Azulene Unit Fused Cyclopentadienide, Fulvene, and Calicene

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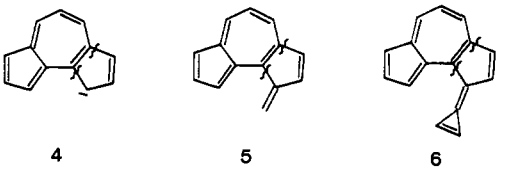
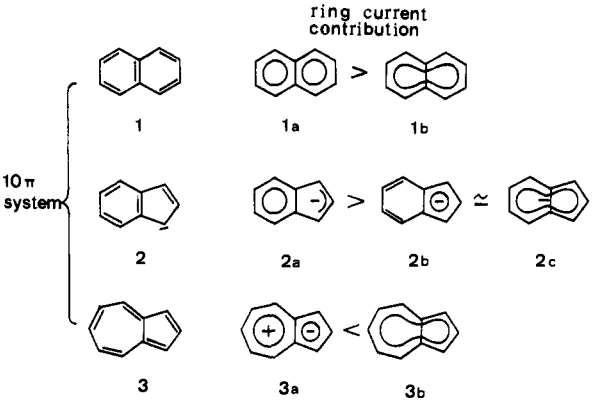
Abstract: The π-conjugation mode of cyclopent[*e*]azulenide (**4**), a new tricyclic anionic system, is elucidated from ^1H and ^{13}C NMR spectra, pK_a value, and MO calculation. Consequently, it is demonstrated that **4** is a considerably stable aromatic anion and that the peripheral 14π-conjugation structure rather than the azulene-type 10π- or cyclopentadienide-type 6π-conjugation structure plays an important role for the ground state of **4**. This contrasts dramatically with the case of benzene unit fused polycyclic anionic systems (e.g., indenide) where the benzene-type 6π-conjugation structure prevails. As perturbed systems of **4**, its fulvene and fulvalene derivatives (**19a**, **19b**, and **20**) are synthesized. On the basis of the NMR data, the π-electron delocalization of their tricyclic anionic parts is discussed in connection with the contribution of polarized structures.

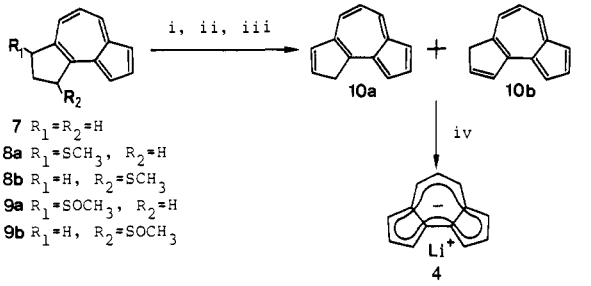
The π-conjugation mode in polycyclic conjugated π-systems containing more than one $(4n+2)$ π-electron-conjugation loop is an intriguing subject from both theoretical and experimental viewpoints, For instance, as shown in Scheme I, naphthalene (**1**), an alternant bicyclic π-conjugated system, is stabilized by the two benzene-type 6π-conjugations (**1a**) more than by the peripheral 10π-conjugation (**1b**).[1] The same type of stabilization is observed for benzene unit fused bicyclic anionic systems, For example, it is well-known that indenide (**2**) is stabilized by the large contribution of the benzene 6π- + allyl anion 4π-type conjugation (**2a**) rather than by the cyclopentadienide 6π- + butadiene 4π-type conjugation (**2b**) or peripheral 10π-type conjugation (**2c**), as is obvious from the ^1H and ^{13}C NMR spectra of **2** and the pK_a value of its conjugate acid,[2] As discussed above, in polycyclic neutral and anionic systems involving a benzene unit, the benzene (6π) type conjugation does significantly contribute to the ground state and outweighs the peripheral π-conjugation. On the contrary, azulene, a nonalternant bicyclic π-conjugated system has a crucial contribution of the peripheral 10π-conjugation (**3b**).[1] Under those circumstances, the π-conjugation mode in nonalternant tricyclic anionic systems is of particular interest. In this paper, we wish to disclose the aromaticity and π-conjugation mode of cyclopent[*e*]azulenide (**4**), one isomer of the azulene unit fused cyclopentadienides, based on its ^1H and ^{13}C NMR spectral data and on MO considerations. In addition, the π-conjuation mode of the other two possible azulene unit fused cyclopentadienides (**15** and **16**) will be discussed by the examination of ring currents in various loops in these molecules, Furthermore we wish to describe the synthesis of quite new systems, azulene unit fused fulvene **5** and calicene **6** as the perturbed system of **4** and to discuss the possible π-conjugation mode in both **5** and **6**.



Scheme I



Scheme II[a]



[a] (i) (1) LDA, (2) CH_3SSCH_3; (ii) $NaIO_4$, CH_3OH; (iii) CCl_4, Δ; (iv) *n*-BuLi, −30 °C.

Results and Discussion

Characterization of Cyclopent[*e*]azulenide. Cyclopent[*e*]azulenide (**4**) was prepared by *n*-butyllithium treatment of a mixture of 1*H*- and 3*H*-cyclopent[*e*]azulenes (**10a** and **10b**) synthesized from 4,5-cyclopentenoazulene (**7**)[3] as previously reported (Scheme II).[4] **4** was shown to be stable in tetrahydrofuran. For example,

Table I, Comparison of ^1H and ^{13}C NMR Spectral Data between **4** and Azulene[5]

H_1, 6.26[a]	C_1, 103.2[a]	$H_{1,3}$, 7.24[b]	$C_{1,3}$, 118.1[c]
H_3, 6.60	C_3, 109.5		
H_2, 6.69	C_2, 124.2	H_2, 7.75	C_2, 137.1
C_{3a}, 132.3	C_{9b}, 135.3	C_{3a}, 140.3	
H_4, 7.56	C_4, 133.3	$(H_4 + H_6)/2$, 7.73	$(C_4 + C_6)/2$, 136.8
H_5, 6.05	C_5, 107.9	H_5, 6.89	C_5, 122.7

[a] In THF-d_8 (δ). [b] In CCl_4 (δ). [c] In $CDCl_3$ (δ).

(1) Ring currents induced in constituent π-electron rings of **1** and **3** are as follows: **1a**, 0.504((I_0)2); **1b**, 0.589I_0; **3a**, cycloheptatrienyl part −0.043I_0, cyclopentadienyl part 0.038I_0; **3b**, 1.111I_0, where I_0 is the ring current of benzene. Resonance energy of a polycyclic conjugated π-system is known to be given by the sum of the resonance energy of each ring which is proportional to the quotient of the ring current divided by the ring area.[11]

(2) (a) Jackman, L. M. "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: London, 1969; p 266. (b) Buncel, E. "Carbanions: Mechanistic and Isotopic Aspects"; Elsevier: Amsterdam, 1975; p 8.

(3) Jutz, C.; Schweiger, E. *Synthesis* **1974**, 193.

