ClO_4$: C, 75.51; H, 4.95%.

The filtrate from the above procedure was washed with 10% NaCl, dried ($MgSO_4$), and evaporated to give 0.368 g of the crude product, which was then separated by preparative TLC (C_6H_6–n-C_6H_{14}(1 : 4)/SiO_2) repeated twice. From the fraction with R_f 0.55 was obtained triphenylmethane (0.123 g; 50.9% based on Ph_3C^+), identified by comparison of the IR and ^{1}H NMR spectra with those of the authentic sample. From the fraction with R_f 0.30 was isolated the hydrocarbon $C_{32}H_{22}$ (0.923 g; 46.3% based on **$5_{n=2}$**), determined to be the triphenylphenanthrene **15**, as white crystals: mp 219.1—219.6 °C; IR (KBr) 3060, 3030, 1600, 1592, 1575, 1495, 1480, 1440, 1160, 1070, 1025, 1000, 920, 820, 782, 763, 750, 727, 700 cm^{-1}; for UV, see text; ^{1}H NMR (CCl_4) δ 7.78 (d, J=8 Hz, 1H), 7.50—7.05 (m+br s×2, 21H); MS m/e 406. Found: C, 94.18; H, 5.77%. Calcd for $C_{32}H_{22}$: C, 94.54; H, 5.46%. From the fraction with R_f 0.1 was obtained triphenylmethanol (0.0846 g; 32.9% based on Ph_3C^+), identified by comparison of the IR and ^{1}H NMR spectra with those of the authentic sample.

The cation $C_{32}H_{25}ClO_4$ was reduced with $NaBH_4$ as follows. A solution of $C_{32}H_{25}ClO_4$ (0.116 g; 0.228 mmol) in MeCN (3 ml) was added dropwise to a stirred suspension of $NaBH_4$ (0.0182 g; 0.481 mmol) in MeCN (2 ml) with ice-bath cooling under nitrogen. After stirring for 30 min, the mixture was hydrolyzed with H_2O and worked up in the usual way to give 0.0985 g of the crude product, which showed mainly one spot at R_f 0.41 on an analytical TLC plate (C_6H_6–n-C_6H_{14} (1 : 4)/SiO_2). Purification with preparative TLC afforded a pale yellow solid (0.0741 g; 79.3%), supposed to be an isomeric mixture of substituted cycloheptatrienes ($C_{32}H_{26}$) corresponding to the cation $C_{32}H_{25}^+$ (supposedly **16**): IR (KBr) 3040, 2970, 2860, 1600, 1575, 1495, 1485, 1452, 1442, 1380, 1070, 1030, 755, 735, 705 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.17 (br s, 10H, Ph), 6.95 (br s, 5H, Ph), 6.55—5.80 (br m, 4H, =CH–), 5.50—5.00 (br m, 1H, =CH–), 2.85—1.85 (br m, 6H, $-CH_2-$); MS m/e 410.

The Complex Salt of Ethylenebis(diphenylcyclopropenium) Dication (**$4_{n=2}$**). A solution of the 1,2-dicyclopropenylethane **$5_{n=2}$** (0.411 g; 1.00 mmol) in CH_2Cl_2 (5 ml) was added dropwise to a stirred solution of $SbCl_5$ (1.44 g; 4.80 mmol) in CH_2Cl_2 (10 ml) with ice-bath cooling under nitrogen during 10 min. After stirring the resulting dark-gray suspension for 1 h, dry ether (180 ml) was added to the mixture to cause the formation of additional dark green precipitates. The precipitates were filtered, washed with dry ether, and dried *in vacuo* to give grayish powder (0.601 g; 93.2%) analyzed as $C_{32}H_{24}\cdot 0.55SbCl_6\cdot 1.45Cl$: mp>300 °C. Found: C, 59.62; H, 3.43%. Calcd for $C_{32}H_{24}Cl_{4.75}Sb_{0.55}$: C, 59.62; H, 3.75%.

