

COMMUNICATION

**Participation of Several Different Electronically-
Excited Biradical Structures in the Ground States
of Bicyclic Tricalicene and Tricyclic Tetracallicene**

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The solid ESR measurement of bis(*tert*-butylthio)-substituted derivatives of bicyclic tricalicene (**2**) and tricyclic tetracallicene (**3**), the next higher analogues of cyclic bicalicene (**1**), suggests that at least two and three different low energy electronically-excited biradical structures are involved for **2** and **3**, respectively.

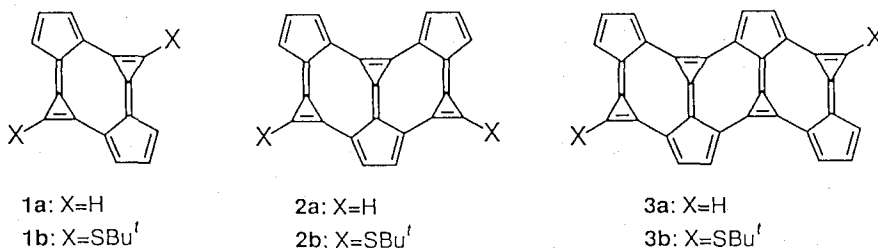
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The organic molecules, whose electronically-excited biradical structures are not so apart from the ground structure in energy, are of much interest in unique ground-state electronic structures as well as in novel optical, magnetical and electrical properties.¹⁾ However, such examples are very rare. We have very recently reported participation of electronically-excited biradical structures in the ground states of cyclic bicalicene (**1a**) and its bis(*tert*-butylthio)-substituted derivative (**1b**),²⁾ which provide a first example evidenced in non-alternant hydrocarbon system.³⁾ The biradical structure in a low-energy singlet in thermal equilibrium with its counterpart triplet, makes a partial contribution to stabilization of ground-state electronic structure of **1** involving an energetically unfavorable antiaromatic 16π electron conjugation. This finding prompted us to investigate as to whether there is participation of electronically-excited biradical structures also in higher analogues of **1a**, bicyclic tricalicene (**2a**) and tricyclic tetracallicene (**3a**), in which cyclic bicalicene conjugation mode still preferentially contributes.⁴⁾ Herein we wish to report the evidence on such a participation from the ESR measurement of the bis(*tert*-butylthio)-substituted derivatives of **2a** and **3a**, (**3b** and **3b**).

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The fresh microcrystalline solids of **2b** and **3b** obtained by recrystallization from $\text{CHCl}_3\text{-CH}_3\text{OH}$,⁵⁾ respectively, were used for the ESR measurement. In the solid ESR spectra at room temperature⁶⁾ one sharp and weak signal was observed near $g=2$. However, by lowering temperature a remarkable change was observed in the spectra. Thus, for **2b** at both wings of the central signal one pair of very weak signals appeared at 90 K, which are presumably due to fine structure of a triplet. The width between the signals is ca. 13 G.⁷⁾ On the other hand, when the ESR spectrum of **3b** was measured at 169 K, the signal due to $\Delta m_s = \pm 2$ transition, which is also characteristic of a triplet, was observed near 1633 G albeit in very low intensity. These results strongly suggest involvement of electronically-excited biradical structures also in the ground states of **2b** and **3b**, as has already been realized in **1a** and **1b**.³⁾

The temperature (T) dependence of the signal intensity (I)⁸⁾ was investigated (see Fig. 1a and 1b). The I value tends to gradually decrease with a lowering temperature till ca. 30–50 K, and then to reversely increase below the temperature. In comparison of such a I–T relation in **2b** and **3b** with that in **1b**, it should be noted that for the two former cyclic polycalicycenes the I value still increases beyond room temperature, while for the latter case the maximum occurs at ca. 250 K and at the higher temperatures a gradual decrease in I is observed.³⁾ The I–T behavior in **2b** and **3b** can well be analyzed by assuming involvement of several low energy singlet biradicals in thermal equilibrium with their counterpart triplets together with an impurity monoradical. By using a Bleaney–Bowers equation relating between I and T,⁹⁾ i. e.,

$$I = N_m g^2 \mu_B^2 \cdot 1/2(1+1/2)/3kT +$$

$N_b(i) g^2 \mu_B^2 \cdot 1(1+1)/3kT \{1+1/3 \exp(\Delta E_i/kT)\}$, where N_m and $N_b(i)$ are amounts of a monoradical and an i -th biradical, respectively, μ_B is Bohr magneton, k is Boltzmann constant, and ΔE_i is energy separation between a low energy singlet and its thermally-accessible triplet of an i -th biradical, the values of N_m , $N_b(i)$ and ΔE_i were determined so as to fit the calculated I–T curve with the observed one. The simulation demonstrates that the two and three biradicals are at least involved in **2b** and **3b**, respectively.¹⁰⁾ This makes remarkable contrast to involvement of one biradical in **1b**.³⁾ The $N_b(i)$ and ΔE_i values of each biradical involved in **2b**, **3b** and also for comparison **1b** are summarized in Table 1.¹¹⁾ For **2b** and **3b** such a biradical (b_1) with a large ΔE (2–3 kcal/mol) participates that is not involved in **1b** at all. On the other hand, the second biradical (b_2) with the smaller ΔE value of 600–800 cal/mol is involved in each cyclic polycalicycene. The contribution of b_1 to the ground