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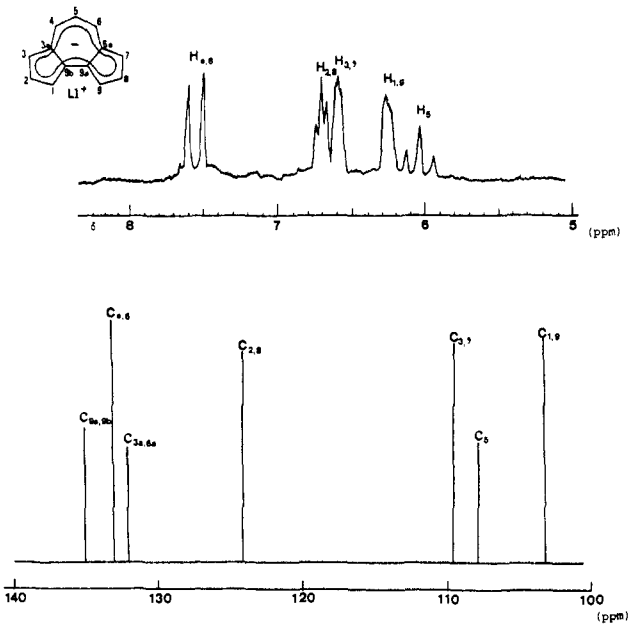


Figure 1. ^1H and ^{13}C NMR spectra of **4** in THF-d_8 at −30 °C.

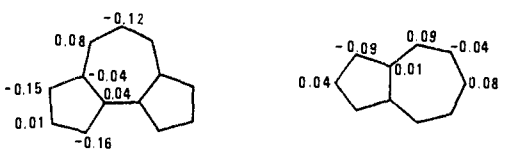
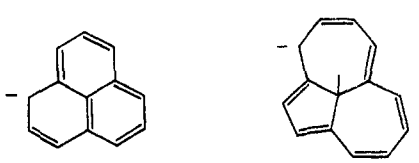


Figure 2. Charge distribution of **4** (left) and azulene (right) by MINDO/3.

UV spectra of **4** did not change even at room temperature for a long time (>1 week) under a thoroughly oxygen- and moisture-free environment. The ^1H and ^{13}C NMR spectra are shown in Figure 1 (equivalent signals for $H_{1,9}$, $H_{2,8}$, $H_{3,7}$, and $H_{4,6}$ and seven signals in the ^{13}C NMR spectra), from which it is evident that **4** possesses a time-averaged C_{2v} molecular symmetry. From comparison of ^1H and ^{13}C chemical shift values of **4** with those of azulene,[5] all the protons (0.2–1.1 ppm) and carbons (2,9–14.9 ppm) of **4** are demonstrated to be shifted to higher magnetic field than those of azulene (Table I). These results indicate the distribution of anionic charge on the peripheral framework of **4** and delocalization of 14π-electrons on the periphery. Further evidence for the peripheral conjugation in **4** can be given by the appearance of a diamagnetic ring current expected for a peripheral 14π-system. Thus, when compared with the ^1H chemical shifts (δ 5.2–5,9) of phenalenide (**11**),[6] a nonaromatic, tricyclic anionic system with



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an isoelectronic π-structure to **4**, all the protons of **4** appear at somewhat lower magnetic field (δ 6.1–7,6), albeit not as low as those in [13]annulenide (**12**) (δ 7.1–8.2), an aromatic tricyclic anionic system with an isoelectronic π-structure to **4**.[7]

Though, in accord with the interpretation of NMR data, MINDO/3 calculation shows that all the carbons of **4** are more negatively charged than those of azulene (Figure 2), an unbalanced charge distribution is observed in **4** (C_1, −0,16; C_2, 0,01; C_4, 0,08). This suggests that contributions of the 10π-conjugation structure of the azulene part and 6π-conjugation structure of the cyclopentadienide part are not negligible.

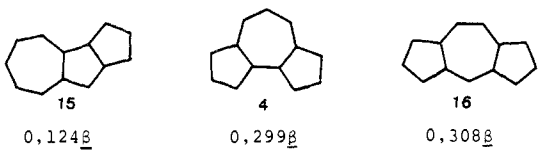
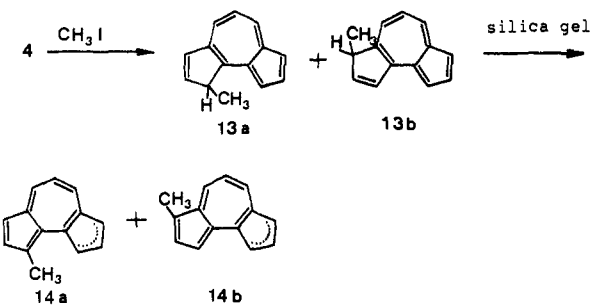
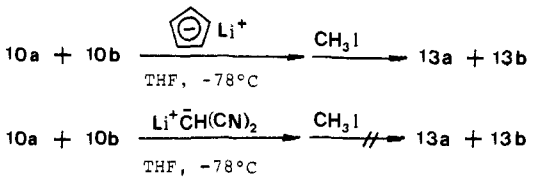


Figure 3. Resonance energies of **4**, **15**, and **16**.

Scheme III



Scheme IV



The reactivity of **4** toward electrophiles was examined in connection with the question of charge distribution. Treatment of a tetrahydrofuran solution of **4** with excess iodomethane was shown to afford a mixture of 1- and 3-methylcyclopent[*e*]azulenes (**13a** and **13b**) in a ratio of ca. 6;1 from its 400-MHz ^1H NMR spectrum. Thus, a dominant pair of olefinic ^1H signals appears at δ 6.81 (dd, 1 H, J = 5.5, 1.2 Hz) and 6,52 (dd, 1 H, J = 5.5, 2,0 Hz), which are assigned to H_2 and H_3 of **13a** from the correspondence with the chemical shift values of $H_{2,3}$ of **10a**. The methyl ^1H signals for **13a** are observed at δ 1.50 (d, 3 H, Me, J = 7,4 Hz), while **13b** exhibits the corresponding signals at δ 1.31 (d, 3 H, Me, J = 7,4 Hz),[8] Formation of 1- and 3-methyl derivatives of **4** by the attack of iodomethane accords with the expectation from the MINDO/3 charge distribution (Scheme III). On treatment with silica gel, the mixture suffered isomerization to give the thermodynamically more stable isomers (**14a** and **14b**). Also, in the reaction of **4** with triethyloxonium tetrafluoroborate, the 1-ethyl derivative was mainly obtained together with the 3-ethyl derivative in analogy with the case of the reaction with iodomethane.

