

## Overall view of cyclic polycalicenyls

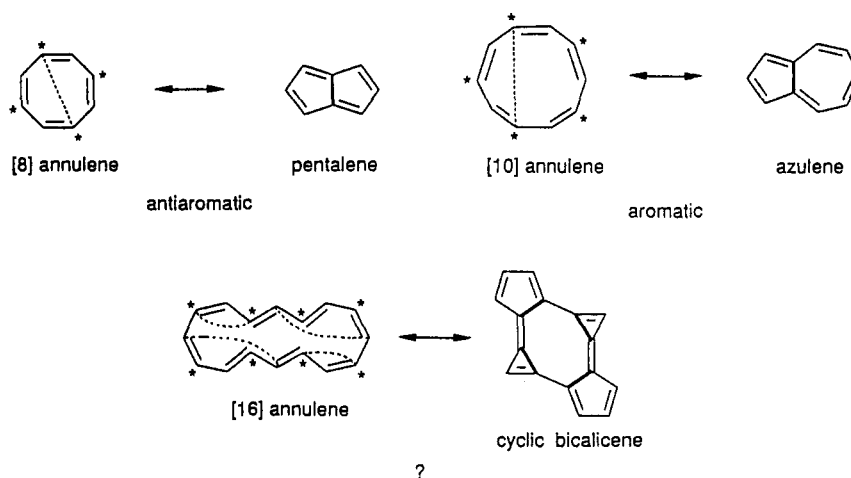
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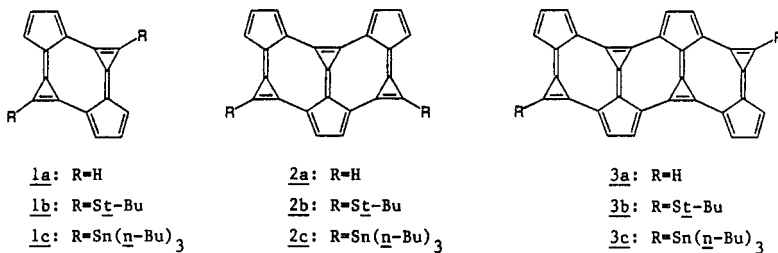
**Abstract** - Cyclic bicalicene (1a) and bicyclic tercalicene (2a), and their bis(tert-butylthio)-substituted derivatives (1b and 2b), and bis(tert-butylthio)-substituted derivative (3b) of tricyclic tetracalicene (3a) were synthesized, in which two, three and four calicene units are joined in a head-to-tail manner, respectively. The X-ray structure analyses of 1a, 1b and 2b indicate that each skeleton of cyclic bicalicene, bicyclic tercalicene, and presumably tricyclic tetracalicene takes almost a complete planar structure. Based on the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR results peripheral 16-, 22-, and 28- $\pi$  conjugations have an unexpectedly small contribution for 1a, 2a, and 3a, respectively, and rather a large polarization of each calicene unit occurs irrespectively of kinds of cyclic polycalicenyls. This conclusion was also supported by modified SCF MO and graph-theoretical calculations.

### INTRODUCTION

Perturbation MO method can predict aromaticity in even nonalternant polycyclic systems containing two or more nonadjacent odd-nonnumbered rings. For typical examples pentalene (ref. 1), azulene, and heptalene (ref. 2) can be derived by intramolecular union from their corresponding even alternant monocyclic polyenes, [8]-, [10]-, and [12]-annulenes, respectively, that form their perimeters. Since the union takes place between atoms of like party in an even alternant system, it leads to no first-order change in  $\pi$ -binding energy. Accordingly, pentalene, azulene, and heptalene should be regarded as a slightly perturbed version of [8]-, [10]- (ref. 3), and [12]-annulenes (ref. 4), respectively, with essential single bond character of new bonds. In fact, these even nonalternant bicyclic systems resemble their original even alternant monocyclic systems in both stability and reactivity (pentalene, heptalene, [8]- and [12]-annulenes: antiaromatic; azulene and [10]annulene; aromatic). The analogous argument might of course be applied to [16]annulene (ref. 5) and its possible polycyclic systems, one of which is cyclic bicalicene (1a), an objective compound discussed here. In addition to 1a, its next higher analogs, bicyclic tercalicene (2a) and tricyclic



tetracalicene (3a) were also successfully synthesized and their electronic structures were examined on the basis of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopies, X-ray structure analyses, and MO and graph-theoretical calculations in order to clarify whether 1a is antiaromatic as expected.



