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Study of Conformation of Anion Radicals of Some Thermochromic Ethylenes by Electron Spin Resonance Spectroscopy and Semi-empirical Molecular Orbital Calculations[1]

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The perpendicularly twisting conformation of an anion radical of 10-(α-(*o*-tolyl)-benzylidene)-9(10*H*)-anthracenone was studied by the use of electron spin resonance (ESR) measurement. By comparison with previous results on 10-diphenylmethylene-9(10*H*)-anthracenone and 10(9-xanthenylidene)-9(10*H*)-anthracenone, it was found that this structural feature of the compound was a result of the presence of the carbonyl group.

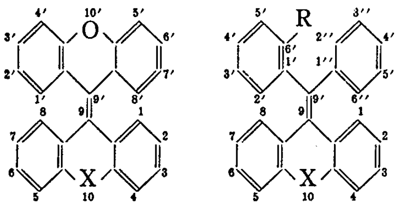
Semi-empirical molecular orbital calculations with an open shell model revealed a correlation between the twisting angle about the central double bond of anion radicals of some thermochromic ethylenes and the π-electronic charge distribution on the double bond, and were found to be in reasonable agreement with the conclusion obtained from ESR measurements. It became apparent that twisting decreased the double bond character of the central double bond. A qualitative interpretation of the distribution of the unpaired electron in the molecule is presented.

Keywords——anion radical; conformation; ESR; PPP-MO; thermochromic ethylene

Thermochromic ethylenes typified by bianthron have become of interest by reason of their reversible color change with change of temperature.[2)]

Harnik and Schmidt, in an X-ray crystallographic study, showed that the molecule of bianthrone has a double-folded structure in the crystal state.[3)] Recently, it was estimated by Agranat and Tapuhi that the molecules of bianthrone derivatives show some rotation about the axis of the central double bond, but the origin of the twisting of the double bond is still obscure.[4)] The authors measured the electron spin resonance (ESR) spectra of anion radicals of 10-(9-xanthenylidene)-9(10*H*)-anthracenone (I), 10-diphenylmethylene-9(10*H*)-anthracenone (II), 10-(α-(*o*-tolyl)benzylidene)-9(10*H*)-anthracenone (III), 9-(diphenylmethylene)xanthene (IV) and 9,9′-bixanthenylidene (V). The structural formulae are given in the following scheme, and the number of 9′ of compounds II, III and IV is used as a matter of convenience.

In a previous paper,[5)] we clarified that the compounds can be classified into two groups. The first group, including compounds I and II, is twisted perpendicularly, and the second



I: X=CO
V: X=O

II: X=CO, R=H
III: X=CO, R=CH$_3$
IV: X=O, R=H

Chart 1

Table I. Spin Densities of 10-(α-(*o*-Tolyl) benzylidene)-9(10*H*)-anthracenone

Position	Obs.	Calc.
2′	0.374	0.283
3′	0.090	−0.061
4′	0.134	0.141
5′	—	−0.009
6′	0.040	0.036
2″, 6″	0.045	0.031
3″, 5″	—	−0.011
4″	0.045	0.039

one, including compounds IV and V, twisted by 80° and 20°. It was also suggested that the origin of the perpendicular structure of the first group may be large polarity caused by a local distribution of π-electronic charge to the carbonyl group so that the central double bond character is decreased and the molecules may be easily twisted.

We report here the results of ESR measurement of compound III in comparison with previous data, and the effect of twisting of the central double bond on the values of the charge densities and the bond-orders is discussed on the basis of PPP–MO calculations.

Experimental

The ESR measurements of anion radicals of compounds I, II, IV and V were described in a previous paper.[5] Compound III was prepared by a method similar to that used for compound II, as described elsewhere.[6] The purity of the compound was confirmed by elemental analysis and mass spectrometry.

The PPP-MO calculations were carried out on an NEC ACOS 77-500 computer by using a FORTRAN program modified from a published program.[7]

The π-bond-orders and the π-electronic distributions of anion radicals of compounds I, II, III, IV and V were obtained in the range of 0—80° or 0—90° twisting angle along the axis of the central double-bond.

We calculated the three-dimensional coordinates of the atoms in the molecules by Eyring's method[8] and displayed them by using a curve plotter.