In order to examine the stability of **4** in comparison with cyclopentadienide and indenide, an average pk_a of **10** was estimated by reference to acidities of other compounds. The reaction of **10** with an equimolar amount of lithium cyclopentadienide in tetrahydrofuran at −78 °C gave a reddish purple solution as observed above, which afforded the methylated products (**13a** and **13b**) in quantitative yield by treatment with an excess of iodomethane (Scheme IV). On the other hand, when in the above reaction lithium malononitrile was used in place of lithium cyclopentadienide, no formation of **13a** and **13b** was observed, suggesting that an average pk_a value of **10** ranges from 12 to 15, the respective pk_a values of malononitrile and cyclopentadiene. It is noteworthy that the stability of **4** presents a striking contrast to

(4) Yoshida, Z.; Shibata, M.; Sugimoto, T. *Tetrahedron Lett.* **1983**, *24*, 4585.
(5) Llinas, J. R.; Roard, D.; Derbesy, M.; Vincent, E. J. *Can. J. Chem.* **1975**, *53*, 2911.
(6) Prinzbach, H.; Freudenberger, V.; Scheidegger, U. *Helv. Chim. Acta* **1967**, *50*, 1087.
(7) Becker, B. C.; Neumann, G.; Schmickler, H.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 241.

(8) The olefinic protons of **13b** cannot be assigned because of the overlap with those of **13a**.

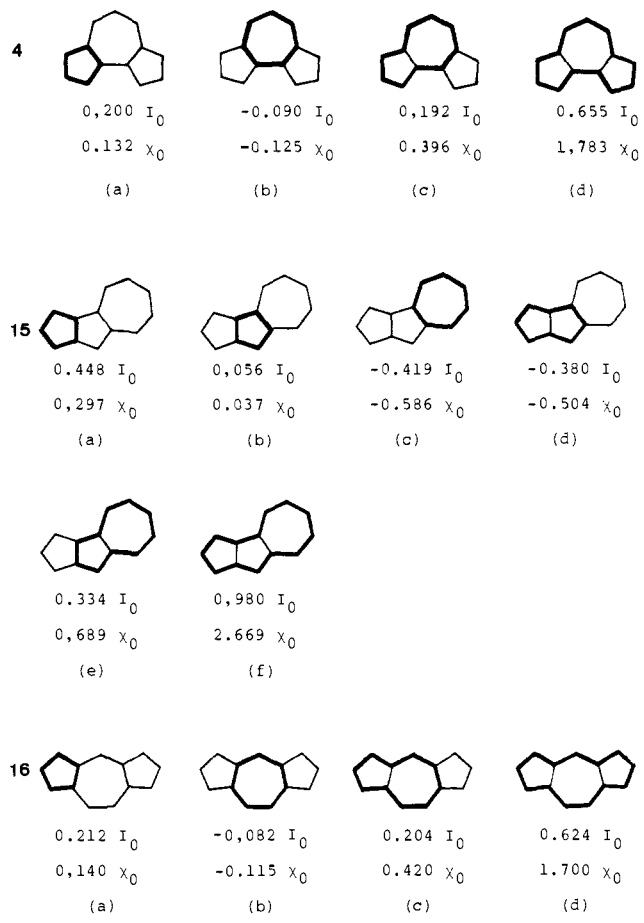


Figure 4. Ring currents and magnetic susceptibilities of **4**, **15**, and **16** (I_0 = ring current of benzene, χ_0 = magnetic susceptibility of benzene).

that of cyclopent[*a*]azulenide (**15**), one of three isomers of azulene unit cata-fused to cyclopentadienides,[9] whose conjugate acid was estimated to have a very high pk_a value (ca. 22) comparable with those of phenalene and indene.

Theoretical Estimation of Resonance Energy, Ring Current and Magnetic Susceptibility of Three Azulene Unit Fused Cyclopentadienides (4, 15, and 16). Resonance energies of possible isomers of cyclopentazulenyl anions were estimated using Aihara's method.[10] The results are summarized in Figure 3. Obviously, **4** has a considerably large resonance energy compared with that of **15**. This is in good accord with the estimated pk_a value. Also, it should be noted that cyclopent[*f*]azulenyl anion (**16**), which is still an unknown compound, has a comparable resonance energy with **4**, suggesting that **16** should be a relatively stable anion. Ring currents and magnetic susceptibilities of **4**, **15**, and **16** were also calculated by Aihara's method.[11] The results are shown in Figure 4. As for **4**, the diamagnetic effect due to the peripheral 14π-structure (i.e., structure d: $0.655I_0$) is the main contributor to the total magnetic effect, although a small contribution comes from the diamagnetic effect of the cyclopentadienyl anion part (i.e., structure a: $0.200I_0$) and azulene part (i.e., structure c: $0.192I_0$) and the paramagnetic effect due to the cycloheptatrienyl anion part (i.e., structure b: $-0.090I_0$). A similar tendency is observed for **16** (Figure 4). Thus the theoretical consideration suggests that peripheral 14π-conjugation plays a crucial role in the stablization of **4** and **16**. This conclusion accords with the experimental results concerning **4**. As for **15**, a significant contribution of the peripheral 14π-structure (i.e., structure f: $0.980I_0$) is also expected. However, the considerably large antiaromatic contributions due to the cycloheptatrienyl anion structure (i.e., structure c: $-0.419I_0$) and pentalene structure (i.e., structure d: $-0.380I_0$) should bring about the destabilization of **15**. The estimated pk_a (22) of the conjugate acid of **15**[9] accords with this interpretation.

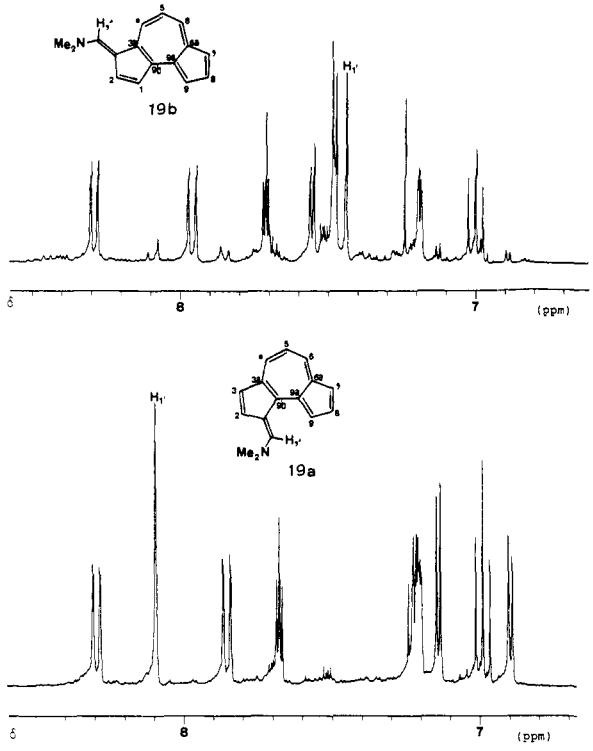
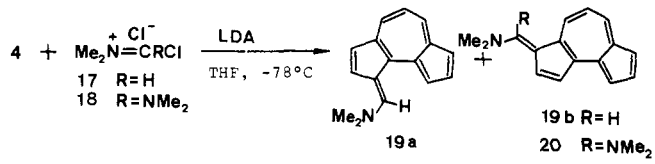


Figure 5. ^{1}H NMR 400 MHz, spectra of **19a** and **19b** in $CDCl_3$.

