CIDEP Studies of the Formation of Cyclohexadienyl-Type Radicals in the Photoreduction of Aromatic Ketones¹

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Photoreduction of benzophenone, acetophenone, and 2-acetonaphthone with tri-n-butylstannane at room temperature in some solvents was studied by CIDEP. The ketyl radicals were shown to be produced in the 2-propanol solution of benzophenone and in the benzene and n-heptane solutions of acetophenone. On the other hand, cyclohexadienyl-type radicals were found to be produced in the 2-propanol, benzene, and n-heptane solutions of acetophenone and 2-acetonaphthone. These two types of radicals, ketyl and cyclohexadienyl-type ones, were shown to be produced through the $n\pi^*$ and $\pi\pi^*$ characters of triplet ketones, respectively.

Introduction

The hydrogen abstraction reaction by aromatic aldehydes and ketones in their triplet states is one of the most essential photochemical processes.^{2,3} The high reactivity of these triplet states has been ascribed to either the $n\pi^*$ character of the carbonyl group² or the creation of charge-transfer (CT) complexes of the triplet states with amines.^{2,3} The formation of the ketyl radicals in these two types of reactions has been well established by analysis of the reaction products⁴ and by direct measurement with timeresolved optical absorption (TROA)⁵ and chemically induced dynamic electron polarization (CIDEP)⁶ techniques.

On the contrary, the $\pi\pi^*$ triplet states of aromatic aldehydes and ketones^{2,3} have been believed to be much less reactive than the $n\pi^*$ triplet states and CT complexes. On the other hand, such a strong hydrogen donor as tri-n-butylstannane has been known to enhance very much the reactivity of the hydrogen abstraction reactions even from the $\pi\pi^*$ triplet states.⁷ However, the primary processes of these reactions have scarcely been studied with the aids of TROA^{8,9} and CIDEP techniques.

Recently, we carried out CIDEP studies of the photoreduction of xanthone¹⁰⁻¹² with such special hydrogen donors as sodium borohydride, triethylgermane, and tri-n-butylstannane and found for the first time the formation of the cyclohexadienyl-type radical in some solvents. The characteristic point of this new reaction

(8) Davis, G. A.; Carapenucci, F. A.; Szoc, K.; Gresser, J. D. J. Am. Chem.
Soc. 1969, 91, 2264.
(9) Scaiano, J. C. J. Am. Chem. Soc. 1980, 102, 7747.
(10) Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. J.; Mochida, K.
Chem. Phys. Lett. 1985, 120, 401.
(11) Sakaguchi, Y.; Hayashi, H. J. Phys. Chem. 1986, 90, 550.
(12) Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. J. Abstracts of Papers, 52nd National Meeting of the Chemical Society of Japan, Kyoto, 10966 (Chemical Society of Japan, Kyoto, 10966) 1986; Chemical Society of Japan: Tokyo; Abstract No. 2F09.

is that a hydrogen atom adds to the aromatic part of xanthone instead of the carbonyl group, where the hydrogen abstraction has been undoubtedly believed to take place in the photoreduction through the $n\pi^*$ triplet states and CT complexes of aromatic aldehydes and ketones.^{2,3}

From the solvent dependence of the photoreduction of xanthone with tri-*n*-butylstannane,¹¹ the cyclohexadienyl-type radical was found to be produced through the $\pi\pi^*$ character of triplet xanthone. On the contrary, the photoreduction through its $n\pi^*$ character was found to give the ketyl radical. In the present paper, we have undertaken an investigation as to whether the above rules can be applied generally to the photoreduction of aromatic ketones with tri-n-butylstannane, taking three representative molecules, benzophenone, acetophenone, and 2-acetonaphthone, as examples.¹ The lowest $n\pi^*$ triplet state of benzophenone has been shown to be much lower in energy than its lowest $\pi\pi^*$ triplet one.^{2,3} The lowest $n\pi^*$ and $\pi\pi^*$ triplet states of acetophenone have been believed to be close to each other.^{13,14} The lowest $\pi\pi^*$ triplet state of 2-acetonaphthone has been shown to be much lower than its lowest $n\pi^*$ triplet one.^{2,3}

Experimental Section

Benzophenone (BP) and 2-acetonaphthone (2AN) were recrystallized repeatedly from an ethanol-water mixture and ethanol, respectively. Acetophenone (ACP) was vacuum-distilled. Trin-butylstannane (Bu₃SnH) supplied by Kanto Chemical Co. was stored in a cold nitrogen atmosphere before use and was used without further purification. Benzene, 2-propanol, and n-heptane of guaranteed reagent grade were used as solvents without further purification.

