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RAPID RACEMIZATION OF THE RADICAL ANIONS OF 1,1'-BINAPHTHYL AND 9,10-DIHYDRO-3,4;5,6-DIBENZOPHENANTHRENE

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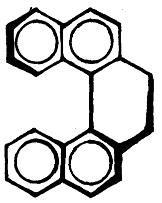
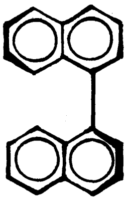
The radical anions of 1,1'-binaphthyl and 9,10-dihydro-3,4;5,6-dibenzophenanthrene racemize more rapidly than the corresponding neutral compounds without cleavage of the 1,1' bond.

It has been reported by Colter and Clemens that, in the charge transfer (CT) complexes, (+)-9,10-dihydro-3,4;5,6-dibenzophenanthrene (DDPH) and (+)-1,1'-binaphthyl (BN), which are acting as donors, racemize more rapidly than in a neutral molecular state.[1] Although the cause of this effect has not been cleared up by them, it can be presumed that this effect is relating to the ion radical-character of the CT complex.[2] On this supposition, it may be expected that the radical ions derived from these binaphthyls racemize more rapidly than the corresponding neutral molecules. We report some evidences suggesting that DDPH$^{\bar{\cdot}}$ and BN$^{\bar{\cdot}}$ racemize more rapidly than the corresponding neutral molecules without cleavage of the 1,1'-bond.

(S)-(+)-DDPH ($[\alpha]_D$ = +1100 in benzene) and (S)-(+)-BN ($[\alpha]_D$ = +130 in dioxane) were synthesized by the reported methods.[3,4] A half-life period ($T_{1/2}$) and activation energy (E_a) of the racemization of DDPH are reported to be 120 min at 108° and 30.8 kcal/mole, respectively.[1,4] $T_{1/2}$ and E_a of BN are 13 min at 50° and 22 kcal/mole, respectively.[1,5] Preparations of the radical anions and measurements of the spectra were described previously.[6,7] By contact with metal chip DDPH turned reddish purple. This solution showed well resolved esr spectrum, which was safely assigned to DDPH$^{\bar{\cdot}}$.



S-(+)-DDPH



S-(+)-BN

The esr signals were stable for a few days at room temperature. By the γ-irradiation of DDPH in methyltetrahydrofuran (MTHF) at -196°, a reddish purple glassy solution was obtained. The CD and absorption spectra of $DDPH^{\bar{\cdot}}$ produced by γ-irradiation were shown in Fig. 1 with solid lines. The magnitudes of the CD bands ($\Delta A/A$) of $DDPH^{\bar{\cdot}}$ were comparable to those of neutral molecule (ca. 7×10^{-4}). After DDPH was reduced by contact with sodium metal in a cooled methanol bath