### CYCLIC BICALICENE

By the reaction of 1,2-bis(*tert*-butylthio)-3,3-dichlorocyclopropene (**4**) obtained by thionyl chloride treatment of bis(*tert*-butylthio)cyclopropenethione (**5**) with lithium cyclopentadienide (2 equiv.) bis(*tert*-butylthio)derivative of **1a** (**1b**) was obtained as reddish purple crystals (mp 190–200 °C (dec)) in 10% yield. Subsequent reaction of **1b** with tri-*n*-butyltin hydride (3 equiv.)/2,2'-azoisobutyronitrile (1 equiv.) in hot chlorobenzene gave 3,11-bis(tri-*n*-butylstannyl)cyclic bicalicene (**1c**) (orange crystals, mp 60–61 °C) in 88%. Treatment of **1c** with sodium methoxide (0.1 equiv.) in benzene-methanol (1:1, v/v) afforded **1a** as orange plates (mp 125–130 °C (dec)) in 98% yield (ref. 6). In contrast with calicene, a dream compound still now, **1a** is unexpectedly stable even in air.

Their X-ray analyses were performed. The molecular structures of **1a** and **1b** are shown by the ORTEP drawing in Figure 1. The outer 16-membered ring is nearly planar, the mean atomic

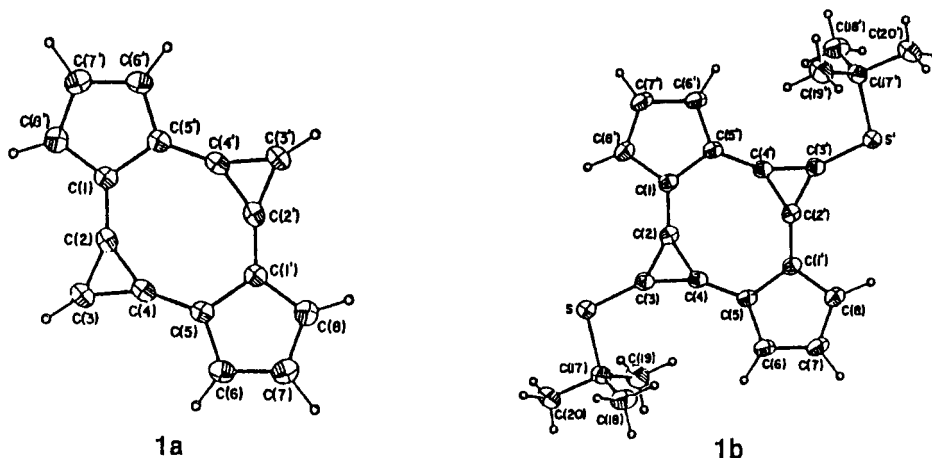


Fig. 1. ORTEP Drawings of **1a** and **1b**.

deviation from the least-squares plane ( $\Delta$ ) being 0.023 and 0.026 Å for **1a** and **1b**, respectively. The inner 8-membered ring makes a complete plane ( $\Delta=0.003$  and 0.006 Å for **1a** and **1b**, respectively). The dihedral angles between the 8- and 5-membered ring planes, and the 8- and 3-membered ring planes are 0.6 and 0.8° for **1a** and 1.6 and 4.5° for **1b**, respectively. Thus, the cyclic bicalicene skeleton has a planar molecular structure, although the molecular planarity is higher in **1a** than **1b**. The bond distances and angles of chemically equivalent but crystallographically independent parts show good coincidences for both **1a** and **1b**: the mean differences for bond distances and angles are 0.005 Å and 0.4° for **1a**, and 0.007 Å and 2.3° for **1b**, respectively. Consequently, both **1a** and **1b** are essentially of  $D_{2h}$  symmetry, although there is some deformation due to steric bulkiness of two *tert*-butylthio substituents.