Scheme V



Synthesis of Azulene Unit Fused Fulvene and Calicene. As perturbed systems of **4**, (dimethylamino)fulvene (**19**) and bis(dimethylamino)fulvene (**20**) were prepared by the reaction of **4** with (chloromethylene)dimethylammonium chloride (**17**) and tetramethylchloroformamidium chloride (**18**), respectively (Scheme V).[12] In the former case both the 1- and 3-isomers were isolated as green crystals in respective yields of 5% and 27%. In the latter reaction there was obtained only the 3-isomer **20** as green crystals in 28% yield, Although the formation of the 1-substituted isomer was realized, its isolation was unsuccessful because of rapid decomposition on purification by column chromatography. The substitution mode was determined from the 400-MHz ^{1}H NMR spectral data of **19a**, **19b**, and **20** (Figure 5). Thus, when the average chemical shift values (δ_{av}) of protons on the cyclopent[*e*]azulenyl ring are compared for the two isomers (**19a** and **19b**), the value of **19a** (7,41 ppm) is shown to be smaller than that of **19b** (7.58 ppm), thereby suggesting that much more negative charge is distributed on the ring of **19a**. Furthermore, the 1'-proton of **19a** (8.09 ppm) appeared at lower magnetic field compared with that of **19b** (7.44 ppm). The similar tendency was also found for the chemical shift of the methyl protons of the dimethylamino group (**19a**, 3.37; **19b**, 3.24 ppm). These results demonstrate that a dipolar structure contributes more to the ground state of **19a** than to that of **19b**. This difference is explained as follows. In

(9) Fleischer, R.; Hafner, K.; Wildgruber, J.; Hochmann, P.; Zahradnĭk, R. *Tetrahedron* **1968**, *24*, 5943.
(10) (a) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750. (b) Aihara, J. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3540.
(11) (a) Aihara, J. *J. Am. Chem. Soc.* **1979**, *101*, 5913. (b) Aihara, J.; Horikawa, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1853.
(12) Eilingsfeld, H.; Neubauer, G.; Seefelder, M.; Weidinger, H. *Chem. Ber.* **1964**, *97*, 1232.

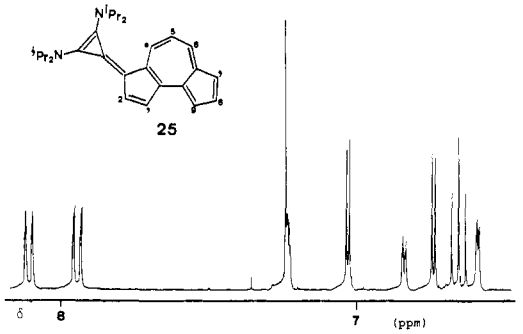
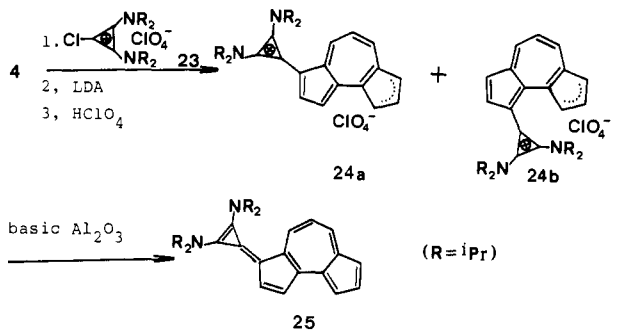
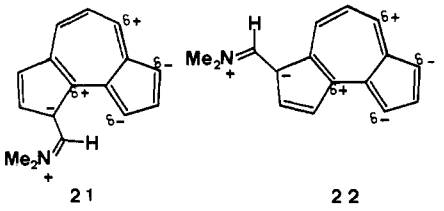


Figure 6, ^1H NMR, 400 MHz, spectrum of **25** in $CDCl_3$.

Scheme VI



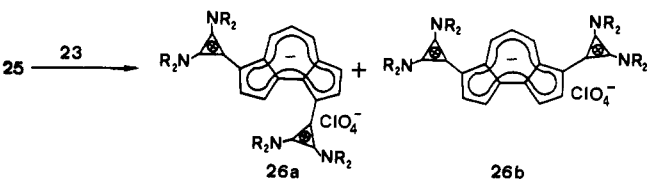
the case of **19a** the induced negative charge can be stabilized by the polarization of an azulene ring, where a positive charge mainly distributes at C_{9b}, C_6, and C_4 of the cycloheptatrienyl part as shown in **21**, while such a stabilization is less effective in the case of **19b**



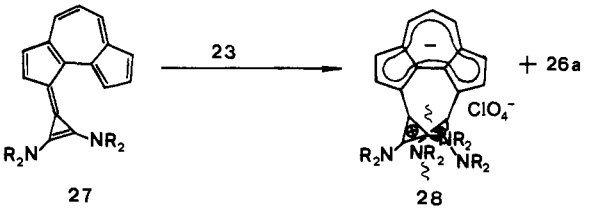
(see **22**). The substitution mode in **20** was determined as the 3-substituted one by reference to the ^1H NMR data of **19a** and **19b**. Replacement (**20**) of the dimethylamino group in **19b** with a bis(dimethylamino) group provided increased polarization as is obvious from the δ_{av} value of **20** (7.42 ppm). However, from the comparison of the δ_{av} value of cyclopent[*e*]azulenyl ring of **19a**, **19b**, and **20** with that of **4** (6.70 ppm), it should be concluded that contribution of the dipolar structure to the ground state of each azulenofulvene is considerable but not so large.

Azulenocalicene can be prepared according to the Scheme VI. Thus, **4** was reacted with chlorobis(diisopropylamino)cyclopropenium perchlorate (**23**), followed by treatment with an equimolar amount of lithium diisopropylamide and then with aqueous perchloric acid solution to afford a mixture (87% yield) of cyclopent[*e*]azulenes substituted with bis(diisopropylamino)-cyclopropenylium group **24a** and **24b** in a ratio of 71:29.[13–15] 3-[Bis(diisopropylamino)cyclopropenylidene]cyclopent[*e*]azulene (**25**) was isolated as unstable reddish purple crystals in 32% yield by chromatography of the mixture of **24a** and **24b** on basic alumina. However, 1-[bis(diisopropylamino)cyclopropenylidene]-

Scheme VII

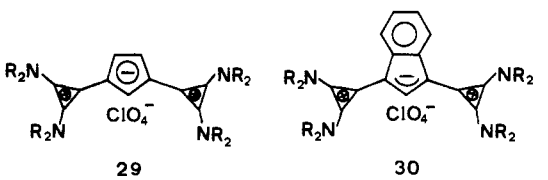


Scheme VIII



cyclopent[*e*]azulene (**27**) was not eluted at all, probably because of its rapid decomposition on the column. The position of the diaminocyclopropenylidene group in **25** could not be determined directly to be the 1- or 3-position from its 400-MHz ^1H NMR spectrum (Figure 6). However, it was determined to be the 3-substituted one from examination of the bis(diaminocyclopropenylio)cyclopent[*e*]azulenides obtained by the reaction of **25** with **23**. As shown in Scheme VII, the reaction gave a mixture of 1,7- and 3,7-bis(diaminocyclopropenylio)cyclopent[*e*]azulenides **26a** and **26b** in 98% yield (**26a**:**26b** = 2:3), which clearly indicate that **25** is the 3-substituted one and has the azuleno[5,4-*a*]calicene structure. If **25** were the 1-substituted one (**27**), it would be difficult to explain that both products (**26a**,**b**) are stable and are formed in a ratio of 2:3, because the reaction of **27** with **23** should lead to formation of the very overcrowded unstable product **28** together with **26a** as shown in Scheme VIII.

