# Electronic structure of diindeno[1,2,3-cd:1',2',3'-lm]perylene radical anion

Y. KUBOZONO, M. ATA and Y. GONDO\*

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812,

Japan

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Abstract—The electronic structure of diindeno[1,2,3-cd:1',2',3'-lm]perylene (periflanthene) radical anion has been studied on the basis of the ESR, electronic absorption, and linear dichroism spectra. The observed results are interpreted in terms of the SCF MO calculations within the framework of the  $\pi$ -electron approximation.

## INTRODUCTION

The electronic structures of planar  $\pi$ -conjugated polyatomic radical anions have been extensively studied by use of various spectroscopic methods [1], inclusive of the linear dichroism (LD) [2] and induced circular dichroism (ICD) [3] methods. In this work, we have undertaken a study of the electronic structure of diindeno[1,2,3-cd:1',2',3'-lm]perylene (periflanthene) radical anion (DIP<sup>--</sup>) as well as the radical cation (DIP<sup>+</sup>), since we are interested in an ionization potential of 8.59 eV comparable with that of perylene and a fairly large electron affinity of 4.03 eV, both predicted for neutral DIP from a semiempirical MO calculation; actually DIP- has been prepared successfully, whereas against our expectation, DIP + has not yet, the reason thereof being unknown. Thus, we here report on the ESR, electronic absorption, and LD spectra of DIP<sup>--</sup> as well as the LD spectrum of neutral DIP for comparison. The experimental results have been discussed on the basis of the restricted Hartree-Fock open shell SCF MO calculations in the  $\pi$ -electron approximation. No spectroscopic study of DIP<sup>--</sup> has been made so far except for an ESR measurement by LEWIS et al. [4] where no detailed information on the electronic structure could be deduced since the ESR spectrum of DIP<sup>-</sup>, prepared by thermal decomposition was poor in resolution [4].

#### **EXPERIMENTAL**

DIP (Aldrich) was used without further purification. For ESR and unpolarized absorption measurements, DIP<sup>--</sup> was generated by reduction with metallic potassium in tetrahydrofuran (THF) under vacuum. The radical anion obtained was fairly unstable even under high vacuum. The red solution of DIP turned blue when brought into contact with metallic potassium, indicating the formation of the radical anion. For LD absorption measurements, stretched polyethylene films were used. Commercially available polyethylene film (1 mm thick) was washed with chloroform (Dotite, spectrosol) during 5 h refluxing, and then the chloroform was evapor-

ated under vacuum. The polyethylene films were soaked in a saturated s-butylamine (Tokyo Kasei, GR) solution of DIP for a few days, dried in air, and stretched by 500%. DIP<sup>--</sup> was prepared in the stretched films by  $^{60}$ Co  $\gamma$ -ray irradiation at a dose of  $1.5 \times 10^6$  rad at 77 K.

ESR spectra were recorded on an X-band ESR spectrometer (Echo Electronics) combined with an electromagnet (JEOL, JM-360) with 100 kHz field modulation. ESR capillary cells of 5 mm, o.d., were used. Unpolarized and LD absorption spectra were measured on a u.v.-vis spectrophotometer (Shimadzu, MPS-50L), the LD spectra being recorded by use of a sheet polarizer (Polaroid, NH38).

By applying the stepwise reduction procedure of MICHL et al. [5] to the LD absorption spectra,  $E_{||}(\lambda)$  and  $E_{\perp}(\lambda)$ , observed in stretched polyethylene films, the long- and shortmolecular-axis polarized components,  $A_1(\lambda)$  and  $A_s(\lambda)$ , were derived. Here,  $E_{||}(\lambda)$  and  $E_{\perp}(\lambda)$  denote the observed absorptions polarized along and perpendicularly to the film stretching direction, respectively, while  $A_1(\lambda)$  and  $A_s(\lambda)$  are represented in terms of  $E_{||}(\lambda)$  and  $E_{\perp}(\lambda)$  as follows:

$$A_{1}(\lambda) = E_{||}(\lambda) - d_{||}^{0}E_{\perp}(\lambda)$$
$$A_{s}(\lambda) = E_{\perp}(\lambda) - d_{\perp}^{0}E_{||}(\lambda),$$

where  $d_{\parallel}^0$  and  $d_{\perp}^0$  are referred to as the reduction factors ranging from 0 to 1.0, and the  $A_1(\lambda)$  and  $A_s(\lambda)$  as the reduced spectra.

