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Chemically Induced Dynamic Nuclear Polarization in the Photochemical Reaction of Phenanthraquinone with Hydrogen Donors. II.[1] A Consideration of Unusual Nuclear Spin Polarization

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Polarized quartet NMR signals due to methylene protons were observed in the hydrogen-abstraction reactions of phenanthraquinone with *o*-substituted toluenes under the irradiation of light. The relative intensities of these signals could be predicted only by the general treatment of the CKO theory, taking account of the electronic singlet-triplet interactions (S–T_0 and S–T_1) of the radical pair. The scalar electronic-coupling constants, J_e, were evaluated approximately by comparing the theory with the experimental results and were found to be in the order of 7×10^9 sec^{-1}. The rather large value of J_e was discussed in relation to the nature of the reaction system; consequently, the existance of electronic π–π interaction was suggested for the radical-pair intermediate of the reaction.

Fischer and Bargon[2] have proposed a cross-relaxation process between electronic and nuclear-spin systems as the mechanism of the chemically induced dynamic nuclear polarization (CIDNP). However, the observations of combination lines consisting of both absorption and emission lines,[3] and strong nuclear spin polarization[4] over that predicted from the Overhausser effect, can no longer be explained on the basis of the cross-relaxation mechanism alone.

In the present stage, the theory developed by Closs and Trifunac[5] and by Kaptein and Oosterhoff,[6] *i.e.*, the CKO theory, seems to give a more reasonable interpretation of the CIDNP mechanism. This theory is principally based on the formation of a radical-pair intermediate during rapid radical reactions; then reaction products are formed through the radical pair in the electronic-spin singlet state brought about by the mixing of the electronic singlet and triplet states. In the CKO theory as approximated in large magnetic fields, only the mixing between the singlet (S) and triplet state with $m_s=0(T_0)$ is taken into

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[1] Previous paper, K. Maruyama, H. Shindo, T. Otsuki, and T. Maruyama, This Bulletin, **44**, 2756 (1971). This work has been done at the Department of Chemistry, College of Liberal Arts and Science, Kyoto University.

[2] H. Fischer and J. Bargon, *Z. Naturforsch.*, **22a**, 1556 (1967).

[3] H. R. Ward and R. G. Lawer, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

[4] G. L. Closs and L. E. Closs, *ibid.*, **91**, 4550 (1969).

[5] G. L. Closs, *ibid.*, **91**, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183 (1970).

[6] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

account; the other two triplet states with $m_s = \pm 1 (T_1$ and $T_{-1})$ are neglected. Though the aproximate CKO theory has described the major features of CIDNP, it has failed to explain the reactions proceeding in small magnetic fields[7] and, rarely, it could not even predict the nuclear-spin polarization of products resulting from the radical pair, the individual components of which have the same g-value.[8]

The methylene protons of the 1,2-photo-adducts[9] show strongly polarized NMR quartet signals in the photochemical reactions of phenanthraquinone with o-substituted toluenes. The intensities of such quartet signals differed from those predicted from the approximate CKO theory. It was shown, by a more general treatment of the CKO theory, that the S–T_1 interaction as well as the S–T_0 interaction must be taken into account in accounting for the nuclear polarization observed in our experiments.

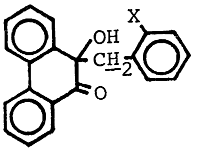
Experimental

The phenanthraquinone was prepared by the oxidation of phenanthrene with potassium dichromate and was purified by recrystallization from an acetic acid solution. Hydrogen-abstraction reactions of phenanthraquinone (0.04M) in a solution of toluene, o-xylene, o-chlorotoluene or o-bromotoluene were photochemically induced at 70°C inside an NMR probe modified for photochemical reactions; the method of modification has been reported in a previous paper.[10] The NMR spectra were observed at 60 MHz by means of a C-60HL-type spectrometer(JEOL. CO., Ltd.) under light.

