Redox Behaviour and Stable Anion Radicals of Cyclic Polycalicenes

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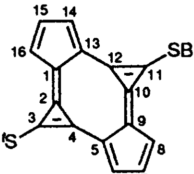
Cyclic polycalicenes (cyclic bicalicene **1**, cyclic tercalicene **2**, and cyclic quatercalicene **3**) have been characterized by cyclic voltammetry and EPR spectroscopic measurements. The redox waves are completely reversible at −70 °C in the reduction process but remain irreversible in the positive voltage region. The cyclic polycalicenes with larger π conjugations are more easily reduced, irrespective of the 16π, 22π and 28π conjugations at the periphery. In particular, **1** shows large reduction potentials, indicating an 'aromatic' system with a 16π-electron periphery. The spin density distribution of the anion radicals ($\mathbf{1}^{\cdot-}$, $\mathbf{2}^{\cdot-}$ and $\mathbf{3}^{\cdot-}$) indicates a localization of the unpaired electron, to some extent, on the five-membered rings, implying a polar structural contribution. It has also been shown that the relatively long chemical bonds at specific positions in the cyclic polycalicenes influence the spin density distribution. The EPR results obtained from the cyclic polycalicenes are quite different from those of the anion radical of calicene itself.

Cyclopropenylidenecyclopentadienide (calicene) is a cross-conjugated π system consisting of one three-membered and one five-membered ring, both unsaturated. This parent compound still remains a synthetic challenge,[1] although a number of its derivatives bearing strong electron-donating and/or electron-withdrawing substituents on the three- and/or five-membered ring have been isolated.[2] Physical and chemical properties of those derivatives have been extensively studied, and it has been shown that a polar structure with 2π and 6π electrons in the three-membered and five-membered rings, respectively, contributes significantly to the ground state.[3,4]

However, cyclic bicalicene **1**, which is composed of two calicene units in a head-to-tail orientation, has been prepared by our group. The X-ray structural analysis, ^1H and ^{13}C NMR spectra, and theoretical calculations indicated that **1** comprises an unprecedented 'aromatic' system with a 16π-electron periphery, owing to a significant contribution of the calicene polar structure to the electronic structure in the ground state.[5,6] Recently, in addition to the covalent and polar structures, the possibility of other structural contributions, such as a biradical structure, has been suggested.[7] Moreover, new syntheses of cyclic tercalicene **2** and cyclic quatercalicene **3** have been reported.[8] These compounds are the next highest homologues with 22π and 28π-electrons in the periphery, respectively. In a series of cyclic polycalicenes the peripheral 16π, 22π and 28π conjugations seem to have an unexpectedly small contribution for **1**, **2** and **3**, respectively; rather, each calicene unit is subjected to a large polarization irrespective of the type of cyclic polycalicene.[9]



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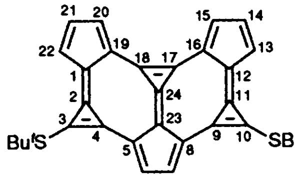

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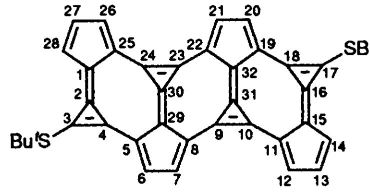

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In this paper we report physicochemical properties of these cyclic polycalicenes (**1**–**3**) as revealed by cyclic voltammetry (CV) and electron paramagnetic resonance (EPR). Their redox potentials and the spin density distributions of their reduced species are discussed, with emphasis placed on the electronic structures of cyclic polycalicenes.

Experimental

Stable *tert*-butylthio derivatives (R = Bu^{t}S) were treated in this paper. Their syntheses have been reported in the literature.[5,6,8]

CV measurements were carried out at −70 °C in CH_2Cl_2–CH_3CN (2:3, v/v) with a supporting electrolyte, tetrabutylammonium perchlorate (Bu_4NClO_4). The redox potentials were determined in the voltage range +2.0 to −2.0 V *vs.* Ag/AgCl by reference to the redox potential of tetrathiafulvalene (+0.27 V *vs.* Ag/AgCl at 25 °C).