### **RESULTS AND DISCUSSION**

Figure 1(a) shows the ESR spectrum of DIP observed at room temperature, which is well resolved and isotropic in pattern. The spectrum is composed of the five main envelopes exhibiting the intensity ratio of 1:4:6:4:1, and can be interpreted straightforwardly in terms of the four different proton groups each with four equivalent protons. The hyperfine coupling (hfc) constants have been determined by the computer simulation shown in Fig. 1(b). Figure 2 shows the carbon skeleton of DIP and a schematic presentation of the SOMO  $(b_{2g})$  of DIP<sup>-.</sup> obtained by the  $\pi$ electron SCF MO calculation as well as the spin densities derived thereof. The observed hfc constants are parallel with those calculated from the spin densities,  $\rho$ , through MCCONNELL's formula [6], as shown in Table 1.

Now, we turn to the electronic spectra. Owing to the absorption of the sheet polarizer employed, the LD measurements were restricted to the region below

<sup>\*</sup>To whom correspondence should be addressed.



Fig. 1. ESR spectra of DIP<sup>-.</sup> observed in THF at room temperature (a), and simulated with the hfc constants in Table 1 (b).



Fig. 2. The carbon skeleton of DIP (a) and a schematic representation of the SOMO and the spin densities derived thereof (b); the diameters of the circles are proportional to the coefficients multiplying AO's, the open and solid circles refer to different signs, and the numerical values are the calculated spin densities.

 $30,000 \text{ cm}^{-1}$ , so that detailed discussions are restricted to this region. Figure 3(a) shows the unpolarized absorption spectrum of neutral DIP in THF and the reduced spectra of neutral DIP in stretched films, together with the theoretical results. The absorption spectrum of neutral DIP in THF is similar to that in trichlorobenzene reported by LANG *et al.* [7]

Table 1. Observed and calculated hfc constants, a<sup>H</sup>, in DIP<sup>--</sup>

Atomic position*	$a_{\rm (obsd)}^{\rm H}/G^{\dagger}$	$a^{ m H}_{ m (calcd)}/G^{ m \dagger}$
1	0.16	-0.22
2	0.26	-0.38
5	0.54	-0.75
6	2.03	-1.22

\*See Fig. 2.

 $\dagger 1 G = 10^{-4} T$ . A value of -23.7 G is taken as  $Q^{\rm H}$  in McConnell's formula,  $a^{\rm H} = Q^{\rm H} \rho$  [6].

An absorption band maximum is located at  $18,660 \text{ cm}^{-1}$ , which makes the solution red. The long-molecular-axis component appearing around 20,000 cm<sup>-1</sup> is assigned to the theoretical first transition. The component shows clearly three progression peaks separated by ca.  $1500 \text{ cm}^{-1}$ . The two short-axis polarized transitions theoretically predicted in the range 25,000–30,000 cm<sup>-1</sup> could not be found in the region studied.

Figure 3(b) shows the absorption spectrum of DIP<sup>--</sup> observed in THF and the reduced spectra of DIP<sup>--</sup> in stretched films, together with the theoretical results. The weak absorption around 20,000 cm<sup>-1</sup> indicates that the neutral species partially remained unchanged. The long-axis component at 12,500 cm<sup>-1</sup>



Fig. 3. The observed and calculated electronic absorption spectra of (a) DIP and (b) DIP<sup>-+</sup>; the solid, broken and dotted curves refer to the unpolarized spectrum, long- and short-molecular-axis polarized components,  $A_1(\lambda)$  and  $A_2(\lambda)$ , respectively. The calculated spectra are represented with the sticks and circles; the stick lengths represent the logarithmic oscillator strengths, and the circles, and symbols L and S refer to the forbidden, long-, and short-molecular-axis polarized transitions, respectively.

is assigned to the first transition theoretically predicted at  $12,380 \text{ cm}^{-1}$ , and the intense long-axis polar-ized component appearing from 13,500 to 16,500  $\text{cm}^{-1}$  is ascribed consistently to the second transition. Though the long-axis component around 20,000 cm<sup>-1</sup> observed in stretched films and ascribed to the remaining neutral species is intense, the corresponding band was observed to be rather weak in the spectrum of DIP<sup>-,</sup> generated by alkali metal reduction. This spectral difference seems very interesting as an indication of different mechanisms of radical formation in different media. The short-axis component at 17,600  $\text{cm}^{-1}$  corresponds to the fourth transition, and the short-axis component above 25,000 cm<sup>-1</sup> can be assigned to the sixth and ninth transitions. Thus, the electronic structure of DIP as well as that of DIP are explained consistently in terms of the  $\pi$ -electron

SCF MO CI calculations, as far as the ground and lower excited electronic states are concerned.

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