50-Ω load resistor and was analyzed by using a Tektonix 7912 AD transient digitizer liked to a Tektronix WP2252 signal processing system. All alkenes were distilled before use, and spectrograde solvents were employed. Further details appear above (see Discussion section), where particulars of the studies with p-$CF_3C_6H_4CBr$ and p-$CH_3OC_6H_4CF$ are described.

Acknowledgment. We thank the National Science Foundation for support of this work at both Rutgers and Columbia Universities. Additionally, the Columbia authors thank the Air Force Office of Scientific Research for financial support.

Registry No. 1, 95911-65-2; **2**, 87282-19-7; **3**, 4460-46-2; **4**, 4222-25-7; **5**, 95911-64-1; TME, 563-79-1; p-$F_3CC_6H_4CBr$, 104197-52-6; PhCBr, 14541-26-5; PhCCl, 19807-41-1; PhCF, 17825-75-1; p-$MeOC_6H_4CF$, 104197-53-7; 1-hexene, 592-41-6; 1-bromo-1-(p-trifluoromethyl)phenyl)-2-n-butylcyclopropane, 104197-48-0; 1-fluoro-1-(p-methoxyphenyl)-2-n-butylcyclopropane, 104197-49-1; 1-fluoro-1-(p-methoxyphenyl)-2,2,3,3-tetramethylcyclopropane, 104197-50-4; 1-bromo-1-(p-(trifluoromethyl)phenyl)-2,2,3,3-tetramethylcyclopropane, 104197-51-5.

Electronic Structure of Cyclic Bicalicenes

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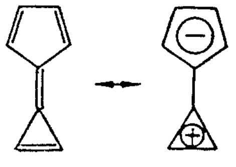
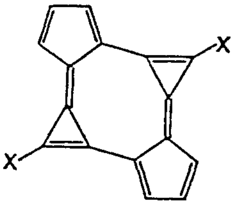
Abstract: The novel π-electron system, pentacyclo[11.3.0.0^{2,4}.0^{5,9}.0^{10,12}]hexadeca-1,3,5,7,9,11,13,15-octaene ("cyclic bicalicene") has been prepared, in which two calicene units are joined in a head-to-tail manner. The X-ray crystallographic analysis indicates that the cyclic bicalicene skeleton is completely planar; i.e., the molecule has D_{2h} symmetry. Cyclic bicalicene is shown to have a characteristic absorption band at around 500 nm, which is interpreted as an intramoleculer charge-transfer band by a SCF-CI MO method. From the ^{1}H NMR spectra, the paramagnetic ring current due to peripheral 16π conjugation is not observed. The ^{1}H and ^{13}C NMR chemical shifts suggest that a considerably large polarization of each calicene unit occurs in the cyclic system. The alternating polarization in cyclic bicalicene is also supported by the graph-theoretical and SCF MO calculations.

Cyclopropenylidenecyclopentadienide (calicene) (**1**) is a cross-conjugated π system, whose synthesis and characterization have been of keen interest.[1] Thus far, the parent calicene has not been isolated. However, a number of calicene derivatives substituted with strong electron-donating and/or electron-withdrawing groups at the cyclopropenyl and/or cyclopentadienyl rings have been isolated as stable compounds. From the investigation of their electronic character, it has been shown that a polar structure (**1B**) contributes significantly to the ground state.[2]



(1A) (1B)

Recently, we have succeeded in the isolation of the 3,11-bis(*tert*-butylthio) derivative **2a** as a stable crystalline compound.[3] This compound contrasts in stability to 5,6-bis(*tert*-butylthio)calicene,[1i] which is unstable even at −78 °C and which evidences a large contribution of covalent structure (**1A**) based on NMR and IR spectral data. Furthermore, the parent system **2b** has been isolated as stable crystals by the reductive desulfurization of **2a**.[3] As we briefly reported before, since **2b** is an unprecedented "aromatic" system with a 16π-electron periphery, we have investigated its electronic structure and π-conjugatin mode based on ^{1}H and ^{13}C NMR spectral data, X-ray structural analysis, and graph-theoretical and a modified Pariser-Parr-Pople-type SCF MO methods ("the variable integrals method I") and elucidated the cause of stabilization. In addition, acyclic bicalicene has been synthesized as a reference π system for cyclic bicalicene. Since the electronic spectrum of cyclic bicalicene is very characteristic, the character of electronic transition is interpreted by using the



(2a) : X=SBu^t

(2b) : X=H

(2c) : X=SnBu$^n_3$

[†] Kyoto University.

[‡] Osaka University.

[§] The Institute of Physical and Chemical Research.

(1) (a) Johns, W. M.; Pyron, P. S. *J. Am. Chem. Soc.* **1965**, *87*, 1608. (b) Ueno, M.; Murata, I.; Kitahara, Y. *Tetrahedron Lett.* **1965**, *6*, 2967. (c) Kende, A. S.; Izzo, P. T. *J. Am. Chem. Soc.* **1965**, *87*, 4162. (d) Prinzbach, H.; Fischer, U. *Angew. Chem.* **1965**, *77*, 258. (e) Bergmann, E. D.; Agranat, I. *Tetrahedron* **1966**, *22*, 1275. (f) Prinzbach, H.; Fischer, U. *Helv. Chim. Acta* **1967**, *50*, 1669. (g) Prinzbach, H.; Woischnik, E. *Helv. Chim. Acta* **1969**, *52*, 2472. (h) Prinzbach, H. *Pure Appl. Chem.* **1971**, *28*, 281. (i) Yoshida, Z. *Pure Appl. Chem.* **1982**, *54*, 1059.

(2) (a) Dewar, M. J. S.; Gmeidner, G. J. *Tetrahedron* **1965**, *21*, 3423. (b) Nakajima, T.; Kohda, S.; Tajiri, A.; Karasawa, S. *Tetrahedron* **1967**, *23*, 2189.

(3) Yoneda, S.; Shibata, M.; Kida, S. Yoshida, Z., Kai, Y.; Kasai, N. *Angew. Chem.* **1984**, *96*, 75; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 63.

