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Participation of Several Different Electronically-Excited Biradical Structures in the Ground States of Bicyclic Tricalicene and Tricyclic Tetracalicene (Commemoration Issue Dedicated to Professor Shigeo Tanimoto On the Occasion of His Retirement)

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

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The solid ESR measurement of bis(tert-butylthio)-substituted derivatives of bicyclic tricalicene (2) and tricyclic tetracalicene (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.

KEY WORDS: Cyclic polycalicene / ESR / Ground state / Electronically-excited biradical structure

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. 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), which provide a first example evidenced in non-alternant hydrocarbon system. 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 tetracalicene (3a), in which cyclic bicalicene conjugation mode still preferentially contributes. 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).
The fresh microcrystalline solids of 2b and 3b obtained by recrystallization from CHCl₃–CH₃OH, respectively, were used for the ESR measurement. In the solid ESR spectra at room temperature 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. On the other hand, when the ESR spectrum of 3b was measured at 169 K, the signal due to Δmₓ = ± 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.

The temperature (T) dependence of the signal intensity (I) 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 polycalicenes 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. 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, i.e.,

\[ I = N_m g_s^2 \mu_B^2 \cdot \frac{1}{2(1+1/2)} / 3kT + \]
\[ N_b(i) g^2_\beta \mu_B^2 \cdot 1(1+1) / 3kT \{ 1+1/3 \exp(\Delta E_i / kT) \} \]

where \( N_m \) and \( N_b(i) \) are amounts of a monoradical and an \( i \)-th biradical, respectively, \( \mu_B \) is Bohr magneton, k is Boltzmann constant, and \( \Delta E_i \) is energy separation between a low energy singlet and its thermally–accessible triplet of an \( i \)-th biradical, the values of \( N_m \) and \( N_b(i) \) 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. This makes remarkable contrast to involvement of one biradical in 1b. The \( N_b(i) \) and \( \Delta E_i \) values of each biradical involved in 2b, 3b and also for comparison 1b are summarized in Table 1. For 2b and 3b such a biradical (b₃) with a large \( \Delta E(2-3 \text{ kcal/mol}) \) participates that is not involved in 1b at all. On the other hand, the second biradical (b₂) with the smaller \( \Delta E \) value of 600–800 cal/mol is involved in each cyclic polycalicene. The contribution of b₁ 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 (—•—): (•) 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.

<table>
<thead>
<tr>
<th>cyclic polycalicene</th>
<th>Nb(1)*</th>
<th>ΔE1*</th>
<th>Nb(2)*</th>
<th>ΔE2*</th>
<th>Nb(3)*</th>
<th>ΔE3*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>6.0x10^9</td>
<td>2940</td>
<td>6.2x10^9</td>
<td>640</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>2.2x10^9</td>
<td>2380</td>
<td>9.6x10^4</td>
<td>750</td>
<td>9.2x10^7</td>
<td>260</td>
</tr>
<tr>
<td>1b</td>
<td></td>
<td></td>
<td>2.3x10^4</td>
<td>810</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*molecules/mol. °cal/mol.
states of 2b and 3b is comparable to or slightly larger than that of b2, as shown from comparison between the $N_n(1)$ and $N_n(2)$ values. Furthermore, 3b also involves a small amount of the third biradical (b3), whose $\Delta E$ value is very small (260 cal/mol). Judging from the amount and $\Delta E$ of the electronically-excited biradical structures involved, it is supposed that both b1 and b2 are apart in comparatively low and almost the same energy from both ground structures, while b3 in 3b is in higher energy compared with those of b1 and b2. 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 polycalicene constructs a quite unique non-alternant hydrocarbon system having participation of low energy electronically-excited biradical structures in its ground state.

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References and Notes


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$_2$Cl$_2$ 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.


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 $\Delta E$ value can not be ruled out.

11) The $N_n$ values are $1.8 \times 10^{18}$, $3.9 \times 10^{17}$, and $2.0 \times 10^{17}$ 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.