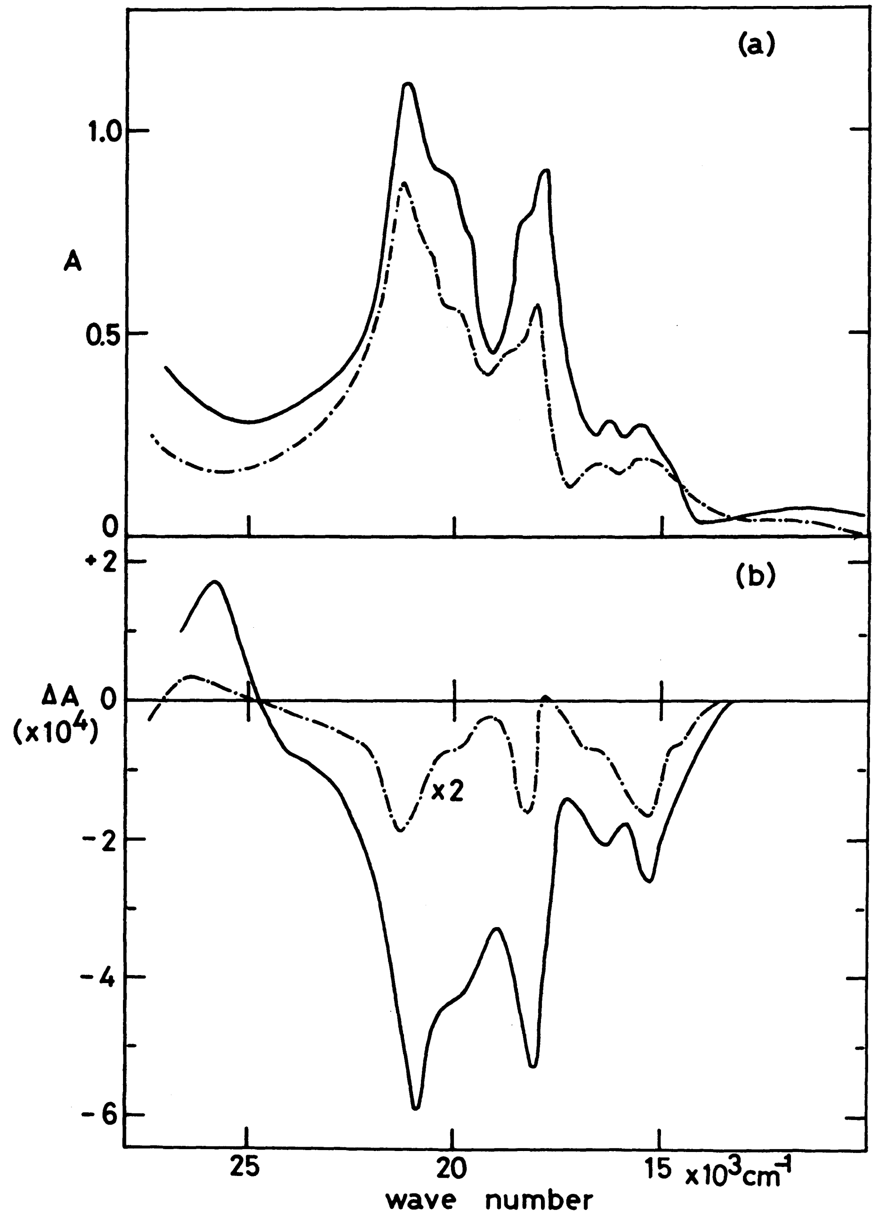


Fig. 1. Absorption (a) and CD (b) spectra of the (S)-(+)-DDPH radical anion produced by γ-irradiation (——) and sodium metal reduction (—·—) in MTHF at -196° (10^{-3} mole/l in 2 mm cell).

(-50°) for 5 min, the CD and absorption spectra were measured at -196° (—·— in Fig. 1). The absorption spectrum obtained by metal reduction was essentially the same as that obtained by γ-irradiation, although the magnitudes of the CD bands were extremely small compared with the corresponding CD bands obtained by γ-irradiation (ca. 1/7). Since both absorption spectra resemble each other, the different magnitudes of the CD bands could not be attributed to the different structures of $\mathrm{DDPH}^{\cdot-}$. Thus, the optical activity of $\mathrm{DDPH}^{\cdot-}$ might vanish appreciably before the $\mathrm{DDPH}^{\cdot-}$ solution formed by metal reduction was cooled to -196°. Before the CD measurement in rigid matrix, the solution had to be warmed up to room temperature for a few minutes to remove the viscous methanol attached to the surface of the optical cell. Rapid decrease of the optical activity of $\mathrm{DDPH}^{\cdot-}$ may occur during this procedure.

To examine whether the rapid disappearance of the optical activity was caused either by the rotation around the 1,1' bond or by the cleavage of this bond, neutral molecule was recovered from the radical anion solution. Sulfur dioxide was introduced in the $\mathrm{DDPH}^{\cdot-}$ solution which was maintained at -50° for 30 min. Electron transfer reaction from $\mathrm{DDPH}^{\cdot-}$ to sulfur dioxide gave DDPH and sodium dithionite, which was insoluble in MTHF.8) The filtered solution showed the same absorption spectrum as that of the authentic DDPH, although the recovered DDPH did not show optical activity at all. Thus, it was confirmed that the racemization of $\mathrm{DDPH}^{\cdot-}$ occurred rapidly without cleavage of the 1,1' bond and that the reactions observed above proceeded according to the following schemes:

$$(+)\text{-DDPH} + e^- \longrightarrow (+)\text{-DDPH}^{\cdot-} \qquad (1)$$

$$(+)\text{-DDPH}^{\cdot-} \rightleftharpoons (-)\text{-DDPH}^{\cdot-} \qquad (2)$$

$$\text{racemic DDPH}^{\cdot-} + SO_2 \longrightarrow \text{racemic DDPH} + 1/2\ S_2O_4^{2-} \qquad (3)$$

The contribution of the dianion of DDPH to the observed rapid racemization must be examined, since the dianion may be formed by the disproportionation reaction of the radical anions or by the heterogeneous reaction on the surface of the alkali metal. In the $\mathrm{DDPH}^{\cdot-}$ solution formed by the electron transfer from the naphthalene radical anion ($N^{\cdot-}$) under the condition of $2[\mathrm{DDPH}] \geq [N^{\cdot-}]$, the formation of the dianion may be depressed on the ground of chemical stoichiometry. The CD spectrum of this solution at -196° gave a similar spectrum to that obtained by the metal reduction as shown in Fig. 1. Thus, it is evident that the rapid racemization observed above is caused by the radical anion itself.

In the case of the $\mathrm{BN}^{\cdot-}$, the CD bands measured immediately after the metal reduction by the same procedure as adopted in DDPH$^{\overline{\cdot}}$ were too small to distinguish from noises, although the CD spectrum of BN$^{\overline{\cdot}}$ obtained by the γ-irradiation had similar magnitude to that of neutral molecule. By the electron transfer experiments, it was confirmed that the optical activity of BN$^{\overline{\cdot}}$ also decreases rapidly in solution without cleavage of the 1,1' bond.

In this study, unfortunately, the difference between the rotational barriers of the radical anion and neutral molecule could not be estimated, since the rate of the racemization of the radical anion was too fast to measure quantitatively. In the neutral binaphthyl derivatives, it is known that large difference of the rate of racemization is not always caused by the large differnce of the activation energy. For example, $T_{1/2}$ at 70° and E_a of 8-methyl-1,1'-binaphthyl are 5.35 hr and 25.3 kcal/mole, respectively, although corresponding values of 8-methyl ester are 36.1 min (at 50°) and 23.6 kcal/mole.9) On the other hand, it is reported that the rotational barrier of the radical anion of biphenyl derivative is smaller than that of neutral molecule.10,11) The rotational barrier of 9,10-dihydrophenanthrene was estimated to be $\lesssim$ 9 kcal/mole by a nmr measurement by Oki, Iwamura, and Hayakawa,10) while that of the radical anion was 6.1 kcal/mole by an esr measurement by Iwaizumi, Matsusaki, and Isobe.11) Thus, it can be presumed that, in the case of 1,1'-binaphthyls, addition of an electron decreases the rotational barrier considerably.

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