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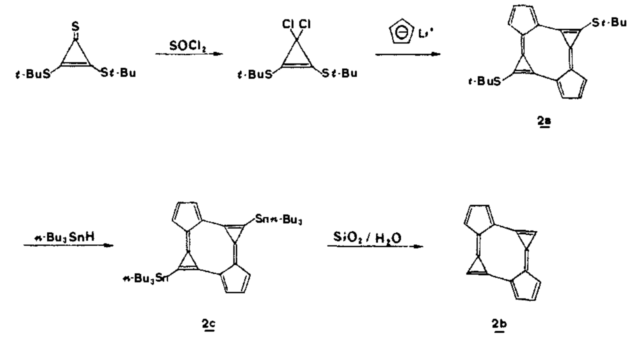
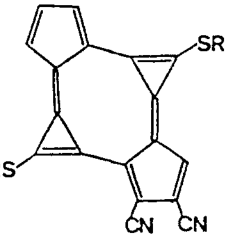
Scheme I



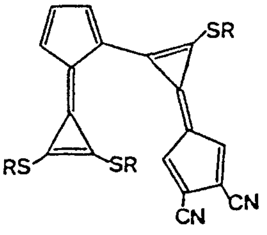
configuration interaction method combined with the SCF MO method mentioned above.

Results and Discussion

Synthesis of 2a, 2b, 3, and 4 and X-ray Structure Analysis of 2a and 2b. When 1,2-bis(*tert*-butylthio)-3,3-dichlorocyclopropene, obtained by the thionyl chloride treatment of bis(*tert*-butylthio)cyclopropenethione,[4] was reacted with 2 equiv of lithium cyclopentadienide in THF at −70 °C, **2a** was isolated as a reddish purple solid in 10% yield. The reaction of **2a** with tri-*n*-butylstannyl hydride in the presence of AIBN gave 3,11-bis(tri-*n*-butylstannyl) cyclic bicalicene (**2c**) (orange crystals, 42% yield). Conversion of **2c** into **2b** was unsuccessful by the usual acids or bases. It was, however, readily achieved by standing **2c** on silica gel for 0.5 h at room temperature (yield 40%) (Scheme I). Silica gel is considered to act as a mild acid catalyst for the Sn–C bond fission. Acyclic bicalicene **4** was formed by the reaction of 1,2-bis[bis(*tert*-butylthio)cyclopropenylio]cyclopentadienide[5] with tetramethylammonium 1,2-dicyanocyclopentadienide[6] in dichloromethane at 0 °C as an unstable yellow solid in 5% yield along with **3** (13% yield). When **4** was allowed to stand in dichloromethane at room temperature, **3** was obtained as reddish purple crystals in 73% yield.



(3)



(4)

The single crystals of **2a** and **2b** were obtained by recrystallization from dimethoxyethane and chloroform, respectively. X-ray crystallographic analysis of **2a** determined the centrosymmetric molecular structure shown in Figure 1 along with the selected bond distances and angles. No bond alternation is observed in the outer sixteen-membered and inner eight-membered ring systems. The outer sixteen-membered ring is nearly planar, the mean atomic deviation from the least-squares plane (Δ) being 0.026 Å. The inner eight-membered ring is planar (Δ = 0.006 Å). The diheral angles between the eight- and five-membered rings (Δ = 0.003 Å) and between the eight- and three-membered rings are 1.6° and 4.5°, respectively. Thus, the molecular structure excluding the *tert*-butylthio substituent has approximate D_{2h} symmetry. The chemically equivalent but significantly different structural parameters in a crystal structure are as follows: C_1–C_2 (1.388 Å) and C_4–C_5 (1.401 Å), C_1–C_2–C_3 (151.6°) and C_3–C_4–C_5 (156.4°), C_2–C_3–S (143.1°) and S–C_3–C_4 (155.6°), and C_8–C_1–C_2 (127.5°) and C_4–C_5–C_6 (130.8°). All the bond angles along the S–C_3–C_4–C_5 system are larger than those along the S–C_3–C_2–C_1 system with the same trend of a slight elongation in C_4–C_5 bond compared with the C_1–C_2 bond, indicating that the sixteen-membered ring deforms significantly from the D_{2h} symmetry. This deformation can be attributed mainly to the steric effect of the *tert*-butylthio substituent. The nonbonded distance between C_{18} and H_6 is 3.23 Å, which represents a normal van der Waals contact in considering the van der Waals radii of methyl carbon (2.0 Å) and hydrogen (1.2 Å).

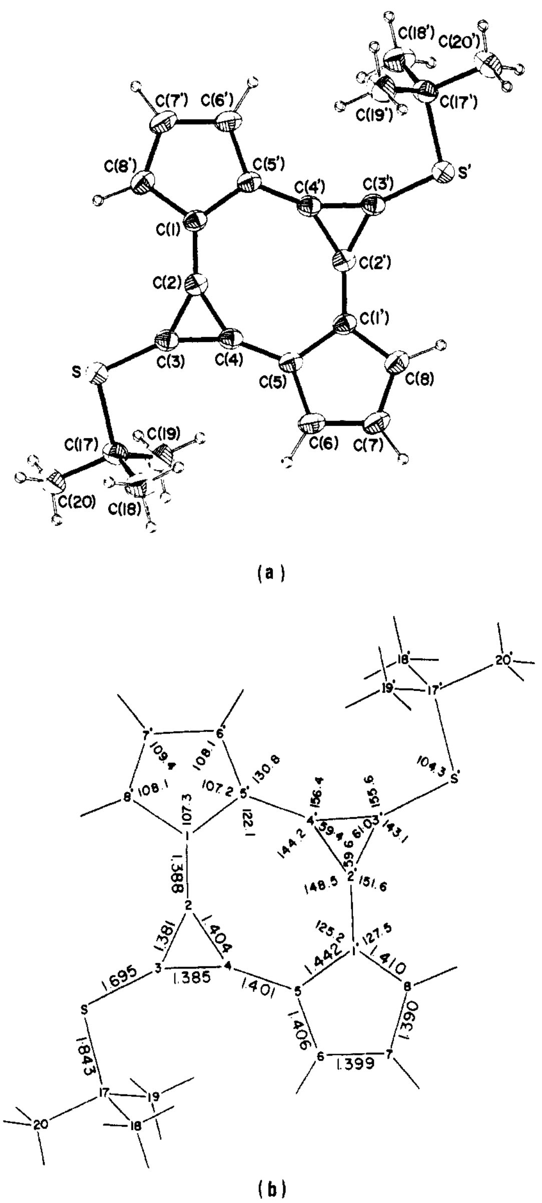


Figure 1. (a) Molecular structure of **2a** shown by the ORTEP-II drawing. Thermal ellipsoids for non-hydrogen atoms are drawn at the 30% probability level. The hydrogen atoms are shown as the spheres with radii of 0.1 Å. (b) Selected bond distances and angles in the molecular structure of **2a**. The estimated standard deviations are 0.002 Å for C–S and 0.003–0.004 Å for C–C bonds, 0.1° for C–S–C and 0.1–0.2° for S–C–C and C–C–C angles. Distances and angles omitted in the figure are as follows: C_{17}–C_{18} = 1.522 Å, C_{17}–C_{19} = 1.524 Å, C_{17}–C_{20} = 1.534 Å, S–C_{17}–C_{18} = 109.5°, S–C_{17}–C_{19} = 109.9°, and S–C_{17}–C_{20} = 103.4°.