A Varian E-109 X-band ESR spectrometer was used for the CIDEP study without field modulation. A Molectron UV24 nitrogen gas laser ($\lambda = 337.1$ nm) was used as the exciting light source. The output signal from a preamplifier of the above instrument was further amplified and introduced to an NF BX-531 boxcar integrator. Throughout the present experiments, the CIDEP spectra were measured at room temperature at a time delay of 1.2 μ s after laser excitation with a gate width of 0.2 μ s. The concentrations (c) of the employed ketones were arranged so as to fulfill the condition where ϵc is 1-3 mm⁻¹. Here ϵ is the molar extinction coefficient at 337.1 nm, and the depth of the flat ESR quartz cell was 0.3 mm. The solution was bubbled with pure nitrogen gas prior to the CIDEP measurement and flowed through

⁽¹⁾ A preliminary report of this work has appeared: Hayashi, H; Sakaguchi, Y.; Murai, H.; I'Haya, Y. J. Abstracts of Papers, 52nd National Meeting of the Chemical Society of Japan, Kyoto, 1986; Chemical Society of Japan: Tokyo; Abstract No. 2F10.
(2) For review, see: Scaiano, J. C. J. Photochem. 1973, 2, 81.
(3) For review, see: Cohen, S. G.; Parola, A.; Parsons, Jr., G. H. Chem.

Rev. 1973, 73, 141.

⁽⁴⁾ For example, see: Moore, W. M.; Hammond, G. S.; Foss, R. P. J. Am.

<sup>Chem. Soc. 1961, 83, 2789 and references cited therein.
(5) For example, see: (a) Porter, G.; Wilkinson, F. Trans. Faraday Soc.
1961, 57, 1686. (b) Lutz, H.; Brehert, E.; Lindqvist, L. J. Phys. Chem. 1973,</sup> 77, 1758.

⁽⁶⁾ For reviews, see: (a) Wan, J. K. S.; Elliot, A. J. Acc. Chem. Res. 1977, 10, 161. (b) Hore, P. J.; Joslin, C. G.; McLauchlan, K. A. Chem. Soc. Rev. 1979. 8. 29

⁽⁷⁾ Hammond, G. S.; Leermarkers, P. A. J. Am. Chem. Soc. 1962, 84, 207.

⁽⁸⁾ Davis, G. A.; Carapellucci, P. A.; Szoc, K.; Gresser, J. D. J. Am. Chem.

⁽¹³⁾ Lamola, A. A. J. Chem. Phys. 1967, 47, 4810.

⁽¹⁴⁾ Lutz, H.; Duvai, M. C.; Brehert, E.; Lindqvist, L. J. Phys. Chem. 1972, 76, 821



Figure 1. CIDEP spectra on the low-field side observed with the 2propanol solution of BP (0.133 mol dm^{-3}) (a) without and (c) with Bu₃SnH (0.074 mol dm^{-3}) (microwave power, 1 mW). Spectrum b is the simulated absorption spectrum of the BP ketyl radical (see text).

the cell in the ESR cavity. The flow rate was kept constant at about 20 mL/h. The details were the same as those published before.¹⁵

Results and Discussion

1. CIDEP Studies of Benzophenone. The CIDEP spectrum was observed with the 2-propanol solution of BP (0.133 mol dm⁻³). The CIDEP spectrum observed on the low-field side is shown in Figure 1a. This spectrum agrees well with that reported in the literature,¹⁶ where the signals due to the BP ketyl and 2-propanol radicals were obtained. The absorption spectrum of the ketyl radical was simulated with the reported hyperfine coupling (hfc) constants¹⁷ and a line width of 0.4 G,¹⁸ and the result is illustrated in Figure 1b. As shown in Figure 1a, the ketyl and 2-propanol radicals have E (emission)/A (absorption) phase patterns.