In the electronic spectra of **25**, its longest wavelength band (526 nm) is very close to that of **4** (525 nm), and its next longest absorption band appears at 403 nm. The latter band can be attributed to an intramolecular charge-transfer transition from the cyclopent[*e*]azulenide ring to the diaminocyclopropenylium group because this absorption band shifts to a much longer wavelength region with the decreasing polar nature of solvent (acetonitrile, 382 nm; dichloromethane, 403 nm; benzene, 424 nm).[16] In the NMR spectrum the δ_{av} value (7.14 ppm) of **25** is much smaller than that of **20** (7.42 ppm), In particular, it is noted that the chemical shift of each ring proton is close to that of **4**. These spectral data clearly indicate the large contribution of the dipolar structure to the ground state of **25**, in which the anionic part, cyclopent[*e*]azulenide, should have the peripheral 14π-conjugated structure. From this discussion, **25** should not be regarded as an azulene unit fused calicene but as a perturbed triatridecafulvalene. Also, **26** has a considerably smaller δ_{av} value (**26a**, 7.31 ppm; **26b**, 7.34 ppm). Therefore it is suggested that both cations have the tripolar mesomeric structure as shown in formula **26a** and **26b**. In our laboratory similar tripolar mesomeric salts, **29** and **30**, were already prepared, and their electronic



structures were elucidated.[17] However, in the latter case the anionic part was a monocyclic or bicyclic system which is different

(13) Both **24a** and **24b** contain a mixture of 3*H* and 1*H* regioisomers. The ratios of isomers were determined to be 57:14 for **24a** and 19:10 for **24b** from their 400-MHz ^1H NMR spectra.

(14) In the reaction of **4** with chloroiminium salts (**17**, **18**, and **23**), 3-substituted products (**19b**, **20**, and **24b**) were preferentially obtained in contrast with the preference for 1-substitution in the reaction of **4** with iodomethane. We are now investigating this difference of reaction position.

(15) Protonation of purified **25** with dilute aqueous perchloric acid solution gave **24a** quantitatively.

(16) In the UV spectra of **20** in dichloromethane, the absorption band at 420 nm shifts to a slightly longer wavelength region with the decreasing solvent polarity (acetonitrile 417 nm, dichloromethane 420 nm, benzene 426 nm). In the case of **19a** and **19b**, such a solvent effect was not observed.

(17) Yoshida, Z.; Araki, S.; Ogoshi, H. *Tetrahedron Lett.* **1975**, *16*, 19.

from the former case where the anionic part is a tricyclic ring system.

Experimental Section

Melting points were determined with a YANACO MP-micro melting point apparatus and are uncorrected. Microanalyses were performed at the Microanalysis Center, Kyoto University. NMR spectra were recorded on a JEOL FX-90Q (^{13}C), JEOL JNM-GX400 (^1H), JEOL JNM-PMX-60 (^1H), or Varian HA-100D (^1H) spectrometer, and chemical shift values are given in δ (ppm) relative to internal tetramethylsilane. Mass spectra were obtained with a JEOL JMS-DX300 spectrometer and IR spectra with a JASCO A-102 diffraction grating infrared spectrophotometer. Electronic spectra were obtained on a Hitachi 340 recording spectrophotometer.

3′- and 5′-(Methylthio)-4,5-cyclopentenoazulenes (8a and 8b). To a solution of 4,5-cyclopentenoazulene[3] (1.04 g, 6.18 mmol) in 70 mL of dry THF under argon was added 0.227 M LDA in dry THF (30 mL, 6.80 mmol) at −70 °C. The resulting brown solution was stirred for 0.5 h at the same temperature, and then dimethyl disulfide (0.84 mL, 9.27 mmol) was added. The mixture was warmed up to room temperature, poured into water (150 mL), and extracted twice with hexane (100 mL). The blue organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo, followed by column chromatography on silica gel (hexane:dichloromethane = 5:1 as an eluant) to give a mixture of **8a** and **8b** (0.464 g, 35%) as a blue oil: ^1H NMR ($CDCl_3$) δ 8.10 (d, 1 H, J = 10.0 Hz), 7.73 (t, 1 H, J = 4.0 Hz), 7.44 (d, 1 H, J = 10.0 Hz), 7.31 (d, 1 H, J = 3.5 Hz), 7.15 (d, 1 H, J = 3.5 Hz), 6.92 (t, 1 H, J = 10.0 Hz), 5.82 (dd, 1 H, J = 6.5, 1.5 Hz), 3.7–3.3, 3.1–2.7, and 2.6–2.2 (m 4 H), 1.98 (s, 3 H); IR (KBr, cm^{-1}) 3080, 2920, 1570, 1440, 1420, 1383, 782; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 246 (4.40), 280 (4.58), 314 (3.67), 326 (3.62), 341 (3.65), 354 (3.21), 382 (2.67), 404 (2.65), 600 (2.65); MS, m/e (M^+) calcd 214.0815, obsd 214.0831.

3′- and 5′-(Methylsulfinyl)-4,5-cyclopentenoazulenes (9a and 9b). To a solution of a mixture of **8a** and **8b** (450 mg, 2.10 mmol) in methanol (50 mL) was added sodium metaperiodate (494 mg, 2.31 mmol) in water (1 mL) at 0 °C. After addition, the temperature was raised to room temperature, and stirring was continued overnight. The reaction mixture was filtered, and the precipitate was washed several times with methanol (25 mL). The combined filtrate was dried over anhydrouds sodium sulfate and concentrated in vacuo to give a blue solid of a mixture of **9a** and **9b** (480 mg) in quantitative yield: ^1H NMR ($CDCl_3$) δ 8.25 (d, 1 H, J = 10.0 Hz), 7.87 (t, 1 H, J = 3.5 Hz), 7.58 (d, 1 H, J = 10.0 Hz), 7.44 and 7.19 (d, 1 H, J = 3.5 Hz), 7.31 (d, 1 H, J = 3.5 Hz), 7.11 (t, 1 H, J = 10.0 Hz), 5.39 and 4.75 (dd, 1 H, J = 8.4, 1.4 Hz), 3.8–2.3 (m, 4 H), 2.58 (s, 3 H); IR (KBr, cm^{-1}) 3050, 2900, 1562, 1440, 1418, 1380, 1350, 1030, 780; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 244 (4.09), 277 (4.41), 326 (3.41), 342 (3.48), 354 (2.82), 384 (2.41), 408 (2.41), 600 (2.65); MS, m/e (M^+) calcd 230.0765, obsd 230.0726.