Theory

The photochemical reaction of phenanthraquinone occurs through its optically-activated triplet state. In the present case, a weakly-coupled radical pair is formed through the hydrogen abstraction of the excited phenanthraquinone from o-substituted toluenes. A finite fraction of the radical pair yields the 1,2-adduct of phenanthraquinone.[11]

Now, let us examine further the particular protons of the adduct, *i.e.*, the methylene protons (underlined) of the 1,2-adduct;



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a. X=H
b. $X=CH_3$
c. X=Cl
d. X=Br

As is shown in Figs. 2 to 5, an unusual polarized NMR quartet of signals of the photo-adduct was observed; these signals are not predicted by the CKO theory based on the S–T_0 mixing alone. This finding encouraged us to investigate the more general CKO theory for AB-spin system.

It has been reported that a weakly-interacting radical pair often shows an unusual hyperfine structure of the electron-spin resonance of the triplet state.[12] This is caused by mixing between the electronic-spin singlet and the triplet states of such a radical pair, whose singlet-triplet separation is comparable to the electronic Zeeman energy or less. The effective spin Hamiltonian for such radical-pair tumbling in a fast rate in a solution can be written (if the nuclear Zeeman term is neglected)[6]:

$$\mathscr{H}_0 = \beta H_0(g_1S_1+g_2S_2) - J_e(1/2+2S_1S_2) + \sum_{i,j} A_{ij}I_iS_j + H_d \tag{1}$$

where β is the Bohr magneton, H_0 is the static magnetic field, S and I are the electronic and nuclear-spin operators, J_e is the scalar electronic exchange coupling constant, and A_{ij} is the hyperfine coupling constant between the ith nuclear and the jth electron. The term of dipole-dipole interaction, H_d, is assumed to be negligible because of the establishment of a thermal equilibrium in the electronic-spin system of the triplet precursor.

As the radical pair will have different values of J_e and A_{ij} from one time to another due to the thermal vibration and the collisions, the Hamiltonian, $\mathscr{H}_0$, should be time-dependent. By denoting the total spin-wave function of the radical pair as $\Psi(t)$, the time-dependent Schrödinger equation for the Hamiltonian, $\mathscr{H}_0$, is given by;

$$i\hbar\frac{\mathrm{d}\Psi(t)}{\mathrm{d}t} = \mathscr{H}_0\Psi(t) \tag{2}$$

The general solution of Eq. (2) produces a linear combination of $U_{ij}{}^0$;

$$\Psi(t) = \sum_{i,j} C_{ij}(t)\mathrm{e}^{-iE_{ij}t}U_{ij}^0 \tag{3}$$

where $U_{ij}{}^0$ represents the eigen function describing both ith nuclear and jth electronic states and where E_{ij} is the eigen value of $U_{ij}{}^0$. According to the CKO model, the triplet state of the radical pair does not lie on the reaction coordinate; hence, the rate of population increase to the final product can be assumed to be proportional to the degree of the singlet character of the radical pair (*i.e.*, the probability of the radical pair in the singlet state). Such a probability of the radical pair can be given by the coefficient of the electronic singlet state, $|C_{is}(t)|^2$ for the ith nuclear spin state, where the suffix s refers to the electronic singlet. Thus, by averaging $|C_{is}(t)|^2$ over the lifetime of the radical pair, τ, the rate of the population increase of the ith nuclear spin state follows Eq. (4);

$$k_i = \frac{k_{\mathrm{SE}}}{n}\int_0^\infty |C_{is}(t)|^2\mathrm{e}^{-t/\tau}\mathrm{d}t \Big/ \int_0^\infty \mathrm{e}^{-t/\tau}\mathrm{d}t \tag{4}$$

where k_{SE} is the specific rate for the product generated from the radical pair in the pure singlet state and where n is the number of spin states of the nuclear spin system in the problem.

Let us now return to the radical pair in our case;

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[7] J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and C. R Morrison, *J. Amer. Chem. Soc.*, **92**, 5761 (1970).

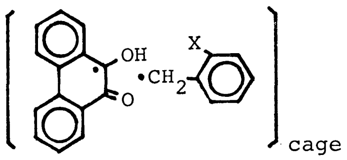
[8] H. Iwamura, M. Iwamura, and T. Nishida, 21st Symposium on Organic Reaction Mechanism, Hiroshima, Oct., 1970.