The IR spectra of **1a** and **1b** revealed characteristic of the methylenecyclopropene double bonds absorptions at 1815 and 1555  $\text{cm}^{-1}$ , and 1782 and 1550  $\text{cm}^{-1}$ , respectively. In the  $^1\text{H-NMR}$  spectra of **1a** and **1b** the 5-membered ring protons appeared at  $\delta$  7.11 (d, 4H,  $J=3.66$  Hz) and 6.58 (t, 2H,  $J=3.66$  Hz) for **1a**, and 6.87 (d, 4H,  $J=3.8$  Hz), and 6.40 (t, 2H,  $J=3.8$  Hz) for **1b**, respectively. On the other hand, the 3-membered ring proton of **1a** appeared as singlet at  $\delta$  7.91. These  $^1\text{H}$  chemical shifts clearly indicate no upfield shift due to a paramagnetic ring current expected from peripheral  $16\pi$  conjugation. The  $^{13}\text{C-NMR}$  spectra were composed of five signals due to cyclic bicalicene skeletal carbons:  $\delta$  135.9, 128.2, 127.5, 123.0, 109.0 for **1b** and 140.9, 130.5, 124.7, 117.8, 110.2. The detailed examination of the  $^{13}\text{C}$  chemical

shifts of 1a provides valuable information on the electronic structure of the cyclic bicalicene system. The 3-membered ring carbons ( $\delta$  117.8, 140.9) appear at lower field than the unsaturated carbon of cyclopropene ( $\delta$  108.7). The lower-field shift is not beyond the value of the cyclopropenium ion ( $\delta$  175.9). On the other hand, the 5-membered ring carbons ( $\delta$  110.2, 124.7, 130.5) are observed at higher field as compared with the olefinic carbons of cyclopentadiene ( $\delta$  133.3 and 132.8). The highest-field shift is not upfield shifted beyond the value of cyclopentadienide ( $\delta$  102.0). The degree of polarization on each calicene unit of 1a, can be estimated from the  $^{13}\text{C}$  chemical shifts of carbon atoms in cyclopropene, cyclopropenium ion, cyclopentadiene, and cyclopentadienide. The average  $^{13}\text{C}$  chemical shifts of carbon atoms in 3- and 5-membered rings of 1a are  $\delta$  133.2 and 121.2, respectively. The 100% polarization of calicene in 1a corresponds to the cyclopropenium-cyclopentadienide structure, and the cyclopropene-cyclopentadiene structure is regarded as a nonpolar structure. Thus, each calicene unit in 1a involves 36-45% polarization, assuming that there is a linear relationship between the degree of calicene polarization and the average  $^{13}\text{C}$  chemical shifts of the 3- and 5-membered ring carbons. The degree of polarization estimated in this manner is nearly consistent with that (51-52%) obtained by modified Pariser-Parr-Pople type SCF MO calculations. Consequently, both a covalent structure with peripheral  $16\pi$  conjugation and a polar structure with a positive charge at the 3-membered ring and a negative charge at the 5-membered ring, respectively, contribute to the ground state of 1a in almost 50% each (ref. 7).