1*H*- and 3*H*-Cyclopent[*e*]azulenes (10a and 10b). A mixture of **9a** and **9b** (450 mg, 1.96 mmol) was dissolved in 50 mL of tetrachloromethane, and the solution was heated to reflux for 4 h. The reaction mixture was concentrated in vacuo until $^1/_4$ volume. The obtained greenish blue solution was chromatographed on neutral alumina with hexane–dichloromethane (5:1). Eluted blue solution was concentrated in vacuo to $^1/_4$ volume (complete evaporation of solvent resulted in almost decomposition of product) and again chromatographed on silica gel to yield a 7:3 mixture of **10a** and **10b** (133 mg, 41%) as a blue oil: ^1H NMR ($CDCl_3$) δ 8.20 (d, 1 H, H_6, J = 9.8 Hz), 7.81 (t, 1 H, H_8, J = 3.7 Hz), 7.60 (d, 1 H, H_4, J = 9.8 Hz), 7.36 (d, 1 H, H_7 or H_9, J = 3.2 Hz), 7.21 (d, 1 H, H_7 or H_9, J = 2.4 Hz), 7.08 (t, 1 H, H_5, J = 9.8 Hz), 6.80 (dt, 1 H, H_3, J = 5.6, 1.8 Hz), 6.40 (dt, 1 H, H_2, J = 5.6, 2.2 Hz), 4.06 (t, 2 H, H_1, J = 2.0 Hz) for **10a**; 8.29 (d, 1 H, H_6, J = 9.5 Hz), 7.83 (t, 1 H, H_8, J = 3.7 Hz), 7.67 (d, 1 H, H_4, J = 9.8 Hz), 7.53 (dtd, 1 H, H_1, J = 5.6, 1.8, 0.7 Hz), 7.48 (d, 1 H, H_7 or H_9, J = 3.9 Hz), 7.33 (d, 1 H, H_7 or H_9, J = 2.9 Hz), 7.00 (t, 1 H, H_5, J = 9.8 Hz), 6.95 (dt, 1 H, H_2, J = 5.6, 2.1 Hz), 3.73 (brs 2 H, H_3) for **10b**; IR (neat, cm^{-1}) 3050, 2900, 1574, 1430, 1380, 1360, 803, 770, 735; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 266 (4.28), 294 (4.36), 340 (3.43), 356 (3.49), 370 (3.34), 384 (3.10), 580 (2.63), 624 (2.59), 690 (2.18); MS, m/e (M^+) calcd 166.0782, obsd 166.0775.

Lithium Cyclopent[*e*]azulenide (4). A solution of a mixture of **10a** and **10b** (50 mg, 0.30 mmol) in THF-d_8 (0.4 mL) was put into an NMR sample tube under argon, cooled to −70 °C, and 1.6 M *n*-butyllithium (0.20 mL, 0.32 mmol) in hexane was added. The resulting reddish purple solution was immediately subject to the ^1H and ^{13}C NMR measurements.

1- and 3-Methylcyclopent[*e*]azulenes (13a and 13b). To a solution of a mixture of **10a** and **10b** (22 mg, 0.13 mmol) in THF (5 mL) was added 1.6 M *n*-butyllithium (0.08 mL, 0.13 mmol) in hexane at −70 °C. The resulting reddish purple solution was reacted with iodomethane (0.08 mL, 1.3 mmol) and then gradually warmed to room temperature. The blue reaction mixture was poured into water and extracted twice with hexane (20 mL). The hexane solution was dried over anhydrous sodium sulfate and concentrated in vacuo to give 6:1 mixture of **13a** and **13b** (23 mg, 96%) as a blue oil: ^1H NMR ($CDCl_3$) δ 8.27 (d, 1 H, H_6, J = 9.7 Hz), 7.88 (t, 1 H, H_8, J = 3.8 Hz), 7.68 (d, 1 H, H_4, J = 9.7 Hz), 7.34 (d, 1 H, H_7 or H_9, J = 3.8 Hz), 7.29 (d, 1 H, H_7 or H_9, J = 3.8 Hz), 7.14 (t, 1 H, H_5, J = 9.7 Hz), 6.81 (dd, 1 H, H_3, J = 5.5, 1.2 Hz), 6.52 (dd, 1 H, H_2, J = 5.5, 2.0 Hz), 4.11 (q, 1 H, H_1, J = 7.5 Hz), 1.50 (d, 3 H, Me, J = 7.5 Hz) for **13a** (the proton signals of **13b** cannot be fully assigned because of partial overlap with those of **13a**); IR (neat, cm^{-1}) 3050, 2950, 2920, 1580, 1560, 1512, 1434, 1353, 800; MS, m/e (M^+) calcd 180.0939, obsd 180.0927. Chromatography of the crude methylated product on silica gel with hexane–dichloromethane (5:1) afforded the pure but isomerized methylcyclopent[*e*]azulenes (**14a** and **14b**) as a blue oil: ^1H NMR ($CDCl_3$) δ 8.22 (d, 1 H, H_4, J = 9.7 Hz), 8.0–6.4 (m, 6 H), 4.13 and 3.55 (brs, 2 H), 2.70 (m, 3 H, Me); IR (neat, cm^{-1}) 3050, 2950, 2910, 1600, 1550, 1430, 1380, 1353, 1224, 1025, 802, 768; MS, m/e (M^+) calcd 180.0939, obsd 180.0931.

Reaction of a Mixture of 10a and 10b with Lithium Cyclopentadienide for the Estimation of Relative pk_a Value. With lithium cyclopentadienide (0.22 mmol) in THF (3 mL) in place of *n*-butyllithium the same reaction of **10a** and **10b** (36 mg, 0.22 mmol) with iodomethane (0.14 mL, 2.2 mmol) was carried out. A mixture of **13a** and **13b** was obtained in quantitative yield. The reaction carried out by using lithium malononitrile in place of lithium cyclopentadienide gave no methylated cyclopent[*e*]azulene.