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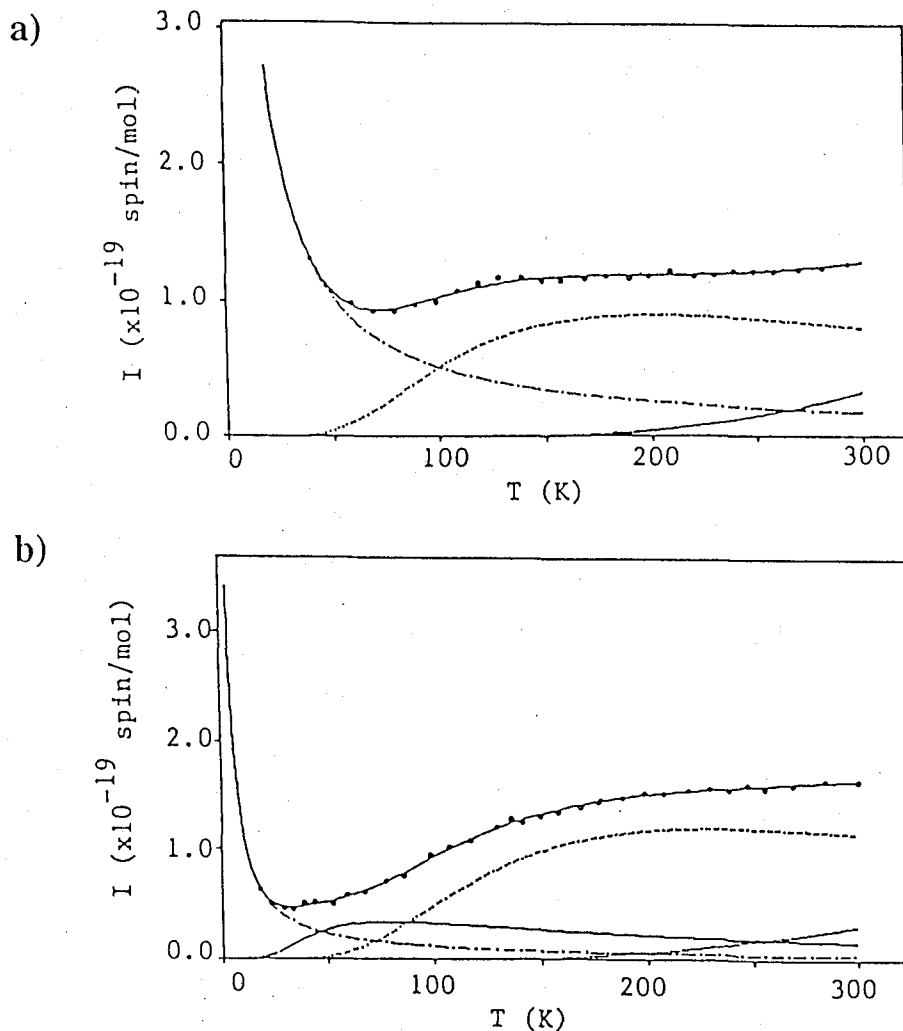


Fig. 1. The temperature (T) dependence of the central signal intensity (I) in the ESR spectra of (a) **2b** and (b) **3b**, and the separation to each contribution due to electronically-excited biradicals in low energy singlet states (—, and ...) and due to an impurity monoradical (---): (\bullet) the observed I at a given temperature and (—) the calculated T dependence of I .

Table 1. The amounts of biradicals involved in the ground states of **2b**, **3b** and a referred **1b**, and the energy separation between the low energy singlet and its thermally-accessible triplet of each biradical.

cyclic polycalicene	Nb(1) ^a	ΔE_1^b	Nb(2) ^a	ΔE_2^b	Nb(3) ^a	ΔE_3^b
2b	6.0×10^{19}	2940	6.2×10^{19}	640		
3b	2.2×10^{19}	2380	9.6×10^{18}	750	9.2×10^{17}	260
1b			2.3×10^{18}	810		

^amolecules/mol. ^bcal/mol.

states of **2b** and **3b** is comparable to or slightly larger than that of b_2 , as shown from comparison between the $N_b(1)$ and $N_b(2)$ values. Furthermore, **3b** also involves a small amount of the third biradical (b_3), whose ΔE value is very small (260 cal/mol). Judging from the amount and ΔE of the electronically-excited biradical structures involved, it is supposed that both b_1 and b_2 are apart in comparatively low and almost the same energy from both ground structures, while b_3 in **3b** is in higher energy compared with those of b_1 and b_2 .¹²⁾ For the three biradicals the low energy spin state is all singlet and its counterpart triplet is in thermal equilibrium with the singlet.

Indeed like **1a** and **1b**, **2b** and **3b** have also participation of electronically-excited biradical structures, respectively, which are in such a low energy as to participate to the ground states albeit in very small content of 0.01–0.00015%. Eventually, cyclic polycalixene constructs a quite unique non-altermant hydrocarbon system having participation of low energy electronically-excited biradical structures in its ground state.

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- 5) Whereas **2b** was obtained as single crystals being suitable for the X-ray structure analysis, **3b** was polycrystalline.
- 6) The ESR spectra were also taken in frozen CH_2Cl_2 solution. The similar spectral pattern was observed.
- 7) This value corresponds to $2D$, where D is the zero-field splitting parameter.
- 8) The I value corresponds to the spin amount, which was determined by using TANOL as a reference.
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- 10) The I-T relation could not be investigated at higher temperatures than ca. 320 K, because **2b** and **3b** began to decompose gradually. The possibility of involvement of the other biradicals with a larger ΔE value can not be ruled out.
- 11) The N_m values are 1.8×10^{18} , 3.9×10^{17} , and 2.0×10^{17} molecules/mol for **2b**, **3b** and **1b**, respectively.
- 12) The lower is the energy of an electronically-excited biradical structure, i. e., the larger the participation in the ground state, the stronger becomes the interaction between the two spins of the biradical structure.