[9] See Structure I.

[10] K. Maruyama, H. Shindo, T. Otsuki, and T. Maruyama, This Bulletin, **44**, 2756 (1971).

[11] The adducts obtained by the reaction of phenanthraquinone with alkyl aromatics are, in general, 1,2-photo-adducts.

[12] See, for example, K. Itoh, H. Hayashi, and S. Nagakura, *Mol. Phys.*, **17**, 561 (1969).



II

which is simply denoted by $[R_1(H_2)\cdot, \cdot R_2]$. Let us evaluate the rate of the population increase of a given nuclear-spin state for methylene protons of the I adduct. Considering the II radical pair, consisting of two electrons and two hydrogen nuclei, one can rewrite Eq. (1) as;

$$\mathscr{H}_0 = \beta H_0(g_1S_1+g_2S_2) - J_e(1/2+2S_1S_2) + (A_{11}I_1+A_{21}I_2)S_1 \tag{5}$$

The four spin functions of the electronic system are taken as $S=1/\sqrt{2}\,(|\alpha\beta>-|\beta\alpha>)$ for the singlet state, and $T_1=|\alpha\alpha>$, $T_0=1/\sqrt{2}\,(|\alpha\beta>+|\beta\alpha>)$, and $T_{-1}=|\beta\beta>$ for the triplet states. Then, the matrix elements of the Hamiltonian, $\mathscr{H}_0$, for these spin functions become as follows;

$$\begin{pmatrix} J_e & -1/2\sqrt{2}\,(A_{11}I_1{}^{+}+A_{21}I_2{}^{+}) & 1/2\beta H_0(g_1-g_2)+1/2(A_{11}I_1+A_{21}I_2) & 1/2\sqrt{2}\,(A_{11}I_1{}^{-}+A_{21}I_2{}^{-}) \\ * & 1/2\beta H_0(g_1+g_2)-J_e+1/2(A_{11}I_1+A_{21}I_2) & 1/2\sqrt{2}\,(A_{11}I_1{}^{-}+A_{21}I_2{}^{-}) & 0 \\ * & * & -J_e & 1/2\sqrt{2}\,(A_{11}I_1{}^{-}+A_{21}I_2{}^{-}) \\ * & 0 & * & -1/2\beta H_0(g_1+g_2)-J_e-1/2(A_{11}I_1+A_{21}I_2) \end{pmatrix} \tag{6}$$

where I^+ and I^- are the nuclear-spin operators, I_x+iI_y and I_x-iI_y respectively, and the element $*$ represents the conjugate of the symmetric elements with respect to the diagonal of the matrix. Matrix (6) shows that the mixing between the electronic singlet and triplet states occurs through off-diagonal elements, *i.e.*, hyperifine coupling constants and g values.

Let us denote the four spin states of the nuclear system as ϕ_i $(i=1\cdots,4)$. A solution of Schrödinger's Eq. (2) for the Hamiltonian (5) can be obtained under suitable initial conditions after solving a secular equation of the matrix with dimensions of 16×16. Such a procedure is very tedious, however, so let us now consider two limiting cases: $2|J_e|\cong|A|$ for case (a) and $|\pm\beta gH_0-J_e|\cong|A|$ for case (b).

Case (a); $2|J_e|\cong|A|$. This is a very important case, one in which the electronic singlet, S, and the T_0 triplet are mixing. As the Zeeman energy is much larger than the hyperfine interaction, the mixing between the singlet, S, and the other two triplets, T_1 and T_{-1}, is negligibly small. Then, we can easily solve the secular equation of matrix (6); we get, as the 16 eigen functions;

$$|T_1\phi_i> \tag{7a}$$

$$|T_{-1}\phi_i> \tag{7b}$$

$$(\cos\theta_i|S>+\sin\theta_i|T_0>)\phi_i \tag{7c}$$

$$(\sin\theta_i|S>-\cos\theta_i|T_0>)\phi_i \tag{7d}$$

$$(i=1,\cdots,4)$$

and, as the 16 eigen values;