The preliminary X-ray structure analysis of **2b** has already been reported.[3] The planarity of **2b** is greater than that of **2a**. The Δ values of the sixteen-, eight-, and five-membered rings are 0.023, 0.003, and 0.010 Å, respectively. The dihedral angles between the eight- and five-membered ring planes and between the eight- and three-membered ring planes are 0.6° and 0.8°, respectively. In addition to the high planarity of the molecule, the bond dis-

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(4) Miki, S. Ph.D. Thesis, Kyoto University, 1978. This compound was synthesized by the reaction of tris(*tert*-butylthio)cyclopropenium perchlorate with sodium bicarbonate in refluxing ethyl acetate in 90% yield.

(5) Yoshida, Z.; Shibata, M.; Kida, S.; Miki, S.; Sugimoto, T.; Yoneda, S. *Tetrahedron Lett.* **1984**, 345.

(6) Webster, O. W. *J. Am. Chem. Soc.* **1966**, *88*, 3046.

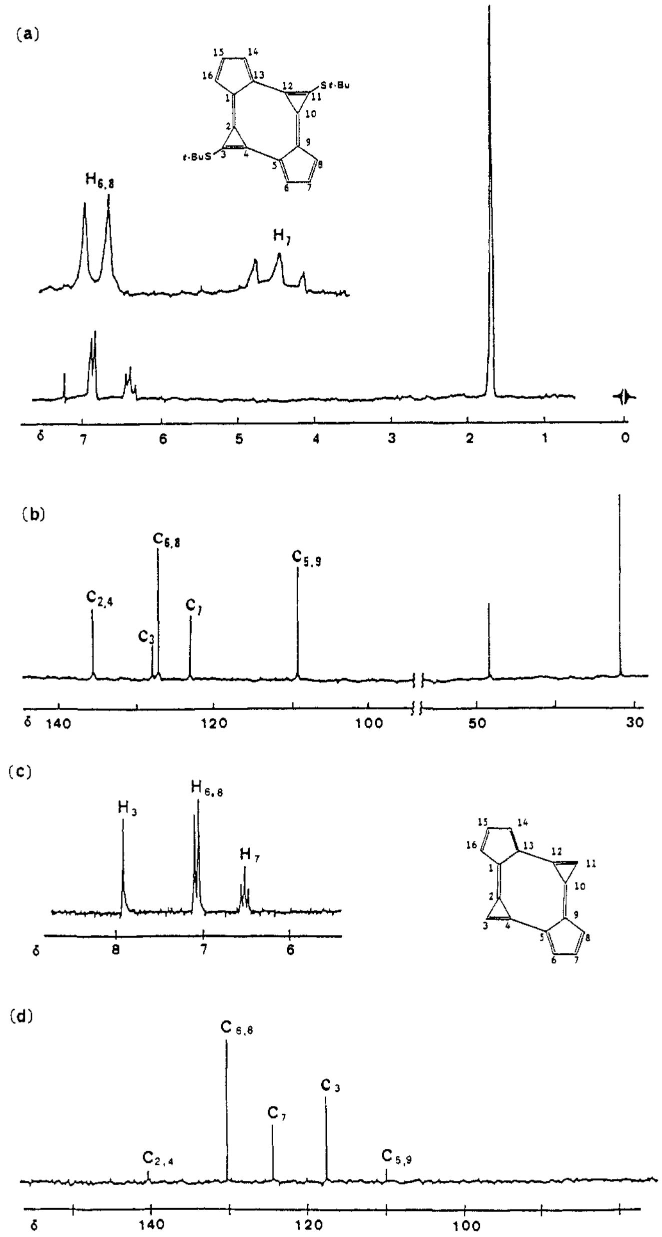

Figure 2. ^1H (a) and ^{13}C (b) NMR spectra of **2a** and the ^1H (c) and ^{13}C (d) NMR spectra of **2b** measured in $CDCl_3$.

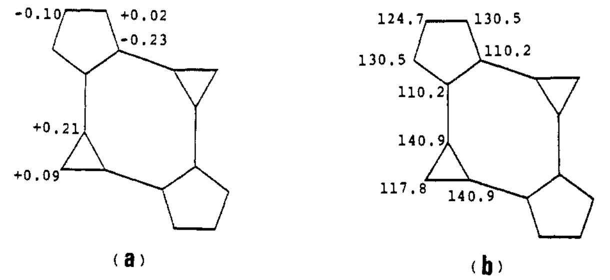

Figure 3. (a) Charge distribution calculated by the VI/1 method. (b) ^{13}C NMR chemical shift values (δ).

tances and angles of chemically equivalent but crystallographically independent parts show good coincidences. Thus, the mean differences are 0.005 Å for bond distances and 0.4° for angles, respectively. In contrast with this, the corresponding values in **2a** are 0.007 Å and 3.5°. From these data, the molecular symmetry of **2b** is concluded essentially to be D_{2h}.

^1H and ^{13}C NMR Spectra. For both of the cyclic bicalicenes (**2a** and **2b**), the ^1H signals of the cyclopentadienyl ring are observed in the normal region (δ 6.4–7.4) (Figure 2), indicating no upfield shift due to a paramagnetic ring current induced by the 16π-electron periphery.[7] Indeed, when the chemical shifts of the ring protons of 3,11-bis(*tert*-butylthio)-6,7-dicyano cyclic bicalicene (**3**) and the corresponding acyclic system 5,6,6′-tris(*tert*-butylthio)-2′,3′-dicyano-1,5′-bicalicene (**4**) are compared, no upfield shift of the cyclopentadienyl protons of **3** is observed compared with those of **4** as is seen in the following data: δ 6.40 (t), 6.95 (dd), and 7.12 (dd) for **3** and 6.60 (t), 7.23 (dd), and 7.37 (dd) for **4**.[8] On the other hand, the ^1H signal of the cyclopropenyl part of **2b** appeared at δ 7.91, which is close to that of methylenecyclopropene.[9] The equivalence of vicinal coupling constants ($J_{6,7}$ = $J_{7,8}$ = 3.66 Hz) in **2a** and **2b** suggests that no bond alternation occurs at the C_6–C_7–C_8 bond of both the compounds. By use of the following equation which relates the vicinal coupling constant (J_{vic}) and π-bond order ($P_{r,s}$), $J_{vic} = 7.12P_{r,s} - 1.18$, the $P_{6,7}$ of the cyclopentadienyl bond of **2b** is estimated to be 0.68.[10] This value is in the range characteristic of aromatic bonds (0.4–0.7) according to Streitwieser's criterion.[10] The ^{13}C NMR of the skeletal carbons of **2b** revealed only five signals (Figure 2), indicating overlap of the $C_{6,8}$, $C_{5,9}$, and $C_{2,4}$ signals. From these results it is concluded that **2a** and **2b** belong to a D_{2h} point group. The ^{13}C–H coupling constants ($J_{^{13}C-H}$) for **2b** are 167.9 Hz for C_6–H_6 (C_8–H_8), 164.4 Hz for C_7–H_7, and 235.5 Hz for C_3–H_3, respectively, so that the hybridizations of the skeletal carbon atoms that take part in the bonding to hydrogen atoms are sp^2 for $C_{6,7,8}$ and sp for C_3, respectively.[11]