Results and Discussion

Figure 1 shows the ESR spectrum of compound III. Its spectral pattern did not vary in the range from $-70°C$ to $+80°C$. This means that the anion radical does not change its

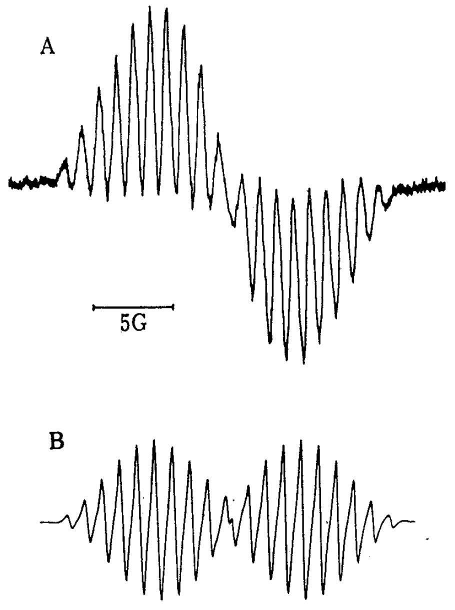


Fig. 1. The ESR Spectrum (A) and the Reconstructed Spectrum (B) of the Anion Radical of Compound III

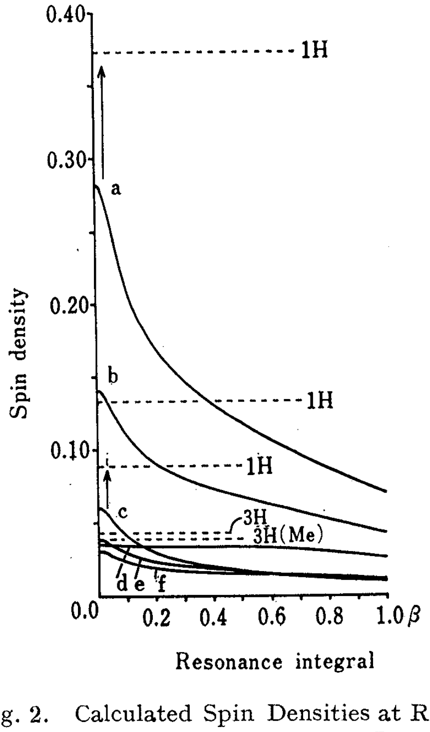


Fig. 2. Calculated Spin Densities at Ring Carbon Atoms *vs.* Resonance Integral about the Central Double Bond

The dotted lines indicate observed spin densities. The symbols 1H and 3H indicate the number of protons from ESR hfs. The solid lines indicate the calculated spin densities on each carbon atom: the curves a, b, c, d, e and f indicate the spin densities of positions 2′, 4′, 3′ (negative sign), 6′, 4″ and 2″(6″), respectively. On positions 5′ and 3″ (5″), the spin densities are negligible (≤ 0.01). Arrowed lines mean that the calculated spin density corresponds to the observed one.

conformation over this temperature range. The behavior at these temperatures is the same as that of compounds I and II.

As shown in Fig. 2, spin densities calculated by the use of McLachlan's method[9] indicate that the anion radical is twisted perpendicularly in a similar manner to compounds I and II. The compound is classified into the first group as described above.

As shown in Fig. 3, the calculated charges at positions 9′ of the anion radicals of compounds I, II and III are large and negative sign (curves b), though they were calculated as positive by use of the closed shell model of the neutral molecules. The charge densities at positions 9 of the radical molecules were calculated as negative for the neutral molecules (curves a). The behavior of the calculated charge reflects the results of ESR measurements, which indicate that the unpaired electron of the anion radicals of the first group is distributed over the moiety of the molecules, including the carbons of positions 9′.

In contrast, compounds IV and V, which have no carnonyl group, have littel difference in charge density between positions 9′ and 9 (curves c and e, for IV respectively, and d for V). It appears that compounds IV and V have a smaller polarity than compounds I, II and III, and the molecules are not twisted easily. This conclusion is consistent with the results of the ESR measurements, indicating that the anion radicals of compounds IV and V are, twisted, but not perpendicularly.