EPR spectra were obtained in the X-band by using a JEOL-ME3X spectrometer equipped with a temperature controller. Anion or cation radicals were produced electrochemically at −80 °C by using a helix-type electrochemical cell described in the literature.[10,11] CH_2Cl_2 was used as a solvent and Bu_4NClO_4 as a supporting electrolyte.

Results and Discussion

Redox Potentials.—In all cases the redox waves were irreversible at room temperature, but the reversibility was improved at −70 °C (Fig. 1). In the negative voltage region, where the cyclic polycalicenes undergo one- and two-electron reduction to afford the corresponding radical anions and dianions, respectively, the redox waves exhibited complete reversibility. On the other hand, the oxidation waves in the positive voltage region were still irreversible. These facts suggest that the radical anions and dianions are stable as compared with the radical cations and dications.

Table 1 Redox potentials of **1**–**3**

Compound	E_{ox}^2/V	E_{ox}^1/V	E_{red}^1/V	E_{red}^2/V
1[a]	+1.16[c]	+0.97[c]	−1.77	−2.5
2[a]	+0.70[c]	+0.49[c]	−1.33	−1.75
3[a]	+0.85[c]	+0.47[c]	−1.14	−1.49
[16]annulene[b]			−1.23	−1.52
[18]annulene[b]			−1.56	−1.90

[a] Measured in CH_2Cl_2–CH_3CN (2:3, v/v) at −70 °C. [b] Measured in DMF at 0 °C. [c] Irreversible steps. Anodic potentials.

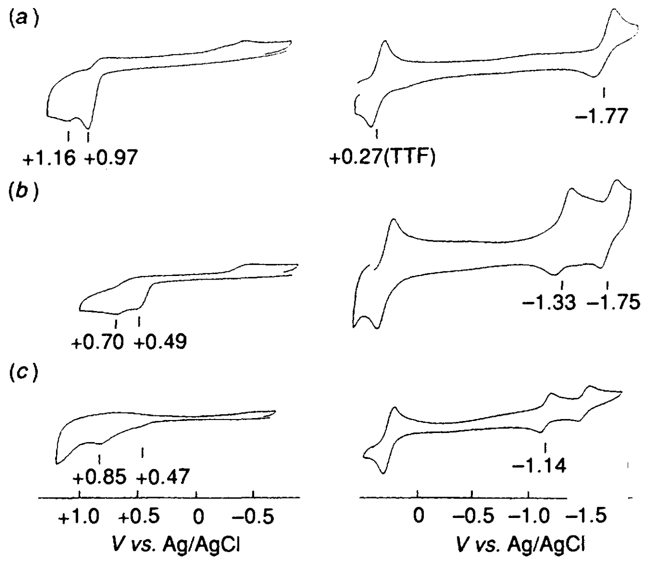

Fig. 1 Cyclic voltammograms of (*a*) **1**, (*b*) **2** and (*c*) **3** in CH_2Cl_2–CH_3CN at −70 °C. TTF is used as a reference, +0.27 V *vs.* Ag/AgCl.

Fig. 2 EPR spectrum of $\mathbf{1}^{\bullet -}$ in CH_2Cl_2 at −80 °C. The *g* value is 2.003 43. On the high-field side the spectrum is a little weakened in intensity, probably because of the decay of the radical.