### BICYCLIC TERCALICENE AND TRICYCLIC TETRACALICENE

Two next higher analogs of 1a, 2a and its 3,19-bis(*tert*-butylthio)-substituted derivative (2b), and 3,18-bis(*tert*-butylthio)-substituted derivative (3b) of 3a, in which three or four calicene units are joined each other in a head-to-tail manner, were also successfully prepared. 3-Cyclopentadienyl-11-(*tert*-butylthio)cyclic bicalicene (14) (reddish purple crystals, mp 197-199 °C) was a key starting material, which was obtained by the reaction of 1b with lithium cyclopentadienide (20 equiv.) in 82% yield. By the reaction of 14 with LDA (2 equiv.) and then with 4 2b was obtained as dark green crystals (mp 195-205 °C(dec)) in 11% yield. The similar method used for the conversion of 1b to 1a was also applied to the conversion of 2b to 2a. Thus, heating a chlorobenzene solution of 2b, tri-*n*-butyltin hydride (10 equiv.) and 2,2'-azobisisobutyronitrile (3 equiv.) for 5-10 min at 110 °C, gave 3,19-bis(tri-*n*-butyltin)-substituted derivative (2c) (8%), and by subsequent treatment of 2c with an excess of acetic acid in methanol-benzene (1:1, v/v) 2a was obtained (59%) as dark brown crystals (mp 110-115 °C(dec)) (ref. 8). On the other hand, 3b was isolated as a black solid (mp 186-200 °C(dec)) in overall yield of 10% by the following four-step reactions: (1) deprotonation of 15 with LDA, (2) reaction of the resultant cyclopentadienide with 8, (3) iodomethane treatment, and finally (4) ring-closure of bis(cyclic bicalicene) with elimination of *tert*-butyl mercaptan (ref. 9). The conversion of 3b to 3a is still now unsuccessful because of both very poor production of 3,18-bis(tri-*n*-butyltin)-substituted derivative and remarkable thermal and acid instability of 3a. In consequence of several attempts to obtain single crystals of 2a, 2b and 3b for X-ray structure analysis, it was successful only for 2b. Very interestingly, the crystal lattice of 2b includes two crystallographically independent molecules, (2b-1 and 2b-2), as shown by ORTEP drawing in Figure 2. The bicyclic tercalicene skeleton takes almost a complete planar structure in both molecules. The remarkable difference between the molecules is the relative position of two *tert*-butylthio substituents: syn for 2b-1 and anti for 2b-2, respectively. In spite of the limited accuracy for the interatomic bond distances, the X-ray analysis revealed the following characteristic features in both molecules: (1) the pinch bond of the central calicene, C(23)-C(24), is longer than those of outer ones, (2) the C(1)-C(19) and C(12)-C(16) bonds are the longest in the 5-membered

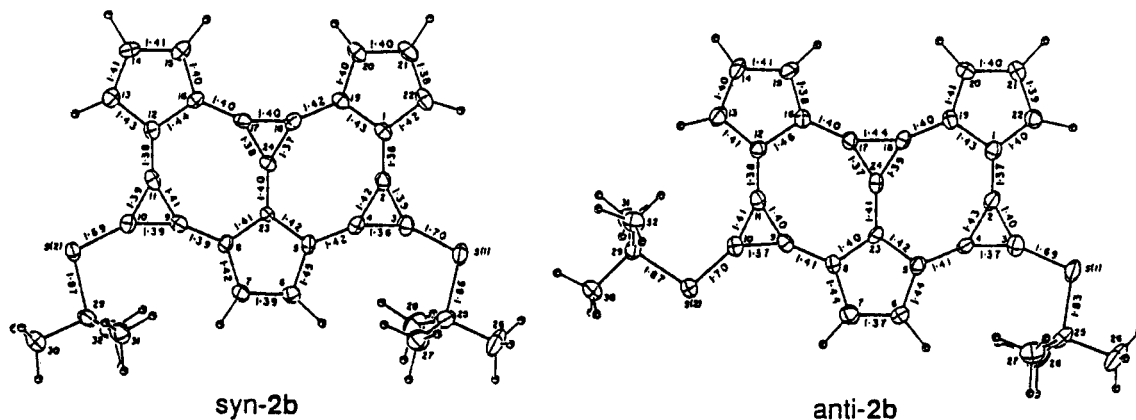


Fig. 2. ORTEP Drawings of two crystallographically independent molecules, syn-2b and anti-2b.

rings of outer calicenes, (3) the C(2)-C(4) and C(9)-C(11) bonds are longer or equal to the other bonds in the 3-membered rings of outer calicenes, (4) the C(6)-C(7) bond is the shortest in the 5-membered ring of central calicene, and (5) the C(17)-C(18) bond is longer than the other bonds in the 3-membered ring of central calicene.