Trimethylenebis(diphenylcyclopropenium) Perchlorate (**$4_{n=3}$**·$2ClO_4^-$). To a stirred suspension of the 1,3-dicyclopropenylpropane **$5_{n=3}$** (0.145 g; 0.342 mmol) in MeCN (2 ml) was added $Ph_3C^+ClO_4^-$ (0.238 g; 0.695 mmol) in one portion at room temp. After stirring at room temp for 15 min and at 60 °C for 15 min, dry AcOEt (10 ml) and dry ether (30 ml) were added to the cooled mixture to cause the formation of yellowish white precipitates, which were then filtered, washed with dry ether, and dried *in vacuo* to give **$4_{n=3}$**·$2ClO_4^-$ (0.200 g; 94.2%) as white powder: mp 214.0—215.0 °C(decomp) after recrystallization from MeCN; ^{13}C NMR (CD_3CN) δ 166.9 (s), 162.3 (s), 139.8 (d), 137.2 (d), 131.4 (d), 120.5 (s), 27.9 (t), 23.9 (t). Found: C, 63.60: H, 4.17%. Calcd for $C_{33}H_{26}Cl_2O_8$: C, 63.78; H, 4.23%.

Tetramethylenebis(diphenylcyclopropenium) Perchlorate (**$4_{n=4}$**·$2ClO_4^-$). In the same way, the reaction of the 1,4-dicyclopropenylbutane **$5_{n=4}$** (0.0975 g; 0.222 mmol) with $Ph_3C^+ClO_4^-$ (0.155 g; 0.452 mmol) was carried out in MeCN (2 ml) to give **$4_{n=4}$**·$2ClO_4^-$ (0.132 g; 93.7%) as white powder: mp 229.8—231.3 °C(decomp) after recrystallization from MeCN; ^{13}C NMR (CD_3CN) δ 167.9 (s), 162.2 (s), 139.6 (d), 137.0 (d), 131.4 (d), 120.5 (s), 27.7 (t), 26.6 (t). Found: C, 64.16; H, 4.35%. Calcd for $C_{34}H_{28}Cl_2O_8$: C, 64.26; H, 4.44%.

Pentamethylenebis(diphenylcyclopropenium) Perchlorate (**$4_{n=5}$**·$2ClO_4^-$). To a stirred solution of the 1,5-dicyclopropenylpentane **$5_{n=5}$** (0.233 g; 0.515 mmol) in CCl_4 (1 ml) and MeCN (2 ml) was added $Ph_3C^+ClO_4^-$ (0.356 g; 1.04 mmol). After stirring at room temp for 20 min and at 60 °C for 30 min, dry AcOEt (15 ml) was added to the cooled mixture. The formed precipitates were filtered, washed with dry AcOEt and dry ether, and dried *in vacuo* to give **$4_{n=5}$**·$2ClO_4^-$ (0.232 g; 69.2%) as white powder: mp 223.4—224.2 °C (decomp) after recrystallization from MeCN; ^{13}C NMR (CD_3CN) δ 168.3 (s), 162.2 (s), 139.5 (d), 137.0 (d), 131.4 (d), 120.6 (s), 29.7 (t), 28.0 (t), 26.3 (t). Found: C, 64.72; H, 4.90%. Calcd for $C_{35}H_{30}Cl_2O_8$: C, 64.84; H, 4.66%.

Hexamethylenebis(diphenylcyclopropenium) Perchlorate (**$4_{n=6}$**·$2ClO_4^-$). Similarly, the reaction of the 1,6-dicyclopropenylhexane **$5_{n=6}$** (0.444 g; 0.950 mmol) with $Ph_3C^+ClO_4^-$ (0.652 g; 1.90 mmol) in MeCN (5 ml) afforded **$4_{n=6}$**·$2ClO_4^-$ (0.545 g; 86.5%) as white powder: mp 229.6—230.3 °C(decomp) after recrystallization from MeCN; ^{13}C NMR (CD_4CN) δ 168.5 (s), 162.2 (s), 139.5 (d), 137.0 (d), 131.4 (d), 120.6 (s), 29.4 (t), 28.1 (t), 26.7 (t). Found: C, 64.88; H, 4.78%. Calcd for $C_{36}H_{32}Cl_2O_8$: C, 65.16; H, 4.86%.