Table 1 summarizes the oxidation (E_{ox}) and reduction (E_{red}) potentials determined. The first oxidation and reduction potentials (E_{ox}^1 and E_{red}^1) gradually become more positive on going from **1** to **2** then to **3**. A similar tendency is also observed for the second oxidation and reduction potentials (E_{ox}^2 and E_{red}^2). These findings indicate that both oxidation and reduction are likely to become easier in the order **1** < **2** < **3**, irrespective of $4n\pi$ and $(4n + 2)\pi$ conjugations in the periphery. Moreover, **1** is in remarkable contrast with [16]annulene ($E_{red}^1 = -1.23$ and $E_{red}^2 = -1.52$ V *vs.* SCE), which has the same peripheral 16π conjugated system as **1**, when the reduction potential difference ($|E_{red}^1 - E_{red}^2|$) is compared between both systems. This value gives an indication as to whether the π-conjugated system is aromatic, non-aromatic or antiaromatic. For antiaromatic systems conversion to the corresponding aromatic systems by oxidation or reduction proceeds favourably, while the reverse case is energetically unfavourable. The value of >0.7 V for **1** as compared to 0.29 V for [16]annulene

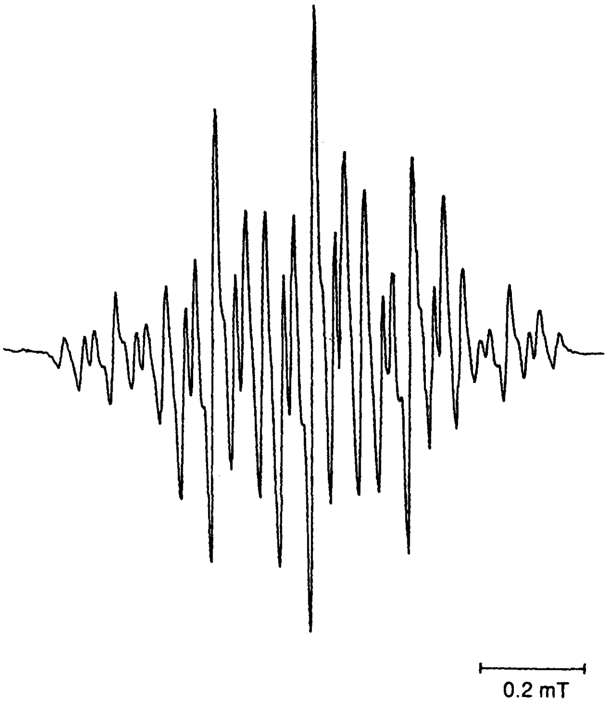

Fig. 3 EPR spectrum of $\mathbf{2}^{\bullet -}$ in CH_2Cl_2 at −80 °C. The *g* value is 2.002 32. See the legend to Fig. 2.

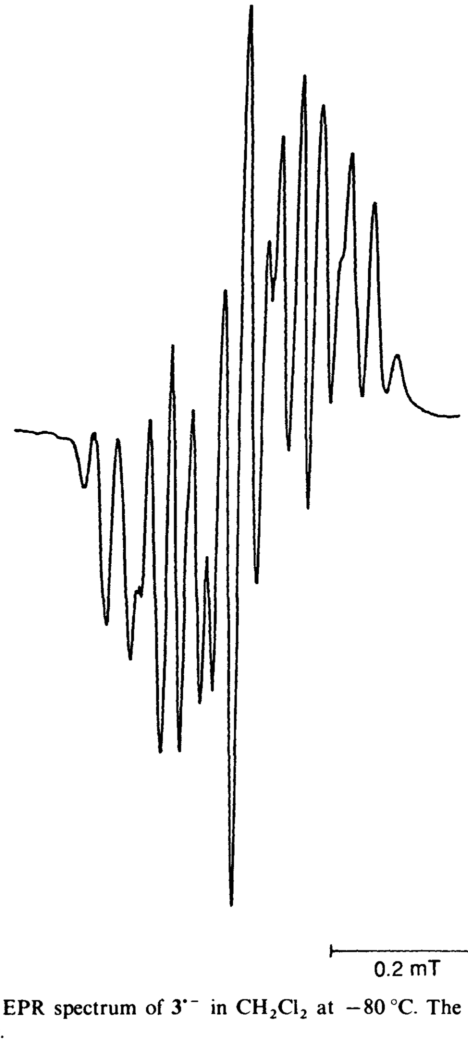

Fig. 4 EPR spectrum of $\mathbf{3}^{\bullet -}$ in CH_2Cl_2 at −80 °C. The *g* value is 2.002 40.