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of 2a, 2b and 3b were measured and compared with those of 1a and 1b. The  $^1\text{H}$  chemical shifts of 1a and 2a, and of 1b, 2b and 3b are shown in Figure 3. Obviously there is almost no change in the chemical shifts of corresponding 3- and 5-membered ring protons between 1, 2 and 3. This result indicates no significant symptom of diamagnetic and paramagnetic ring currents induced by the peripheral 22- and 28- $\pi$  conjugations also in 2a and 3a, respectively, as there was realized no paramagnetism in 1a. Figure 4 summarizes the  $^{13}\text{C}$  NMR chemical shifts of 1a, 1b, 2a and 2b. The  $^{13}\text{C}$  NMR spectrum of 3b was also measured, which revealed 16 signals in correspondence with a tricyclic tetracalicyclic skeleton. Howev-

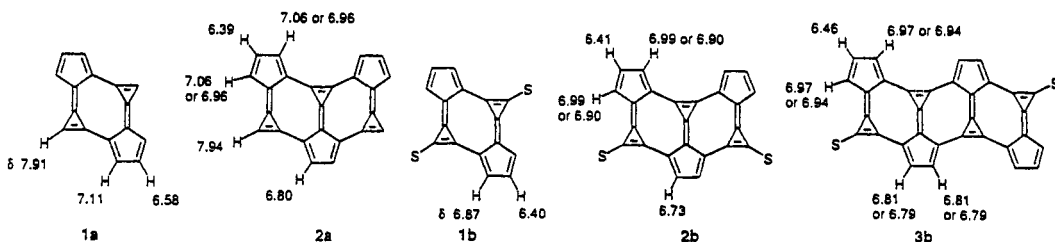


Fig. 3.  $^1\text{H}$  Chemical shifts of 1a, 2a, 1b, 2b, and 3b.

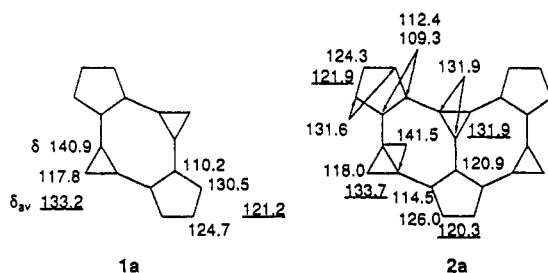


Fig. 4.  $^{13}\text{C}$  NMR Chemical shifts of 1a and 2a.

er, reasonable assignment is not still accomplished. The chemical shifts of both inner and outer 3-membered and outer 5-membered ring carbons of 2a and 2b are almost the same to those of 1a and 1b. However, the situation is remarkably different for the inner 5-membered ring carbons. Thus, the three carbons connected by 3-membered rings showed their chemical shifts at the fairly higher field as compared with those of the remaining two carbons, strongly suggesting the preferential localization of a negative charge at the connected part. Furthermore, the average chemical shifts of each 3- and 5-membered rings were calculated to be 120.3 (119.3), 121.9 (120.5), 131.9 (131.4), and 133.7 (133.0) for central and terminal 5- and 3-membered rings of 2a (2b), respectively. When these values are considered together with those of 1a (121.2 and 133.2 for the 5- and 3-membered rings, respectively) and 1b (119.2 and 133.3), both central and terminal calicene units in 2 are polarized by ca. 50%, and the degree of polarization is almost close to that of 1. In conclusion, alike 1a 2a also has important contribution of a polar structure with a somewhat different structure from that of 1a. On the other hand, as for covalent structures such a 16 $\pi$ -conjugated structure as is participating in 1a is predominant rather than a peripheral 22 $\pi$ -conjugated structure. Eventually, 2a is stabilized by the two cyclic bicalicyclic type of conjugations, laying again great emphasis on the remarkable stabilization of a cyclic bicalicyclic system. Presumably, the similar conclusion can be also brought to 3a, in view of the  $^1\text{H}$  NMR and graph-theoretical calculation results.