$$E_{1i} = 1/2\beta H_0(g_1+g_2) - J_e + 1/2M_i \tag{8a}$$

$$E_{2i} = -1/2\beta H_0(g_1+g_2) - J_e - 1/2M_i \tag{8b}$$

$$E_{3i} = [J_e{}^2+(1/2\beta H_0\Delta g+1/2M_i)^2]^{1/2} \tag{8c}$$

$$E_{4i} = -[J_e{}^2+(1/2\beta H_0\Delta g+1/2M_i)^2]^{1/2} \tag{8d}$$

$$(i=1,\cdots,4)$$

where $\tan 2\theta_i=J_e/M_i$, $\Delta g=g_1-g_2$, and $M_i=<\phi_i|A_{11}I_1+A_{21}I_2|\phi_i>$. By considering that the radical pair, II, was in the triplet state at the initial time, $t=0$, Eq. (2) can be easily solved by means of Eq. (3) in the zeroth-order approximation as follows;

$$\Psi(t) = \frac{1}{2}\sum_{i=1}^{4}\{e^{-iE_{1i}t}|T_1\phi_i>+e^{-iE_{2i}t}|T_{-1}\phi_i>+\sin\theta_i\cos\theta_i \times(e^{-iE_{3i}t}-e^{-iE_{4i}t})|S\phi_i>+(\sin^2\theta_i e^{-iE_{3i}t}+\cos^2\theta_i e^{-iE_{4i}t})|T_0\phi_i>\} \tag{9}$$

The probability that the radical pair transfers after time t from the electronic triplet state to singlet state is given by;

$$|C_{ij}(t)|^2 = \frac{1}{2}\sin^2\theta_i\cos^2\theta_i\{1-\cos(E_{3i}-E_{4i})t\} \tag{10}$$

Then, by using Eq. (4), we obtain k_i as the rate of population increase for the nuclear-spin state, ϕ_i, of the photo-adduct;

$$k_i = \frac{k_{\mathrm{SE}}}{2}\,\frac{(1/2\beta H_0\Delta g+1/2M_i)^2\tau^2}{1+(E_{3i}-E_{4i})^2\tau^2} \tag{11}$$

This is a well-known expression derived by Closs and Trifunac[5] and by Kaptein and Oosterhoff.[6] Since the values of M_i in Eq. (11) differ from one nuclear-spin state to another, the increases in the rates of the adduct are different according to the individual nuclear spin states. Thus, polarization occurs in the nuclear-spin system of the adducts.

Case (b); $|\pm\beta gH_0-J_e|\cong|A|$. This is the case in which the electronic singlet, S, does not mix with the T_0 triplet but with the T_1 or T_{-1} triplet. Let us consider the case of the S–T_1 mixing alone. In this case, the Hamiltonian matrix with dimensions of 16×16 may be expressed as the direct sum of nine submatrices, whose dimensions are eight 1×1 and one 8×8. For the sake of simplicity, let us assume a relationship of hyperfine coupling constants, $A_{11}\cong A_{21}$; this is reasonable because two protons of the radical pair, II, in the problem are attached to the same carbon atom. On denoting the two spin functions of a single nuclear spin by $|+>$ and $|->$, we obtain, as the spin functions for AB-spin system, $s=1/\sqrt{2}\,(|+->-|-+>)$, $t_1=|++>$, $t_0=1/\sqrt{2}\,(|+->+|-+>)$, and $t_{-1}=|-->$. The first function, s, may be reffered to the nuclear-spin singlet, while probably the latter three may be reffered to the nuclear-spin triplets. Thus, we obtain the following four eigen functions concerned with the S–T_1 mixing;

$$\cos\gamma|T_1t_0>-\sin\gamma|St_1> \tag{12a}$$

$$\sin\gamma|T_1t_0>+\cos\gamma|St_1> \tag{12b}$$

$$\cos\delta|St_0>-\sin\delta|T_1t_{-1}> \tag{12c}$$

$$\sin\delta\,|St_0\rangle + \cos\delta\,|T_1t_{-1}\rangle \tag{12d}$$

where $\tan 2\gamma = A/(\beta gH_0 - 2J_e)$ and $\tan 2\delta = A/(\beta gH_0 - 2J_e - 1/2\ A)$. It is acutually found from Eq. (12) that the mixing of the electronic singlet, S, and triplet, T_1, occurs only through the nuclear-spin triplet (t_1, t_0, and t_{-1}), but is not associated with the nuclear-spin singlet(s).