1- and 3-[(Dimethylamino)methylidene]cyclopent[*e*]azulenes (19a and 19b). To a solution of (chloromethylene)dimethylammonium chloride (44 mg, 0.34 mmol) in THF (5 mL) was added a THF solution (5 mL) of **4** prepared from **10** (57 mg, 0.34 mmol) and 1.55 M *n*-butyllithium (0.23 mL, 0.35 mmol) in hexane at −70 °C. After mixture was stirred for 1 h, 0.12 M LDA (3 mL, 0.35 mmol) in THF was added to the solution and then the reaction mixture was gradually warmed to room temperature. The resulting green solution was concentrated in vacuo and the residue was chromatographed on neutral alumina with dichloromethane–hexane (2:1). From the first eluate **19a** was obtained as green crystals (3.8 mg) in 5% yield, and from the second eluate **19b** was obtained as green crystals (20.3 mg) in 27% yield. **19a**: mp 68–72 °C; ^1H NMR ($CDCl_3$) δ 8.29 (d, 1H, H_4, J = 9.5 Hz), 8.09 (s, 1 H, $H_{1'}$), 7.85 (dd, 1 H, H_6, J = 9.5, 0.7 Hz), 7.68 (t, 1 H, H_8, J = 3.8 Hz), 7.22 (m, 2 H, $H_{7,9}$), 7.14 (d, 1 H, H_2, J = 5.2 Hz), 6.99 (t, 1 H, H_5, J = 9.5 Hz), 6.90 (d, 1 H, H_3, J = 5.2 Hz), 3.37 (s, 6 H, NMe_2); IR (KBr, cm^{-1}) 3070, 2920, 1610, 1370, 1324, 1127, 997, 795; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 277 (4.50), 305 (4.18), 387 (4.30), 413 (4.27), 451 (sh, 3.90), 560 (2.82); MS, m/e (M^+) calcd 221.1204, obsd 221.1185. **19b**: mp 50–52 °C; ^1H NMR ($CDCl_3$) δ 8.29 (d, 1 H, H_4, J = 9.9 Hz), 7.96 (d, 1 H, H_6, J = 9.9 Hz), 7.71 (t, 1 H, H_8, J = 3.9 Hz), 7.55 (d, 1 H, H_1, J = 5.0 Hz), 7.48 (d, 2 H, $H_{2,9}$, J = 5.0 Hz), 7.44 (s, 1 H, $H_{1'}$), 7.19 (dd, 1 H, H_7, J = 3.9, 1.5 Hz), 7.00 (t, 1 H, H_5 J = 9.9 Hz), 3.24 (s, 6 H, NMe_2); IR (KBr, cm^{-1}) 3050, 2910, 1610, 1370, 1120, 998, 800, 760; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 255 (4.26), 296 (4.22), 394 (4.38), 412 (4.30), 450 (sh, 3.87), 570 (2.98); MS, m/e (M^+) calcd 221.1204, obsd 221.1197.

3-[Bis(dimethylamino)methylidene]cyclopent[*e*]azulene (20). To a solution of chloroformamidium chloride[12] (66.8 mg, 0.39 mmol) in THF (5 mL) was added a THF solution of **4** prepared from **10** (64 mg, 0.39 mmol) at −78 °C. After the solution was stirred for 1 h, 0.13 M LDA (3 mL, 0.39 mmol) in THF was added and then the reaction mixture was gradually warmed to room temperature. The resulting green solution was concentrated in vacuo and chromatographed on neutral alumina with benzene–acetone (8:2) to give **20** (28.9 mg) as unstable green crystals in 28% yield: mp 185–187 °C dec; ^1H NMR ($CDCl_3$) δ 8.23 (d, 1 H, H_4, J = 9.3 Hz), 7.63 (dd, 1 H, H_8 J = 3.9, 3.7 Hz), 7.51 (d, 1 H, H_6, J = 10.0 Hz), 7.42 (ddd, 1 H, H_9, J = 3.7, 1.5, 0.7 Hz), 7.34 (dd, 1 H, H_1, J = 4.8, 0.3 Hz), 7.19 (d, 1 H, H_2, J = 4.8 Hz), 7.09 (dd, 1 H, H_7, J = 3.9, 1.5 Hz), 6.92 (dd, 1 H, H_5, J = 9.3, 10.0 Hz), 3.09 (s, 12 H, NMe_2); IR (KBr, cm^{-1}) 3060, 2910, 1590, 1530, 1375, 1341, 1000; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 254 (4.39), 300 (sh, 4.13), 336 (sh, 3.74), 420 (4.55), 482 (sh, 3.87), 600 (2.99); MS, m/e (M^+) calcd 264.1627, obsd 264.1641.

7- and 9-[Bis(diisopropylamino)cyclopropenylio]cyclopent[*e*]azulenes (24a and 24b). To a solution of a mixture of **10a** and **10b** (72.6 mg, 0.437 mmol) in THF (12 mL) was added 0.11 M LDA (8 mL, 0.874 mmol) in THF at −78 °C. After the solution was stirred for awhile, was added chlorobis(diisopropylamino)cyclopropenium perchlorate (162 mg, 0.436 mmol). The reaction mixture was gradually warmed to 0 °C and poured into cold dilute aqueous perchloric acid solution and extracted twice with dichloromethane (20 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo to give a blue solid. Recrystallization of the solid from dichloromethane–ether gave a mixture

of **24a** and **24b** as blue crystals (191 mg) in 87% yield: mp 231-234 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.39 (d, 1 H, H_6, J = 9.7 Hz), 7.92 (d, 1 H, H_4, J = 9.7 Hz), 7.71 (d, 1 H, H_8, J = 4.0 Hz), 7.53 (bd, 1 H, H_1, J = 3.9 Hz), 7.41 (brd, 1 H, H_2, J = 3.9 Hz), 7.40 (d, 1 H, H_9, J = 4.0 Hz), 7.23 (t, 1 H, H_5, J = 9.7 Hz), 4.31 and 3.74 (m, 4 H, *i*-Pr), 3.80 (brs, 2 H, H_3), 1.55, 1.46, 1.18 and 1.05 (d, 24 H, *i*-Pr) for 3*H* isomer of **24a**; 8.36 (d, 1 H, H_6, J = 10.0 Hz), 7.88 (d, 1 H, H_4, J = 10.0 Hz), 7.76 (d, 1 H, H_8, J = 4.2 Hz), 7.36 (t, 1 H, H_5, J = 10.0 Hz), 7.35 (d, 1 H, H_9, J = 4.2 Hz), 6.90 (brs, 2 H, $H_{2,3}$), 4.00 (brs, 2 H, H_1) for 1*H* isomer of **24a**; 8.37 (d, 1 H, H_6, J = 9.8 Hz), 7.93 (d, 1 H, H_4, J = 9.8 Hz), 7.82 (d, 1 H, H_8, J = 4.2 Hz), 7.62 (brd, 1 H, H_1, J = 5.4 Hz), 7.18 (brd, 1 H, H_2, J = 5.4 Hz), 3.89 (brs, 2 H, H_3) for 3*H* isomer of **24b**; 8.31 (d, 1 H, H_6, J = 9.5 Hz), 4.17 (s, 2 H, H_1) for 1*H* isomer of **24b** (other signals could not be assigned because of overlap with those of other isomers, but from the integral ratio of methylene protons the ratio of 3*H*-**24a**, 1*H*-**24a**, 3*H*-**24b**, and 1*H*-**24b** isomers was determined to be 57:14:19:10); IR (KBr, cm^{-1}) 2970, 1900, 1548, 1090; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 224 (4.50), 269 (4.65), 305 (4.68), 359 (4.14), 562 (3.10), 600 (sh, 3.08), 660 (sh, 2.70). Anal. Calcd for $C_{28}H_{37}N_2ClO_4$: C, 67.12; H, 7.44; N, 5.59. Found: C, 66.51; H, 7.32; N, 5.65.