Table 2 Observed and calculated hyperfine coupling constants of $1^{\bullet -}$, $2^{\bullet -}$ and $3^{\bullet -}$

Compound	hfcc(obs)/mT[a]	hfcc(cal)/mT[b]	hfcc(cal)/mT[c]	Assignment
$1^{\bullet -}$	0.439	0.316	0.438	6, 8, 14, 16
	0.097	0.098	0.129	7, 15
$2^{\bullet -}$	0.200	0.117	0.238	13, 22
		0.104	0.198	15, 20
	0.061	0.058	0.061	14, 28
	0.043	0.042	0.010	6, 7
$3^{\bullet -}$	0.099	0.076	0.080	14, 28
	0.076	0.021	0.043	12, 26
	0.029	0.014	0.008	13, 27
	<0.001	0.009	0.002	7, 21
		<0.001	<0.001	6, 20

[a] The hfccs were obtained by simulation analysis of the spectra. [b] Calculated from McConnell's relation based on the spin density distribution by McLachlan's method. [c] Calculated from McConnell's relation based on the spin density distribution by McLachlan's method in consideration of bond distances (see text).

implies that **1** is aromatic while the annulene is antiaromatic. Indeed, **1** is a very stable π conjugated system, similar to [18]annulene. According to the redox data of both annulenes listed in Table 1, [16]annulene is more readily reduced to its radical and dianion states than [18]annulene in spite of the smaller π conjugation system. If the peripheral 16π conjugation contributes significantly to the ground state, the high value of the second reduction potential (< -2.5 V) cannot be explained, because the corresponding dianion becomes aromatic with a peripheral 18π conjugation. In the cases of **2** and **3**, however, such a conjugation mode does not always contribute overwhelmingly to the ground states, judging from the slightly smaller $|E_{red}{}^1 - E_{red}{}^2|$ values (0.42 and 0.35 V) than that for **1**.

It can be concluded from the CV measurements that the peripheral 16π, 22π and 28π conjugations make little contribution to the ground states of **1**–**3**. This is consistent with ^{1}H and ^{13}C NMR spectroscopic results which indicated a large polarization of each calicene unit in the cyclic polycalicenes.[6,8] The reversibility of the redox waves suggests that the significant stability of the reduced species, even though at very low temperature, is sufficient for them to be characterized by EPR spectroscopy.

EPR Spectra of the Anion Radicals.—The intermediate radical ions produced electrochemically were investigated by EPR spectroscopy. The de-gassed CH_2Cl_2 solution containing the cyclic polycalicenes (**1**–**3**) and Bu_4ClO_4, a supporting electrolyte, was subject to *in situ* reduction or oxidation at -80 °C. As expected from the CV observations, well-resolved EPR spectra of the radical anions $1^{\bullet -}$, $2^{\bullet -}$ and $3^{\bullet -}$ were observed (Figs. 2–4). The cation radicals, which were rather difficult to generate, were recognized from unidentified EPR spectra. As predicted from the CV results, the radical cations are remarkably unstable, presumably because of the poor solvation effect of the CH_2Cl_2 solvent and/or further reactive processes after the cation radical production.

Spectral analyses of the EPR spectra can be performed very easily, and the hyperfine coupling constants (hfccs) were confirmed by a computer simulation technique. These are summarized in Table 2. The hf values become smaller in the order **1** > **2** > **3**, suggesting that the unpaired electron is distributed much more extensively with increasing size of the π conjugated ring.