Assuming that the radical pair is in the electronic triplet state at the initial time, $t=0$, just after being produced, then we can obtain the rate of the population increase for a given nuclear-spin state of the adduct in the same manner as in the case of Eq. (9);

$$k(s) = k(t_{-1}) = 0 \tag{13a}$$

$$k(t_1) = \frac{k_{\mathrm{SE}}}{2}\,\frac{A^2\tau^2}{1 + [(\beta gH_0 - 2J_e)^2 + A^2]\tau^2} \tag{13b}$$

$$k(t_0) = \frac{k_{\mathrm{SE}}}{2}\,\frac{A^2\tau^2}{1 + [(\beta gH_0 - 2J_e - 1/2A)^2 + A^2]\tau^2} \tag{13c}$$

Eq. (13) leads to an unexpected and interesting conclusion. In the limiting case of the S–T_1 mixing, only the adducts in the states of the nuclear-spin triplets (t_0 and t_1) are exclusively generated from the radical pair in the pure electronic singlet state.

If we consider another limiting case of the S–T_{-1} mixing, it may be deduced that the adducts in the states of the nuclear-spin triplets (t_0 and t_{-1}) are preferentially generated from the radical pair.

Results and Discussion

Signal Observed. The hydrogen-abstraction reactions of phenanthraquinone with toluene, *o*-xylene, *o*-chlorotoluene, and *o*-bromotoluene are photochemically induced to yield their 1,2-adducts. For example, as is shown in Fig. 1, methylene protons of the adduct with *o*-xylene indicate the AB-spin system in the NMR pattern; this system was originally observed by one of the present authors (K.M.). The quartet spectrum of the photo-adduct arises from the fact that the two methylene protons are magnetically different from each other due to the unequality in their conformations.[13]

This was confirmed by the fact that the chemical-shift difference between A and B protons decreased with an increase in the temperature. The absorption line at 226 Hz (down field from TMS) in Fig. 1 is due to a hydroxyl proton of the photo-adduct.

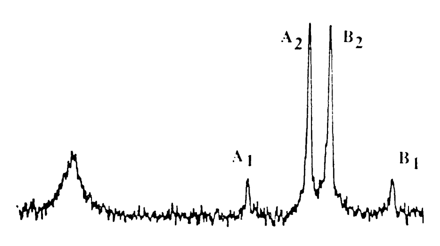


Fig. 1. Normal NMR quartet spectra due to the methylene protons of the 1,2-adduct of phenanthraquinone with *o*-xylene. Chemical shifts are in Hz down-field from TMS.

In Fig. 2 the spectrum (down) was observed for *o*-xylene solution of phenanthraquinone, while the spectrum (up) was recorded in the course of irradiation. The signal at 183 Hz (down-field from TMS) is responsible for a carbon-13 satellite of the methyl group of *o*-xylene, while the small but broad signal at about 180 Hz represents accidental harmonics due to AC power. Strongly-polarized quartet lines are observed during the course of irradiation, where three lines,

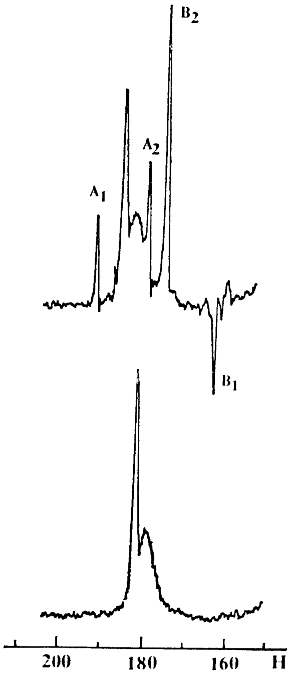


Fig. 2. Polarized NMR signals due to methylene protons of the 1,2-adduct of phenanthraquinone with *o*-xylene in photo-induced reaction.