The bond-orders between positions 9 and 9′, calculated with the open-shell models, have a small value and decrease with increasing twisting angle, as shown in Fig. 4. Curves a and b indicate that compounds I, II and III are more easily twisted than compounds IV and V.

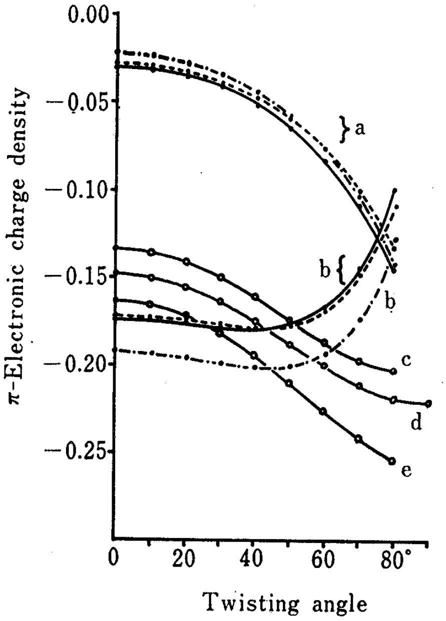


Fig. 3. Calculated Charge Densities *vs.* Twisting Angles about the Central Double Bonds

The curves a indicate the π-electronic charge densities on position 9 and the curves b indicate charges on position 9′ of componds I, II and III (—I, ---II, -·-·-III). The curves c and e indicate charges on position 9′ and 9 of compound IV, and curve d indicates charge on position 9 of compound V.

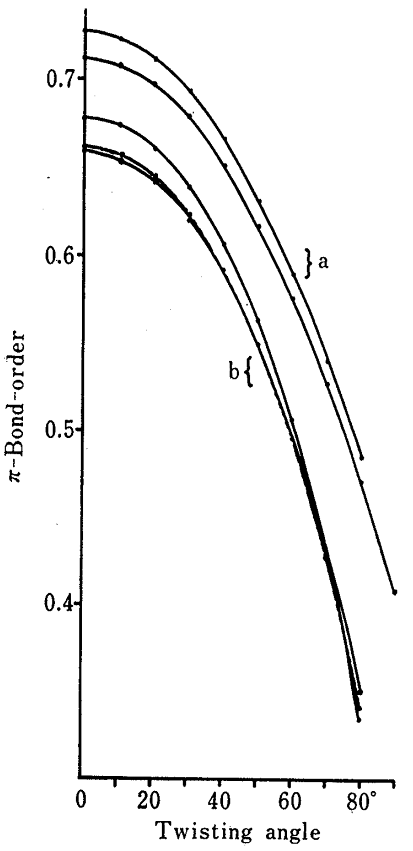


Fig. 4. Calculated Bond-orders between Position 9 and 9′

Curves a indicate the bond-orders of the radicals of compounds IV and V. Curves b indicate those of compounds I, II and III.

It is estimated that the polar structures of compounds I, II and III reduce the double bond characters of the central double bonds, and that the polar structures are held stably by localization the π-electrons on moieties including the carbonyl groups.

It may be considered that when an electron is supplied from an electrode or alkali metal, it is attracted by the positive-charged moieties of the molecules, so that the radical molecules have stable twisting structures with decreased double bond characters.

Although the twisting structure is not expected from the calculated π-electronic energies, which increase with increase in the twisting angle of the central double bond, the anion radicals of compounds IV and V are also twisted.[5] It may be considered that the reduction of the double bond character of the central double bonds allows the anion radicals to twist, but the polarity of the molecules is small (Fig. 3), and thus the radicals are twisted, but not perpendicularly.

In conclusion, simi-empirical MO calculations by using the PPP approximation reflect the relations between the conformations and the polarities of the molecules, It was found that the PPP–MO calculation could give a simple, satisfactory interpretation of the twisting structure of the anion radicals of thermochromic ethylenes. MO calculations including all valence electrons are under way, so that more quantitative data may shortly be available for conformational analysis.

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References and Notes

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Synthesis of 8α,9α- and 8β,9β-Epoxyhexahydrocannabinols

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8α,9α- (IIa) and 8β,9β-epoxyhexahydrocannabinol (IIIa) were prepared from Δ^8-tetrahydrocannabinol (Ia) by three reaction steps. Epoxidation of acetylated Ia with