The detailed examination of the ^{13}C chemical shifts of **2b** provides valuable information on the electronic structure of the cyclic bicalicene system. The three-membered ring carbons (C_3, δ 117.8; $C_{2,4}$, δ 140.9) appear at lower field than the unsaturated carbon of cyclopropene (δ 108.7).[12] The low-field shift of $C_{2,4}$ is not beyond the value of the cyclopropenium ion (δ 175.9).[13] On the other hand, the five-membered ring carbons ($C_{5,9}$, δ 110.2; $C_{6,8}$, δ 130.5; C_7, δ 124.7) are observed at higher field as compared with the olefinic carbons of cyclopentadiene (δ 133.3 and 132.8).[14] The carbons $C_{5,79}$ are not upfield shifted beyond the value of cyclopentadienide (δ 102.0).[15] The degree of polarization on each calicene unit of **2b** can be estimated from the ^{13}C chemical shifts of carbon atoms in cyclopropene, cyclopropenium ion, cyclopentadiene, and cyclopentadienide. The average ^{13}C chemical shifts of carbon atoms in three- and five-membered rings of **2b** are δ 133.2 and 121.2, respectively. The 100% polarization of calicene in **2b** corresponds to the cyclopropenium–cyclopentadienide structure, and the cyclopropene–cyclopentadiene structure is regarded as a nonpolar structure. Thus, each calicene unit in **2b** involves 36–45% polarization, assuming that there is a linear relationship between the degree of calicene polarization

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(7) The ^1H NMR spectral pattern of **2a** and **2b** was not changed even at -80 °C. The measurement at lower temperatures than -80 °C was difficult because of its poor solubility.

(8) Detailed examination of the ^1H chemical shifts together with the ^{13}C NMR data suggests strikingly different polarization between **3** and **4**. Thus, for the former the tetrapolar structure mainly contributes, while the latter has important contribution of the dipolar structure charged positively in the terminal three-membered ring and negatively in the other terminal five-membered ring, respectively. Because of such a dipolarization in **4**, the terminal cyclopentadienyl carbon is preferably subjected to nucleophilic attack of the terminal cyclopropenyl carbon, followed by removal of *tert*-butylmercaptan to give a more stable **3**, in which two alternate charges are dispersed in the four rings.

(9) (a) Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3698. (b) Staley, S. W.; Norden, T. D. *J. Am. Chem.* **1984**, *106*, 3699.

(10) Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; *Wiley*: New York, 1961; p 172.

(11) Being different from the case of ordinary systems, hybrid orbitals around the carbon atoms constructing strained ring systems are not equivalent.

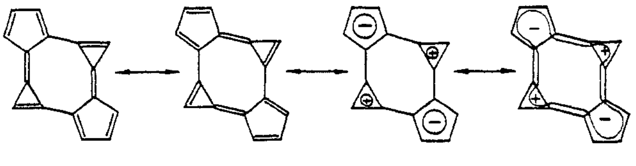
(12) Günther, H.; Seel H. *Org. Magn. Reson.* **1976**, *8*, 299.

(13) Olah, G. A.; Staral, J. S.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 6233.

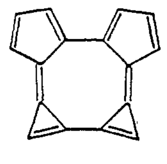
(14) Chertkov, V. A.; Grishin, Yu. K.; Sergeev, N. M. *J. Magn. Reson.* **1976**, *24*, 275.

(15) Spieseke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468.

and the average ^{13}C chemical shifts of the three- and five-membered ring carbons. The above conclusion is well supported by the charge distribution calculated by the variable integrals method I (VI/1 method),[16] as shown in Figure 3. There is satisfactory correspondence between the calicene polarization (51–52%) obtained by the VI/1 method and the above ^{13}C chemical shift values. From both the experimental and computational results, the negative charge is mainly distributed at the C_5, C_7, and C_9 positions of the five-membered ring, while the positive charge is mainly distributed at the C_2 and C_4 carbons in the three-membered ring. On the basis of these data, pentadienyl anion-type and allyl cation-type charge distributions are considered for the five- and three-membered rings, respectively. Therefore, as a polar structure contributing to the ground state of cyclic bicalicene, a tetrapolar [16]annulene structure (**2D**)[17] must be considered in addition to a respresentative structure (**2C**).



2A 2B 2C 2D



(2')

Table I. Resonance Energies (REs) of Cyclic π-Electron-Conjugated Systems

system	RE, β^a	% RE
2b	0.193	0.87
calicene	0.038	0.36
sesquifulvalene	0.023	0.15
fulvene	−0.082	−1.10
triafulvene	−0.145	−2.96
s-indacene	−0.056	−0.35
2'	−0.188	−0.848

^{a}Calculated by the ω (ω = 1.4) technique.