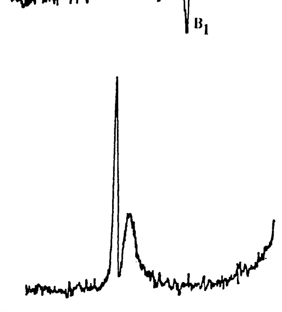


Fig. 3. Polarized NMR signals due to methylene protons of the 1,2-adduct of phenanthraquinone with *o*-chlorotoluene in photo-induced reaction.

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[13] P. M. Nair and J. D. Roberts, *J. Amer. Chem. Soc.*, **79**, 4565 (1957).

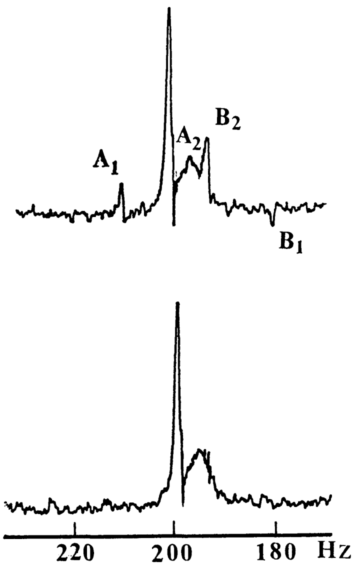


Fig. 4. Polarized NMR signals due to methylene protons of the 1,2-adduct of phenanthraquinone with *o*-bromotoluene in photo-induced reaction.

A$_1$, A$_2$, and B$_2$, at low fields show enhanced absorption, while the remaining line at a higher field (B$_1$), shows emission.

If the irradiation is shut off, the quartet spectrum promptly decays.

The quartet spectra for adducts of *o*-chlorotoluene and *o*-bromotoluene are illustrated in Figs. 3 and 4. It can be seen from these figures that the A$_1$ and B$_2$ lines of the quartet spectra show enhanced absorption, while that the A$_2$ and B$_1$ lines show emission. It was observed for the photo-adduct of toluene that the A$_2$ and B$_2$ lines are strongly enhanced and that the B$_1$ line is emission-enhanced. On the other hand, the A$_1$ line revealed a nearly zero polarization. The parameters of the quartet spectra of these adducts are gived in Table 1.

TABLE 1. DIFFERENCES OF CHEMICAL SHIFTS $\Delta\omega$ SPIN-SPIN COUPLING CONSTANTS J_n AND INTENSITY RATIOS I_{A_2}/I_{A_1} OF QUARTET SPECTRA OF THE PHOTO-ADDUCTS OF PHENANTHRAQUINONE WITH HYDROGEN DONORS

Hydrogen donor	$\Delta\omega$(Hz)	J_n(Hz)	Intensity ratio,I_{A_2}/I_{A_1}
o-Xylene	12.4	13.1	6.52
o-Chlorotoluene	10.5	12.8	7.81
o-Bromotoluene	11.1	13.5	7.77
Toluene	3.6	8.52	23.0

An Interpretation of Results. As was shown in Eq. (14) of a previous paper[10] the population difference, $[Z_i]-[Z_j]$ between the ith and jth nuclear-spin states of the photo-adduct was thus after light irradiation;

$$[Z_i]-[Z_j] = \frac{k_0 k_a (k_i-k_j)\,T_1{}^*}{(k_a+1/\tau_f)\sum\limits_j (k_j+2k_{bd})}(1-e^{-t/T_1{}^*}) \qquad (14)$$

wher k_o and k_a are the specific rate constant for the photo-excited molecule and that for the process of hydrogen abstraction respectively, and where k_i and k_j are the rate constants for the formation of photo-adducts in the ith and jth nuclear spin states respectively. k_{bd} is the rate constant which is associated with the process independent of the nuclear spin. $T_1{}^*$ is the relaxation time of the nuclear-spin system under the irradiation of light, and τ_f is the lifetime of the excited molecules. On assuming that $k_a \gg 1/\tau_f$, Eq. (14) is reduced to;