The Chromium(II) Ion Reduction of Hexamethylenebis(diphenylcyclopropenium) Perchlorate (**$4_{n=6}$**·$2ClO_4^-$). A solution (28.6

ml; 28.6 mmol) of the chromium(II) ion (1.00 M, 1 M=1 mol dm^{-3}) in 10% HCl, which had been prepared as previously reported,[31] was added to a stirred solution of $\mathbf{4}_{n=6}\cdot 2ClO_4^-$ (0.122 g; 0.183 mmol) in 10% HCl (100 ml), which had been deaired by bubbling with nitrogen for 2 h. The mixture was stirred with heating at 75 °C for 3 h. The color of the mixture gradually changed from blue to greenish blue with the concomitant formation of white paste-like precipitates. The mixture was extracted with C_6H_6 and worked up in the usual manner to give the polymeric material (supposedly **7**) (0.0691 g; 81.0%) as a yellowish solid: mp 73.5—99.2 °C; IR (KBr) 3065, 3030, 2930, 2855, 1600, 1577, 1495, 1480, 1460, 1440, 1073, 1030, 917, 760, 700, 680 cm^{-1}; for ^{1}H NMR see text.

Determination of pK_{R^+} *Values.* Buffer solutions of slightly different acidities (pH 2—8) were prepared by mixing a citric acid solution (0.1 M) in 50% aq MeCN (1 : 1 by volume) and a saturated solution of Na_2HPO_4 in 50% aq MeCN, in various proportions. For the preparation of a sample solution, each 1-ml portion of the stock solution, prepared by dissolving 1—2 mg of the cation salt in MeCN (20 ml), was pipetted out and made up to 10 ml by adding H_2O (1 ml) and the buffer solution. The sample solution with higher or lower acidity was made by further addition of 1—3 drops of H_2SO_4 or 10% NaOH. The UV-Vis spectrum was recorded, using a 1-cm cell thermostated at 25 °C, on each cation in 15—20 solutions of buffers spaced through a pH range of about two units on each side of the pK_{R^+}. Immediately after recording the spectrum, the pH of each sample solution was determined on a Horiba Model H pH meter calibrated with standard buffers before use. After complete neutralization of each cation, the reversibility was confirmed by quantitative regeneration of the cation spectrum upon acidification of the solution with H_2SO_4. The observed absorbance at the specific absorption wavelength of each cation was plotted against the pH to give a classical titration curve, whose midpoint was taken as the pK_{R^+}.

Cyclic Voltammetry. The measurements were carried out with a Hokuto-Denko Model HA 104 potentiostat equipped with a Hokuto-Denko Model HB 107A function generator. A three-electrode cell was used, consisting of Pt wire working and auxiliary electrodes and a reference electrode, $Ag/AgNO_3$ (0.01 M) with $Bu_4N^+ClO_4^-$ (0.1 M) in MeCN. The reference electrode was connected to the bulk of the sample solution by a salt bridge made up with a $Bu_4N^+ClO_4^-$ solution (0.1 M) in MeCN. Ferrocene, used as a reference compound (*vide infra*), was found to exhibit $E_{1/2}+0.083$ V against this reference electrode.[32] All the sample solutions were 1 mM in the cation and 0.1 M in $Bu_4N^+ClO_4^-$ as a supporting electrolyte in MeCN, and were deaired by bubbling with nitrogen for 10 min. The measurements were made at the scan rate of 0.1 V/s, and the voltammograms recorded on a Hitachi Model 057 X-Y recorder. Immediately after the measurements. ferrocene (0.2 mM) was added as an internal standard,[33] and the observed cathodic peak potential was corrected with reference to this standard.

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