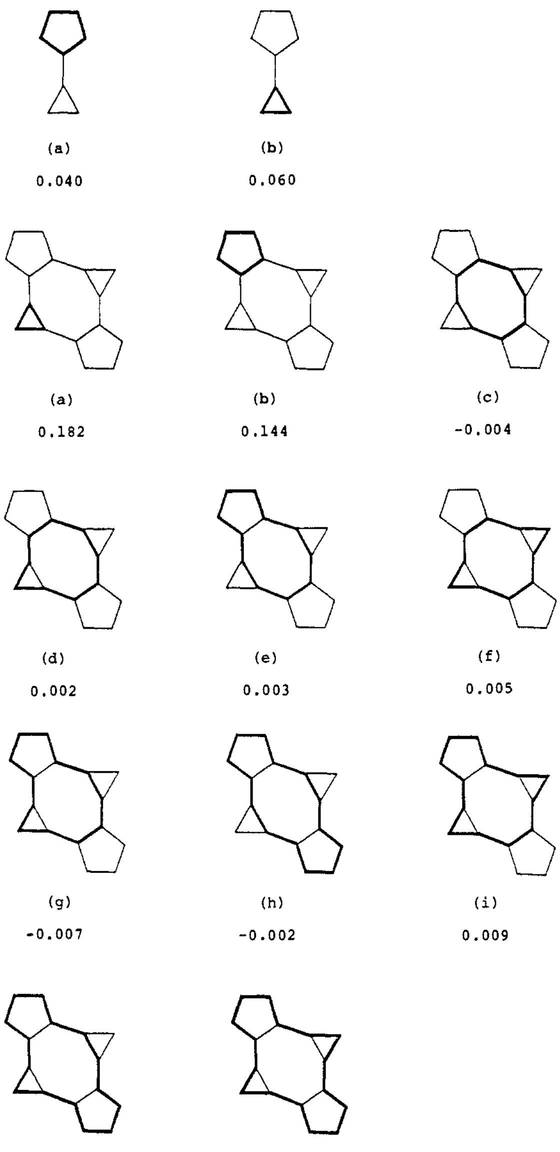


Figure 4. Ring resonance energies (RREs) of each constituent ring of calicene (structures a and b) and **2b** (structures a–k) calculated by the Aihara's $\beta\omega'\omega''$ method.

Graph-Theoretical Calculations. The resonance energy (RE) of **2b** was calculated by using Aihara's graph-theoretical method,[18] and its RE was compared with those of calicene itself, another isomer of cyclic bicalicene (**2'**), and some cyclic π systems (Table I). Also included in Table I are percent resonance energies (%RE's)[19] of these cyclic π systems. The RE (0.193β) and %RE (0.87) of **2b** are much larger than those of calicene (0.038β and 0.36) and sesquifulvalene (0.023β and 0.15). Consequently, from a graph-theoretical standpoint, **2b** can be regarded as a very stable aromatic system, which is supported by experiment. On the other hand, fulvene, triafulvene, and *s*-indacene have negative %RE values. More remarkable is a large negative %RE value (−0.85) for the isomeric cyclic bicalicene, **2'**. These cyclic π systems are anticipated to be antiaromatic. In order to elucidate the cause of the extraordinary stabilization of **2b**, the ring resonance energy (RRE), that is, the resonance energy of each ring of **2b**, was calculated by Aihara's $\beta\omega'\omega''$ method.[20] This result is summarized together with the RRE values of calicene in Figure 4. The RREs of the three- and five-membered rings of **2b** are 0.182β (structure a) and 0.144β (structure b), respectively, which are strikingly larger than the values of the three- and five-membered rings of calicene (0.040β and 0.060β). Furthermore, it is noteworthy that

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(16) (a) Yoshida, Z.; Kobayashi, T. *Theor. Chim. Acta* **1970**, *19*, 377; (b) *Bull. Chem. Soc. Jpn.* **1972**, *45*, 316.

(17) The ^{13}C NMR and MINDO/3 calculations of **2b** indicate similar electron distributions to the pentadienyl anion and allyl cation on the five- and three-membered rings, respectively. This type of polar structure can be regarded as tetrapolar [16]annulene structure **2D**, which is produced by tetrapolarization of the peripheral 16π electrons along the outer σ framework, whose shape could assist this polarization. Such a polarization should have a minor contribution but should be also useful for stabilization of the planar 16π system.

(18) (a) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750. (b) Aihara, J. *Pure Appl. Chem.* **1982**, *54*, 1115.

(19) The %RE is defined as 100 times the resonance energy divided by the energy of the "localized" reference structure. This value is quite consistent with experimental stability for a variety of π-electron-conjugated systems: %RE > 0.50, generally stable; %RE < −0.50, extremely unstable. The %RE values of the other representative π-electron-conjugated systems are as follows: benzene, 3.53; cyclooctatetraene, −5.80; naphthalene, 2.92; azulene, 0.42; [10]annulene, 1.25; [12]annulene, −2.57.

(20) This calculation method is improved by the ω technique considering bond alternation, because of the appearance of significant uncertainty in nonalternant polycyclic π-electron-conjugated systems: (a) Aihara, J. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2689. (b) Aihara, J. *J. Am. Chem. Soc.* **1985**, *107*, 298.

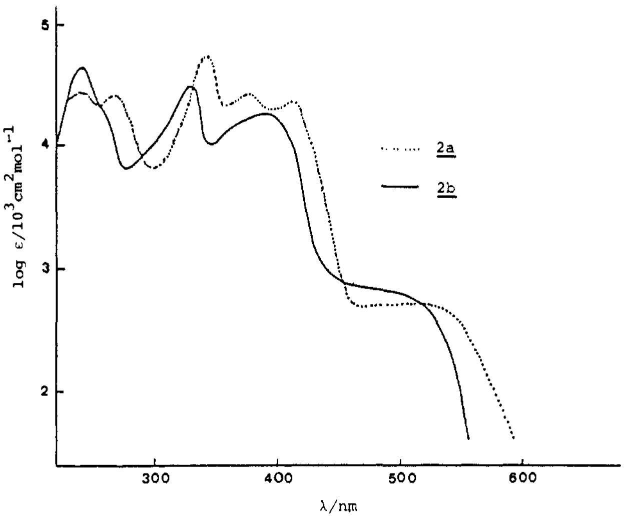

Figure 5. Electronic spectra of **2a** and **2b** in CH_2Cl_2.

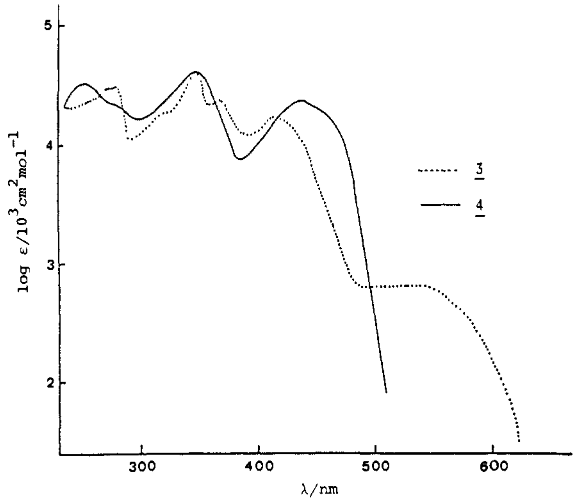

Figure 6. Electronic spectra of **3** and **4** in CH_2Cl_2.

destabilization due to peripheral 16π conjugation is surprisingly small (structure k, RRE = −0.028β): only ca. 9% of resonance energy (−0.295β) of [16]annulene.[21] The other consituent rings (structures c–j) offer a negligibly small contribution to the π conjugation of **2b**. The stability of **2b** can be ascribed to both an increase in the desirable 2π (3-membered ring) and 6π (5-membered ring) conjugation and a decrease in the undesirable 16π (peripheral 16-membered ring) conjugation. The latter could be explained by the large contribution of the polar structure (**2C** and **2D**).