## REDOX

It is well documented that for antiaromatic systems conversion to the corresponding aromatic systems by oxidation or reduction progresses favorably in energy, while the reverse case is energetically remarkably unfavorable. Therefore, investigation on redox of cyclic polycalicyclics can provide strong informations to understanding of their electronic structures. The cyclic voltammetric measurement of 1b, 2b and 3b was carried out in  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{CN}$  (2:3, v/v) at  $-70^\circ\text{C}$  under Ar atmosphere (ref. 10). The redox potentials obtained in the voltage range of +2.0 ~ -2.0 V vs. Ag/AgCl are shown in Table I, along with the values of [16]- (ref. 11) and [18]-annulenes (ref. 12) for comparison. Reversible waves appeared in their reductions, while the waves in their oxidations were irreversible, indicating that their radical anions and dianions are stable as compared with their radical cations and

Table I. Redox potentials of 1b, 2b, 3b, and their related [16]- and [18]-annulenes.

	Redox potential <sup>a</sup>			
	E <sub>1</sub>	E <sub>2</sub>	E <sub>3</sub>	E <sub>4</sub>
<u>1b</u> <sup>b</sup>	+1.16 <sup>d</sup>	+0.97 <sup>d</sup>	-1.77	— <sup>e</sup>
<u>2b</u> <sup>b</sup>	+0.70 <sup>d</sup>	+0.49 <sup>d</sup>	-1.33	-1.75
<u>3b</u> <sup>b</sup>	+0.85 <sup>d</sup>	+0.47 <sup>d</sup>	-1.14	-1.49
[16] annulene <sup>c</sup>			-1.23	-1.52
[18] annulene <sup>c</sup>			-1.56	-1.90



a) V vs. Ag/AgCl. b) Measured in CH<sub>2</sub>Cl<sub>2</sub> - CH<sub>3</sub>CN (2:3 v/v) at -70 °C.  
 c) Measured in DMF at 0 °C. d) Irreversible steps. Anodic peak potentials.  
 e) Not observed within -2.5V.

dications. From comparison of the potentials between 1b, 2b and 3b, both oxidation and reduction tend to become easier in the order of 1b, 2b and 3b, irrespectively of [4n]- and [4n+2]- $\pi$  conjugations in periphery. This makes a marked contrast with the case of [16]- and [18]-annulenes, in which [16]-annulene is more reduced to its radical and dianion than [18]-annulene in spite of the smaller  $\pi$  conjugation system. If peripheral 16-, 22-, and 28- $\pi$  conjugations had significant contribution to the ground state of 1a, 2a and 3a, respectively, a regular change in the potentials should be recognized. That is really not true. Furthermore, the second reduction potential of 1b is remarkably high (<-2.5 V), where the corresponding dianion is produced, a very stable aromatic system if a peripheral 18 $\pi$  conjugation is efficient. An analogous argument can be also applied to the oxidation of 1b. These results are consistent with before mentioned NMR results that indicate large polarization of each calicene unit in cyclic polycalicycnyls.