$$[Z_i]-[Z_j] = C(k_i-k_j) \qquad (15)$$

in the steady-state polarization. Here, C is a constant proper to the reaction system. The relative intensities of the polarized signals of the photo-adduct are proportional to the product of the population difference and to the relative intensities of the normal spectrum (*i.e.*, the transition probability induced by the application of the rf field). Thus, the relative intensities of polarized signals, $I_{ij}{}^*$, in steady-state polarization lead to;

$$I_{ij}^* = (k_i-k_j)I_{ij} \qquad (16)$$

where I_{ij} is the relative intensity of the spectral line in the thermal equilibrium of the spin system. The (k_i-k_j) factor may be referred to as a relative enhancement factor. One can compare the theoretical results with the experimental results by using Eq. (16).

It must first be investigated whether the polarized quartet signals can or can not be interpreted on the basis of the $S-T_0$ mixing alone. In the following calculations, it may be reasonable to assume that the hyperfine coupling constant, A_{11}, is nearly eaqual to A_{21} for the reason previously mentioned.

The rates of population increase for the four spin states of the AB-spin system of the photo-adduct can be calculated by means of Eq. (11). The relative intensities of the polarized signals are given by Eq. (17) as follows for the transitions corresponding to the spectral lines, A$_1$, A$_2$, B$_2$, and B$_1$ in the order of high-resonance frequencies; for lines A$_1$ and B$_2$;

$$I^* = \left\{\frac{1/4(\beta H_0 \Delta g+A)^2\tau^2}{1+4[J_e{}^2+1/4(\beta H_0 \Delta g+A)^2]\tau^2} - \frac{1/4(\beta H_0 \Delta g)^2\tau^2}{1+4[J_e{}^2+1/4(\beta H_0 \Delta g)^2]\tau^2}\right\} \times I \qquad (17a)$$

and for lines A$_2$ and B$_1$;

$$I^* = \left\{\frac{1/4(\beta H_0 \Delta g)^2\tau^2}{1+4[J_e{}^2+1/4(\beta H_0 \Delta g)^2]\tau^2} - \frac{1/4(\beta H_0 \Delta g-A)^2\tau^2}{1+4[J_e{}^2+1/4(\beta H_0 \Delta g-A)^2]\tau^2}\right\} \times I \qquad (17b)$$

It is evident form Eq. (17) that the relative enhancement factor is the same for both the A$_1$ and B$_2$ lines and also for both the A$_2$ and B$_1$ lines. As was illustrated in Fig. 2, in the polarized quartet signals of the photo-adduct of *o*-xylene, the A$_2$ line shows a positive polarization, while the B$_1$ line shows a negative polarization. This fact is substantially inconsistent with the theoretical consideration just mentioned. Thus, we may conclude that the CKO theory approximated to $S-T_0$ mixing is not satisfactory in discussing the photo-induced reaction examined here.

Now, consider a moderate case; $|A| \ll 2|J_e| < \beta g H_0$. In such a case, the rate of the population increase of the photo-adduct may be taken as the sum of the contributions from pure S–T_0, S–T_1, and S–T_0–T_1 interactions. Since the contributions from the former two are generally larger than that from the latter, the contribution from the S–T_0–T_1 interaction may be ignored for the sake of simplicity. Therefore, the rates of population increase may be given by Eqs. (11) and (13). Since the A_1,A_2,B_2, and B_1 spectral lines are assumed to correspond to the $t_1 \rightarrow s$, $t_0 \rightarrow t_{-1}$, $t_1 \rightarrow t_{-1}$, and $s \rightarrow t_{-1}$ transitions,[14] the relative intensities of quartet lines are obtained from Eq. (16). On assuming that $2|J_e|$ and $\beta g H_0 \gg |A|$ and $\beta H_0 \Delta g$, they are as follows for individual lines;