Electronic Spectra and Their Interpretations by the Modified Pariser–Parr–Pople-Type SCF MO Method (Variable Integrals Method I). The cyclic bicalicenes show three main electronic absorption bands at ca. 330, 380, and 500 nm (see Figure 5). The longest wavelength absorption band is very weak and characteristic of the cyclic bicalicene system, as is obvious from comparison of the electronic spectra of **3** and **4** (see Figure 6). In order to understand the character of this absorption, the electronic transitions of **2a** and **2b** were calculated by using the variable integrals method I (VI/1) with configuration interactions.[16] The observed electronic spectral band characteristics with the calculated singlet–singlet (s–s) electronic transitions are summarized in Table II. Also, the HOMOs and LUMOs of **2a** and **2b** are schematically shown in Figure 7. In the case of **2b**, by comparison of the observed and calculated electronic transitions, the weak band observed at 2.58 eV (480 nm) is assigned to the symmetry-forbidden B_{3g} $\pi^* \leftarrow \pi$ transition which is mainly contributed from the LU-π-MO ← HO-π-MO excitation configuration (see Figure 7). The two strong bands at 3.23 eV (384 nm) and 3.73 eV (332 nm) are assigned as the B_{1u} $\pi^* \leftarrow \pi$ and B_{2u} $\pi^* \leftarrow \pi$ bands which are polarized along the long (z) and short (y) molecular axes, respectively. The former is mainly contributed from the LU-π-MO ← second HO-π-MO excitation configuration. The strong band at 5.08 eV (244 nm) may be assigned as the B_{1u} $\pi^* \leftarrow \pi$ transition polarized along the long molecular axis. All the transitions are accompanied by electron migrations (ca. 0.2–0.3 unit) from the five-membered rings to the three-membered rings. Incidentally as for the ground state the present calculation suggests that the tetrapolar structure contributes considerably to the ground state of **2b**. Normally, electronic transitions accompanied by electron migration are significantly influenced by the solvent. However, the electronic spectrum of **2b** (and also **2a**) is not subject to solvent shifts due to the reason that **2b** cannot have a nonzero dipole moment because of its D_{2h} symmetry. A similar tendency is seen for **2a** (Table II). The π-MOs higher than the sixth HO-π-MO are essentially the same as those of **2b** in order and shape, although the former are slightly shifted to higher energy than the corresponding ones of **2b** because of the perturbation of the sulfur atom lone-pair orbitals (see Figure 7). Consequently, the electronic spectrum of **2a** is expected to be rather similar to that of **2b** in the lower energy region.

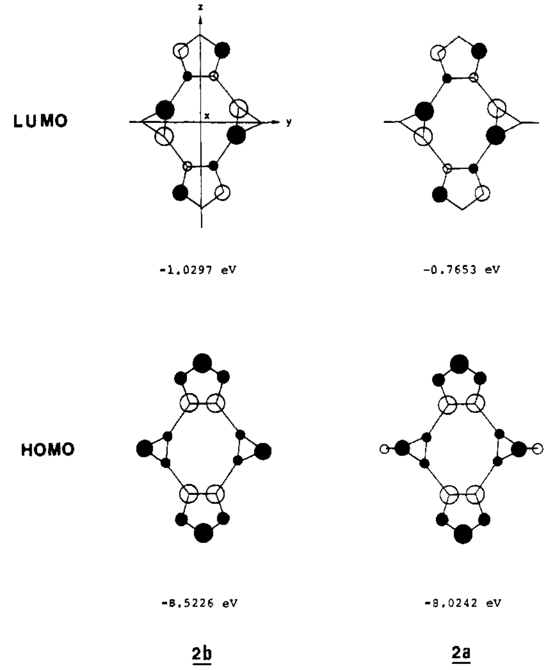

Figure 7. Schematic representations of HOMOs and LUMOs of **2a** and **2b**. The areas of the circles are proportional to the squares of the LCAO coefficients. The blank and filled circles symbolize different signs of these coefficients.

Conclusion

The extraordinary stability of the cyclic bicalicene system is attributed to the unexpectedly large contribution to the ground state of the tetrapolar structures **2C** and **2D** and to the marked suppression of destabilization due to peripheral 16π conjugation (**2A** and **2B**). Thus, the tetrapolar structures, which are characterized by the cyclic and alternate distribution of the charged parts, should be responsible for the highly polarized calicene units.

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(21) In correspondence with this result Randić has shown with his method of conjugated circuits that larger annulene circuits make only a minor contribution compared with smaller ones for both neutral and ionic conjugated polycyclic systems (Randić, M. *Chem. Phys. Lett.* **1976**, *38*, 69, *J. Phys. Chem.* **1982**, *86*, 3970). By using the REPE (resonance energies per π electron) method, Hess and Schaad et al. have also come to a similar conclusion (Hess, B. A., Jr.; Schaad, L. J.; Agranat, I. *J. Am. Chem. Soc.* **1978**, *100*, 5268). However, the exceptional case was found by us in cyclopenta[*e*]azulenide, in which a peripheral 14π circuit contributes much more to the conjugation than the cyclopentadienyl 6π circuit (Yoshida, Z.; Shibata M.; Sakai, A.; Sugimoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 6383). Therefore, further study should be needed for more detailed understanding of the conjugation mode in conjugated polycyclic systems.