3-[Bis(diisopropylamino)cyclopropenylidene]cyclopent[*e*]azulene (25). A mixture of **24a** and **24b** (56 mg, 0.11 mmol) was chromatographed on basic alumina (Woelm B Akt II) with benzene-acetone (7:3) to give **25** as reddish purple crystals (14 mg) in 32% yield: mp 171-175 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.11 (d, 1 H, H_4 or H_6, J = 9.3 Hz), 7.94 (d, 1 H, H_4 or H_6, J = 9.8 Hz), 7.23 (dd, 1 H, H_8, J = 4.2, 3.2 Hz), 7.03 (d, 1 H, H_2, J = 4.4 Hz), 6.84 (d, 1 H, H_7 or H_9, J = 4.2 Hz), 6.74 (d, 1 H, H_1, J = 4.4 Hz), 6.65 (t, 1 H, H_5, J = 9.5 Hz), 6.59 (d, 1 H, H_7 or H_9, J = 3.2 Hz), 3.99 (m, 4 H, *i*-Pr), 1.31 (d, 24 H, *i*-Pr); IR (KBr, cm^{-1}) 3050, 2950, 1890, 1592, 1522, 1300; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 243 (4.25), 273 (4.27), 299 (sh, 4.20), 403 (4.03), 526 (3.73); MS *m/e* (M^+) calcd 400.2878, obsd 400.2851.

1,7- and 3,7-Bis[bis(diisopropylamino)cyclopropenylio]cyclopent[*e*]azulenides (26a and 26b). To a solution of **25** (21 mg, 0.051 mmol) and triethylamine (10 mg, 0.10 mmol) in dry dichloromethane (5 mL) was added chlorobis(diisopropylamino)cyclopropenium perchlorate (19 mg, 0.051 mmol) at room temperature. After stirring under argon overnight, the reaction mixture was concentrated in vacuo to give a reddish purple solid, and recrystallization from dichloromethane-ether afforded a 2:3 mixture of **26a** and **26b** (37 mg) as dark reddish purple crystals in 98% yield: mp 163-168 °C dec; ^{1}H NMR ($CDCl_3$, ppm) δ 8.15 (d, 1 H, H_6, J = 9.5 Hz), 7.86 (d, 1 H, H_4, J = 9.5 Hz), 7.48 (d, 1 H, H_2 or H_8, J = 4.0 Hz), 7.23 (d, 1 H, H_2 or H_8, J = 4.4 Hz), 6.93 (d, 1 H, H_3 or H_9, J = 4.4 Hz), 6.83 (t, 1 H, H_5, J = 9.5 Hz), 6.69 (d, 1 H, H_3 or H_9, J = 4.0 Hz), 4.13 (m, *i*-Pr), 1.56, 1.54, and 1.43 (d, *i*-Pr) for **26a**; 8.04 (d, 2 H, $H_{4,6}$, J = 9.6 Hz), 7.26 (d, 2 H, $H_{2,8}$, J = 4.5 Hz), 6.93 (t, 1 H, H_5, J = 9.6 Hz), 6.91 (d, 2 H, $H_{1,9}$, J = 4.5 Hz), 4.13 (m, *i*-Pr), 1.56, 1.54, and 1.43 (d, *i*-Pr) for **26b** (the protons of isopropyl group of **26a** overlap with those of **26b**); IR (KBr, cm^{-1}) 2970, 1880, 1508, 1460, 1340, 1090; UV (CH_2Cl_2, nm) λ_{max} (log ϵ) 255 (4.23), 322 (4.37), 374 (4.05), 424 (4.00), 564 (4.34). Anal. Calcd for $C_{43}H_{63}N_4ClO_4$: C, 70.23; H, 8.63; N, 7.62. Found: C, 70.22, H, 8.73; N, 7.47.

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Registry No. **4**, 88726-17-4; **7**, 14311-05-8; **8a**, 88726-13-0; **8b**, 88726-14-1; **9a**, 88726-15-2; **9b**, 88726-16-3; **10a**, 228-82-0; **10b**, 13777-90-7; **13a**, 88726-18-5; **13b**, 91861-71-1; **14a** (isomer 1), 91861-72-2; **14a** (isomer 2), 91861-73-3; **14b** (isomer 1), 91861-74-4; **14b** (isomer 2), 91861-75-5; **18**, 30388-20-6; **19a**, 91861-76-6; **19b**, 91861-77-7; **20**, 91861-78-8; 3*H*-**24a**, 91861-81-3; 1*H*-**24a**, 91861-83-5; 3*H*-**24b**, 91861-85-7; 1*H*-**24b**, 91861-87-9; **25**, 91861-79-9; **26a**, 91861-89-1; **26b**, 91861-91-5; chlorobis(diisopropylamino)cyclopropenium perchlorate, 74507-77-0; dimethyl disulfide, 624-92-0; **17**, 3724-43-4.

The $C_4H_7^+$ Potential Surface[1]

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Abstract: MINDO/3 calculations are reported for the $C_4H_7^+$ systems. Contrary to conclusions from ab initio calculations but in agreement with experiment, the cyclopropylcarbinyl cation and "cyclobutyl cation" are *both* predicted to correspond to minima on the potential surface, the latter being indeed the lower in energy and having a nonclassical structure with a relatively strong transannular bond, corresponding to 1-protonated bicyclobutane. The cyclopropylcarbinyl cation is best formulated as a π complex. Interconversion of the two isomers was studied and also their conversions to the α-methylallyl cation. The formation of 1-substituted 3-butenes does not take place via 3-buten-1-yl cation.

Thirty years have now elapsed since Roberts[2] first showed the cyclopropylcarbinyl cation (**1**) to have a nonclassical structure. During this period numerous experimental[3-5] and theoretical[6-10] studies have been reported of **1** and the rearrangements it, and its derivatives, undergo.

The experimental studies indicate that **1** undergoes a rapid degenerate interconversion with the two isomers where different pairs of methylene groups are linked, and also rapid interconversion with the cyclobutyl cation (**2**, **3**). Under ionizing conditions, ionizable derivatives (**4**, **5**) of **1** or **2** (**3**) interconvert rapidly, while a slower rearrangement leads to the corresponding 3-butenyl derivative, **6**. It has usually been assumed that the latter is formed via the corresponding cation (**7**).

Calculations[6] by the Roothaan-Hall (RH; "ab initio SCF") method, using the STO-3G basis set, predicted **1** to be the only minimum of the type $(CH)(CH_2)_3^+$ on the $C_4H_7^+$ potential

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