The calculated spin density, by simple Huckel MO theory, predicts zero spin density at, *e.g.*, the C-7 and C-15 of **1**, where a negative spin density would usually be expected by spin-correlated MO treatment such as McLachlan's method.[12] The calculated hfccs were evaluated on the basis of McConnell's relation between the spin density on the carbon atoms and the hfccs of the protons (A_H) attached to the carbon atoms, with a proportionality constant $Q = -2.70$ mT.[13] Usually one can obtain negative proton hfccs ($A_H < 0$) except for those protons attached to carbon atoms with a negative spin density ($A_H > 0$). Since we have no definite information about this sign, we have summarized, in Table 2, absolute values of the hfccs calculated from the usual McLachlan method and from that derived from a consideration of bond length. The latter problem will be discussed later.

Assignment of the hfcc values is straightforward for **1**, because of the simple EPR spectrum (the quintet of the triplet) and of the molecular symmetry. In the case of **2**, the spectrum simulation concluded four equivalent protons with $A_H = 0.200$ mT in spite of MO calculations and symmetry considerations. Satisfactory assignment was made by taking the order of the calculated value into account. There are many proton pairs with small hfccs for **3**, so that the above-mentioned assignment seems to be insufficient. Although we need more sophisticated experiments to avoid this ambiguity of assignment, the larger hf groups may be reasonable.

All the hf structures come from the protons bonded to the carbon atoms comprising the five-membered rings, and the largest hfcc in each compound always turned out to be remarkably large as compared to the value predicted by simple Huckel MO theory or McLachlan's method. This seems to suggest a contribution from the negatively charged polar structure of the five-membered rings. The suggestion that a significant amount of the unpaired electron is localized on the five-membered rings is controversial if one considers the results for the spin density distributions of the anion radicals of two calicene derivatives, 1,2,3,4-tetrachloro-5,6-diphenylcalicene (PhC) and 1,2,3,4-tetrachlorodipropylcalicene. In those compounds the unpaired electron does not exist, or scarcely exists, on the five-membered ring. Thus, the spin density distribution of $PhC^{\bullet -}$ is almost the same as the (*Z*)-stilbene anion radical.[14] Our EPR data for the cyclic polycalicenes resulted in quite different spin density distributions and significant contributions from the polar structures. The polar structure might have been strengthened by composing two calicene units in a head-to-tail orientation, contributing to the stability of the cyclic polycalicenes.

It has been reported that consideration of bond alternation is desirable for the calculation of the electronic states of PhC.[4] Such a treatment has therefore been taken into account in the EPR study of $PhC^{\bullet -}$.[14] However, a fairly good explanation was obtained by McLachlan's method without bond-length alternation, concluding that consideration of bond-length

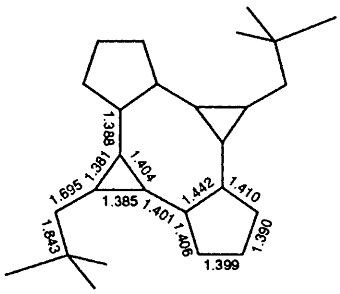

Fig. 5 Interatomic bond distances of **1**

alternation gives no improvement. In our systems, X-ray structural analyses predict more or less such a bond alternation or considerably long C–C bonds at specific positions (Fig. 5).[5,8] For example, the 1–13 or 5–9 bond length of **1** amounted to 1.442 Å. We took these into account, neglecting the other bond alternations. The results are shown in the second column of the calculated hfcc values in Table 2, where the resonance integral β is taken to be 0.5 so that the largest hfcc of each compound may become comparable to the observed value. However, in the case of $\beta = 0.5$, the discrepancy becomes rather prominent for the smaller hfccs. It is true that the long chemical bonds in 1–13 and 5–9 of **1** cause more localization of the unpaired electron on the five-membered rings. Generally speaking, the agreement between the observed and the calculated hfccs can be improved by considering the long bond length at specific positions and reducing the resonance integral parameter.

We can conclude from the EPR measurements that there is a significant polar structural contribution and that long chemical bonds have to be taken into account in the cyclic polycalicenes. These predominant characteristics are in contrast to the anion radical of substituted calicene itself and are derived from cyclization of the calicene unit.

Acknowledgements

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