Table II. Calculated and Observed Electronic Transitions

		calcd				obsd[b]		
sym		E^{s-s}, eV	f	main CI component[a]		λ_{max}, nm	E_{max}, eV	log (ϵ_{max}/ 10^3 cm^2 mol^{-1})
2b	B_{3g}	2.28	0.0	9 ← 8	0.912	480	2.58	2.81
	B_{1u}	3.74	0.957	9 ← 7	0.929	384	3.23	4.20
	B_{2u}	4.09	0.772	9 ← 6	0.668	332	3.73	4.42
				10 ← 8	0.692			
	A_g	4.35	0.0	9 ← 5	0.578			
				10 ← 7	0.742			
	B_{2u}	4.67	0.041	9 ← 6	0.675			
				10 ← 8	−0.682			
	A_g	4.92	0.0	9 ← 8	0.357			
				10 ← 6	−0.566			
				11 ← 5	0.485			
				12 ← 7	0.529			
	A_g	4.94	0.0	9 ← 5	0.668			
				10 ← 7	−0.619			
				11 ← 8	0.385			
	B_{1u}	5.19	0.384	10 ← 5	0.856	244	5.08	4.63
				11 ← 6	−0.339			
	B_{2u}	5.29	0.096	11 ← 7	0.886			
				12 ← 5	0.428			
	B_{3g}	5.33	0.0	10 ← 6	0.686			
				12 ← 7	0.641			
	B_{1u}	5.35	1.245	12 ← 8	0.895			
2a	B_{3g}	2.14	0.0	11 ← 10	0.928	530	2.34	2.74
	B_{1u}	3.66	0.891	11 ← 9	0.933	380	3.26	4.35
	B_{2u}	4.01	0.977	11 ← 8	0.611	341	3.64	4.63
				12 ← 10	0.739			
	A_g	4.24	0.0	11 ← 7	0.594			
				12 ← 9	0.747			
	B_{2u}	4.55	0.047	11 ← 8	0.727			
				12 ← 10	−0.617			
	A_g	4.86	0.0	11 ← 7	0.632			
				12 ← 9	−0.577			
				13 ← 10	0.493			
	B_{3g}	4.87	0.0	11 ← 10	0.317			
				12 ← 8	−0.484			
				13 ← 7	0.480			
	B_{1u}	5.14	1.234	12 ← 7	−0.608	246	5.04	4.43
				13 ← 8	0.345			
				14 ← 10	0.687			
	B_{2u}	5.15	0.093	13 ← 9	0.877			
				14 ← 7	0.420			
	A_g	5.21	0.0	11 ← 7	−0.447			
				13 ← 10	0.832			
	B_{1u}	5.28	0.445	12 ← 7	0.672			
				14 ← 10	0.642			

[a] The transition indicated as $j \leftarrow i$ refers to a one-electron excitation from the valence π orbital i to j. The second column gives the CI coefficient of the configuration $j \leftarrow i$. [b] Solvent: hexane for **2b** and cyclohexane for **2a**.

On the other hand, the latter result is important for understanding the bonding character of 16π electrons in the periphery, although the smaller circuits are considered to make large contributions.[21] As the other different bonding mode, two classical structures (**2A** and **2B**) are conceivable, which are in equilibration. However, the present X-ray analysis and the NMR measurement at −78 °C do not provide enough evidence to support the equilibration.

Experimental Section

Melting points were determined with a YANACO MP-micro melting point apparatus and are uncorrected. Microanalyses were performed by the Microanalysis Center, Kyoto University. NMR spectra were recorded on a JEOL FX-90Q (^{13}C), JEOL JNM-PMX-60 (^{1}H), or Varian HA-100D (^{1}H) spectrometer, and chemical shift values are given in parts per million (ppm) relative to internal tetramethylsilane. Mass spectra were obtained with a JEOL JMS-DX 300 spectrometer and IR spectra with a JASCO A-102 diffraction grating infrared spectrophotometer. Electronic spectra were measured on a Hitachi 340 recording spectrophotometer.

3,11-Bis(*tert*-butylthio) Cyclic Bicalicene (2a). To a solution of cyclopentadiene (1.98 mL, 24 mmol) in THF (100 mL) was added 1.55 M *n*-butyllithium in hexane (15.5 mL, 24 mmol) at 0 °C under argon. After the solution was stirred for 0.5 h, a THF solution of 1,2-bis(*tert*-butylthio)-3,3-dichlorocyclopropene (12.0 mmol), obtained by the reaction of bis(*tert*-butylthio)cyclopropenethione[4] with thionyl chloride, was dropwise added to the solution at −70 °C under argon. After stirring for further 2 h, the reaction mixture was poured into cold water and then extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and concentrated in vacuo. The brown tarry residue was purified by preparative TLC on silica gel with dichloromethane–petroleum ether (1:2), followed by recrystallization from 1,2-dimethoxyethane to give **2a** (235 mg) as reddish purple crystals in 10% yield: mp 190–200 °C dec; IR (KBr) 2950, 1815, 1555, 1418, 1350, 1270, 1072, 740, 721 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) nm (4.51), 266 (4.49), 337 (4.74), 372 (4.43), 413 (4.39), ca. 525 (2.74); ^{13}C NMR ($CDCl_3$) δ 135.9 ($C_{2,4,10,12}$), 128.2 ($C_{3,11}$), 127.5 ($C_{6,8,14,16}$), 123.0 ($C_{7,15}$), 109.0 ($C_{1,5,9,13}$), 48.0 ($\mathit{C}(CH_3)_3$), 31.6 ($C(\mathit{C}H_3)_3$); MS, *m/e* 376 (M$^+$), 320, 264. Anal. Calcd for $C_{24}H_{24}S_2$: C, 76.55; H, 6.42; S, 17.03. Found C, 76.69; H, 6.51; S, 16.97.

3,11-Bis(tri-*n*-butylstannyl) Cyclic Bicalicene (2c). In the presence of AIBN (15 mg, 0.09 mmol), a mixture of **2a** (30 mg, 0.08 mmol) and tri-*n*-butyltin hydride (70 mg, 0.24 mmol) in dry benzene (5 mL) was allowed to reflux for 3 h under argon. After the solvent was evaporated, the residue was chromatographed on silica gel with dichloromethane–hexane (1:2) to afford **2c** (26 mg) and 3-(*tert*-butylthio)-11-tri-*n*-butylstannyl cyclic bicalicene (12 mg) as an orange solid and a purplish orange syrupy oil in 42% and 27% yields, respectively: orange crystals (from MeOH); mp 60–61 °C; IR (KBr) 2910, 1769, 1539, 1410, 1350, 1153, 1080, 740 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) 240 nm (4.76), 313 (4.75), 369 (4.60), ca. 460 (br, 3.21); ^{1}H NMR (CCl_4) δ 6.72 (d, 4 H, $H_{6,8,14,16}$, J = 3.8 Hz), 6.36 (t, 2 H, $H_{7,15}$, J = 3.8 Hz), 0.8–1.8 (br m, 54

H, Bu); MS, *m/e* 778 (M^+). Anal. Calcd for $C_{40}H_{60}Sn_2$: C, 61.73; H, 7.77. Found: C, 61.67; H, 8.00.

Cyclic Bicalicene (2b). A mixture of **2c** (26 mg, 0.33 mmol) and silica gel (10 g, Merck, Kieselgel 60 PF_{254}) was kept for 0.5 h at room temperature and then was extracted with dichloromethane. The solution was concentrated in vacuo to provide an orange-red semisolid, which was purified by preparative TLC on silica gel with dichloromethane–petroleum ether (2:1) to give pure **2b** (2.7 mg) in 40% yield: orange plates (from $CHCl_3$); mp 125–130 °C dec; IR (KBr) 3100, 1782, 1550, 1420, 1346, 1240, 745 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) 241 nm (4.63), 328 (4.51), 390 (4.27), ca. 470 (2.81); MS, *m/e* 200 (M^+), 174, 149, 100. Anal. Calcd for $C_{16}H_8$: C, 95.97; H, 4.03. Found: C, 95.72; H, 4.23.