## THEORETICAL CONSIDERATION

The characteristics of electronic structures of cyclic polycalicycnyls were investigated by using the SCF MO and graph-theoretical calculations. The electron density distributions of 1a, 2a and 3a were calculated by the modified Pariser-Parr-Pople type of SCF MO method (ref. 7, 8, 9). The calculation results show that a considerably large polarization of each calicene unit occurs in any cyclic polycalicycnyl. The degree of polarization is almost 50% irrespectively of number of calicene units and inner or outer position of a calicene unit. The analogous conclusion was also derived from the graph-theoretical calculations, in which resonance energies (RREs) of 3- and 5-membered constituent rings contribute significantly to the overall resonance energy of cyclic polycalicycnyls. Table II summarizes resonance energies of 1a, 2a, 3a and their related  $\pi$ -conjugated hydrocarbon systems calculated by the  $\omega$ -technique method, in which  $\omega=1.4$  was used (ref. 13). Also included in the Table are their percent resonance energies (%REs), the values defined as 100 times the resonance energies divided by the energies of the "localized" reference structures (ref. 14). This %RE value is quite consistent with experimental stability for a variety of  $\pi$ -conjugated hydrocarbon systems: generally stable for %RE>0.50 and extremely unstable for %RE<-0.50. The %RE values of 1a, 2a and 3a are 0.87, 0.63 and 0.57, respectively, indicating that three cyclic polycalicycnyls are indeed aromatic systems, although aromatic stabilization tends to decrease as increasing the number of calicene units. In contrast with these cyclic polycalicycnyls, calicene itself is not aromatic and has rather an olefinic character, as indicated by its smaller %RE value (0.36) than 0.5. Another isomer of 1a, in which two calicene units are joined in a head-to-head manner, has a large and negative %RE value (-0.848). The graph-theoretical calculations are of great advantage to understanding the role of each constituent ring contributing to overall resonance stabilization of such polycyclic  $\pi$ -conjugated systems as cyclic polycalicycnyls. For 1a there are only 11 possible constituent rings, but the numbers increase to 60 and 200 for 2a and 3a, respectively. Therefore, only significant constituent rings were picked up for 2a and 3a and their RRE values were compared with each other. The RRE values of 3- and 5-membered rings composing of calicene were also obtained for comparison with those of cyclic polycalicycnyls. The followings can be pointed out: (1) 3- and 5-membered rings make most important contribution to overall resonance stabilization of cyclic polycalicycnyls; (2) the RRE's of 3- and 5-membered rings contained in each cyclic polycalicycnyl are large (0.14-0.188) as compared with those of calicene (0.04-0.068); (3) aromatic or antiaromatic peripheral 16-, 22- and 28- $\pi$  conjugations are negligibly small. In view of these results, it is exaggeratedly said that cyclic polycalicycnyls are stabilized by polarization of each calicene unit, even if this conclusion must

Table II. Resonance energies (REs) and percent resonance energies (%REs) of **1a**, **2a**, **3a**, calicene, and another isomer of **1a**.

	RE, $\beta^a$	% RE $^b$
<b>1a</b>	0.193	0.87
<b>2a</b>	0.214	0.63
<b>3a</b>	0.257	0.57
	0.038	0.36
	-0.188	-0.848

be taken into consideration with care, since the graph-theoretical calculations are essentially based on Hückel MO method.

### CONCLUSIONS

On the contrary to prediction from perturbation MO method cyclic polycalicylenyls are undoubtedly aromatic. The main causes arises out of a large polarization of each calicene unit producing two stable aromatic systems of cyclopropenium ion ( $2\pi$ ) and cyclopentadienide ( $6\pi$ ). Nevertheless, it must be taken into consideration that a peripheral  $16\pi$  conjugation has also significant contribution to the ground state of any cyclic polycalicylenyl. Very recently, ESR study gave distinct evidence of such a participation. The chemistry of cyclic polycalicylenyls is now in an important position to solving problems of  $\pi$  conjugation modes and possible participation of biradical structure in nonalternant polycyclic systems. On the ground of space limitation there was no description for a number of interesting reactions of cyclic polycalicylenyls. The results will be reported in due time.

### Acknowledgement

The authors are greatly indebted to the late Prof. Shigeo Yoneda who has made a significant contribution at the initial stage of this work, and also Prof. Nobutami Kasai, Prof. Yasushi Kai, Prof. Tsunetoshi Kobayashi, Prof. Jun-ichi Aihara, Dr. Mitsuhiro Shibata, Mr. Akihiko Sakai, Mr. Hiroshi Ando, Mr. Yoshihisa Arai, and Mr. Masashi Sakaguchi for their kind and active collaborations.

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