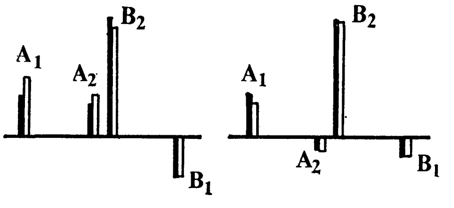
$$I^*_{A_1} = \left\{ \frac{1/4A(2\beta H_0 \Delta g + A)\tau^2}{1+4{J_e}^2\tau^2} + \frac{A^2\tau^2}{1+4(1/2\beta g H_0 - J_e)^2\tau^2} \right\} I_{A_1} \tag{18a}$$

$$I^*_{A_2} = \left\{ \frac{1/4A(2\beta H_0 \Delta g + A)\tau^2}{1+4{J_e}^2\tau^2} + \frac{A^2\tau^2}{1+4(1/2\beta g H_0 - J_e)^2\tau^2} \right\} I_{A_2} \tag{18b}$$

$$I^*_{B_2} = \frac{1/4A(2\beta H_0 \Delta g + A)\tau^2}{1+4{J_e}^2\tau^2} \times I_{B_2} \tag{18c}$$

$$I^*_{B_1} = \frac{1/4A(2\beta H_0 \Delta g - A)\tau^2}{1+4{J_e}^2\tau^2} \times I_{B_1} \tag{18d}$$

The relative intensities of polarized signals in the photo-adduct can be calculated by means of Eq. (18). As for the photo-adducts of *o*-xylene and *o*-chlorotoluene, Fig. 5 (spectra a and b) compares the experimental results with the calculated relative intensities based on the parameters in Table 2; $g=2.0$, $H_0=$ 14000 gauss, $\tau=10^{-9}$ sec, and A, J_e and Δg were adjusted so as to fit the experimental results. The agreement of the experimental results with the calculations is fairly good. However, the polarized quartet signals of the photo-adduct of toluene could not be interpreted whatever parameter values were used. This discrepancy may be due to the neglect of the S–T_0–T_1 interaction of the radical pair.



(a) (b)

Fig. 5. Experimental and calculated quartet spectra due to the methylene protons of 1,2-adducts of phenanthraquinone with *o*-xylene(a) and *o*-chlorotoluene(b) in photo-induced reaction.

▆; Experimental signal intensity

▭; Calculated signal intensity

TABLE 2. PARAMETERS ADJUSTED TO MAKE FIT WITH THE EXPERIMENTAL RESULTS

Hydrogen donor	$\beta H_0 \Delta g/A$	J_e(Hz) $\times 10^9$
o-Xylene	−0.168	7.31
o-Chlorotoluene	−0.053	6.61

The absolute values in Table 2 can not be too significant because of the simplifications adopted in Eq. (18). However, it may be concluded at least that; 1) experimental results are interpreted in terms of the mixing between the electronic singlet (S) and triplet states (T_0 and T_1) of the associated radical pair, and 2) the scalar electronic-exchange coupling constant, J_e, has a positive value intermediate between the Zeeman energy and the hyperfine coupling constant.

The resulting value of J_e is positive and is larger by about one order than the values reported hetherto.[15] As for our present values, it is not unreasonable to consider that an electronic π–π interaction brought about by the aromatic nature of each component of the radical pair may be responsible. There is strong chemical evidence supporting the above considerations.[16,17]

As was pointed out by Garst and his co-workers,[7] the contribution of S–T_1 interaction to nuclear polarization give a chance to observe the polarization from the reactions of diradicals or corresponding radical pairs. The reaction system reported here seems to be an ideal case where both the S–T_0 and S–T_1 interactions are associated with the nuclear-spin polarization.

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[14] Strictly speaking, this is the case when the limiting factor, $J_n/\Delta\omega \rightarrow \infty$, but this assumption does not lead to fatal errors in the results of the present study.

[15] See, for example, G. L. Closs, C. E. Doubleday, and D. R. Paulson, *J. Amer. Chem. Soc.*, **92**, 2185 (1970); G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2186 (1970).

[16] The structural problems of the photo-adducts resulting from the hydrogen-abstraction reactions of phenanthraquinone will be extensively discussed in the near future in this Bulletin by one of the present authors (K. Maruyama).

[17] K. Maruyama, H. Shindo, T. Otsuki, and T. Maruyama, This Bulletin, **44**, 2000 (1971).