3,11-Bis(*tert*-butylthio)-6,7-dicyano Cyclic Bicalicene (3) and 5,6,6′-Tris(*tert*-butylthio)-2′,3′-dicyano-1,5′-bicalicene (4). To a solution of 1,2-bis[bis(*tert*-butylthio)cyclopropenylio]cyclopentadienide[5] (200 mg, 0.338 mmol) in dichloromethane (8 mL) was added tetramethylammonium 1,2-dicyanocyclopentadienide[6] (64 mg, 0.338 mmol) at 0 °C under argon. After stirring at 0 °C overnight, the reaction mixture was concentrated in vacuo. The residue was purified by preparative TLC on silica gel with dichloromethane–petroleum ether to afford **3** (19 mg) and **4** (8 mg) as reddish purple crystals and an unstable yellow solid in 13% and 5% yields, respectively. A solution of **4** (5 mg, 0.01 mmol) in dichloromethane (3 mL) was allowed to stand overnight. After the solvent was evaporated, the residue was purified on silica gel with dichloromethane–petroleum ether to give **3** (3 mg) in 73% yield. **3**: mp 224–227 °C dec; IR (KBr) 2975, 2200, 1818, 1538, 1423, 1320, 1268, 1161, 1050, 750 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) 268 nm (sh, 4.45), 277 (4.49), 310 (sh, 4.21), 344 (4.59), 365 (4.37), 413 (4.25), 520 (2.88); MS, *m/e* (M^+) calcd 426.1224, obsd 426.1206. **4**: IR (KBr) 2960, 2930, 2200, 1803, 1760, 1503, 1320, 1044, 983, 935, 738 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) 246 nm (4.55) 260 (sh, 4.49), 344 (4.60), 432 (4.35), 448 (sh, 4.32).

X-ray Structure Analyses of 2a and 2b. Crystal Data. **2a**: $C_{24}H_{24}S_2$, fw = 376.6, monoclinic, $P2_1/n$, $a = 6.022$ (1) Å, $b = 11.450$ (1) Å, $c = 15.386$ (1) Å, $\beta = 103.44$ (1)°, $U = 1031.9$ (2) Å^3, $Z = 2$, $D_x = 1.212$ g·cm^{-3}, $D_m = 1.22$ g·cm^{-3}, $F(000) = 400$, μ(Cu Kα) = 22.7 cm^{-1}. **2b**: $C_{16}H_8$, fw = 200.2 monoclinic, $P2_1/c$, $a = 9.587$ (1) Å, $b = 5.964$ (1) Å, $c = 9.968$ (1) Å, $\beta = 117.01$ (1)°, $U = 507.7$ (1) Å^3, $Z = 2$, $D_x = 1.309$ g·cm^{-3}, $D_m = 1.30$ g·cm^{-3}, $F(000) = 208$, μ(Cu Kα) = 5.8 cm^{-1}.

X-ray diffraction data were collected on a Rigaku four-circle diffractometer using nickel-filtered Cu Kα radiation. Integrated intensities were measured by the θ–2θ scan technique at a 2θ scan rate of 2 deg min^{-1} and a scan width of $\Delta 2\theta = (2.0 + 0.70 \tan \theta)°$. The background intensities were measured for 10 s at both ends of a scan. Three standard reflections were measured after every 61 reflections in order to monitor the radiation damage and the change of the crystal orientations. No significant intensity decay of the standard reflections was observed for both of the crystals. For the crystal **2b** the two crystallographically equivalent sets of reflections were measured and averaged to improve the accuracy of the structure analysis.

The crystal structures of **2a** and **2b** were solved by use of direct methods (MULTAN-78)[22] and refined by the block-diagonal least-squares procedure (HBLS-V)[23] using the reflections of $|F_o| \geq 3\sigma(F_o)$, the function minimized being $\sum w(|F_o| - |F_c|)^2$. The weighting function used was $|F_o| < F_{max}$, $w = 1$, and $|F_o| \geq F_{max}$, $w = (F_{max}/|F_o|)^{-2}$, where $F_{max} = 20$ for both of the crystals. All the non-hydrogen atoms were refined by supposing the anisotropic thermal parameters together with the hydrogen atoms with isotropic thermal parameters. The final *R* indexes were 0.035 ($R_w = 0.041$) for **2a** and 0.039 ($R_w = 0.045$) for **2b**, respectively.

Computational. Graph-Theoretical Calculation. The resonance energy of cyclic calicene was calculated by Aihara's ω-technique ($\omega = 1.4$) method. The resonance energy of each constituent ring (RRE) of **2b** and calicene itself was also calculated by Aihara's $\beta\omega'\omega''$ method.

Variable Integrals Method I. The electronic states of **2a** and **2b** were calculated by the variable integrals method I (VI/1), a modified Pariser–Parr–Pople-type SCF CI method for π-electron systems which takes into account the changes in π-electron densities in the evaluation of atomic integrals during the SCF procedures. The geometrical structures of **2a** and **2b** were assumed to be of D_{2h} symmetry based on the X-ray diffraction analysis.

X-ray Structure Analysis. The atomic scattering factors for non-hydrogen atoms were taken from International Tables for X-ray Crystallography, Vol. IV,[24] and those for hydrogen atoms from Stewart et al.[25] All the crystallographic calculations were carried out by the use of UNICS System, Osaka, on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

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Registry No. 2a, 72649-42-4; **2b**, 73091-52-8; **2c**, 73625-08-8; **3**, 104464-02-0; **4**, 104464-01-9; 1,2-bis(*tert*-butylthio)-3,3-dichlorocyclopropane, 72649-41-3; 1,2-bis[bis(*tert*-butylthio)cyclopropenylio]cyclopentadienide, 89821-02-3; tetramethylammonium 1,2-dicyanocyclopentadienide, 42491-32-7.

Supplementary Material Available: Figure S1 of the molecular structure of **2b** and Tables S1–SIV and SVI–SVIII listing anisotropic temperature factors for non-hydrogen atoms, final atomic parameters for non-hydrogen atoms, fractional atomic coordinates and isotropic temperature factors for hydrogen atoms, and interatomic bond distances and angles concerning the hydrogen atoms for **2a** and **2b** (9 pages); tables of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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