The CIDEP spectrum was also observed with the 2-propanol solution containing BP (0.133 mol dm⁻³) and Bu₃SnH (0.074 mol dm⁻³). The CIDEP spectrum observed on the low-field side is shown in Figure 1c. As clearly seen in this spectrum, the phase of the ketyl radical is changed from an E/A pattern to an E one upon addition of Bu₃SnH, and the signal intensities of the 2-propanol radical are decreased concomitantly. However, no new signal was obtained with Bu₃SnH. These facts clearly indicate that the BP ketyl radical is produced more efficiently in the photoreduction of BP with Bu₃SnH than that with 2-propanol. Indeed, according to the CIDEP theory,⁶ an E or A phase pattern is shown to be obtained in the reaction faster than or comparable to the relaxation of an electron-spin polarization within the triplet precursor (triplet mechanism), and an E/A pattern is obtained in the relaxation (radical pair mechanism).

The signals due to the stannyl radical (Bu_3Sn^{\bullet}) may disappear because of the fast relaxation of its electron-spin polarization through the spin-orbit interaction within the radical and/or through the exchange reaction of the radical with Bu_3SnH .

From the above experiments, the carbonyl group of triplet BP was proved to abstract a hydrogen from the Sn-H bond of Bu₃SnH in the same manner as from the C-H bonds of such hydrogen donors as alcohols and amines. This agrees well with the fact that the lowest triplet state of BP is $n\pi^*$ in character even in an alcoholic solvent.^{2,14}

2. CIDEP Studies of Acetophenone. The CIDEP spectrum was observed with the 2-propanol solution of ACP (0.216 mol dm^{-3}). The observed spectrum is shown in Figure 2a. In Figure 2b, the signal positions of the 2-propanol radical¹⁹ are represented



Figure 2. CIDEP spectra observed with the 2-propanol solution of ACP (0.216 mol dm⁻³) (a) without (microwave power, 10 mW) and (d) with (microwave power, 1 mW) Bu₃SnH (0.078 mol dm⁻³). Diagram b shows the signal positions of the 2-propanol radical.¹⁹ Spectrum c is the simulated absorption spectrum of the ACP ketyl radical (see text). Diagram e shows the signal positions of a new radical (radical I).

TABLE I: Observed g Values and Proton hfc Constants

| radical | g value | proton hfc constants ^a /G |
|--|-----------------------|--|
| cyclohexadienyl radical ²¹ | 2.0025 | 47.70 (CH ₂); 13.04 (4); 8.99 (2, 6); 2.65 (3, 5) |
| radical I ^b | $2.0027_5 \pm 0.0001$ | 43.6 (>CHCO-); 13.0 (4); 9.0 (2, 6); 2.8 (3, 5) |
| radical II ^b | $2.0037_3 \pm 0.0001$ | 42 (CH ₂); 8 (5); 7 (3); 2 (4, 6); 1 (CH ₂) |
| radical III ^b | | 30 (CH ₂); 11 (1) |

^a The proton positions shown in parentheses are illustrated in Figure 3. The proton positions of the cyclohexadienyl radical are numbered as those of radical I. ^b Observed values in this work (see text for names of radicals).

by a stick diagram. The absorption spectrum of the ACP ketyl radical was simulated with the reported hfc constants²⁰ and a line width of 0.4 G, and the result is shown in Figure 2c. From diagram b and spectrum c of Figure 2, the spectrum in Figure 2a was easily assigned to be a combination of the signals due to the ketyl and 2-propanol radicals. These radicals have E/A^* phase patterns. Here E/A^* means that an A phase pattern is mixed with an E/A one.

Upon addition of Bu_3SnH (0.078 mol dm⁻³) to the above solution, the CIDEP spectrum showed a drastic change as shown in Figure 2d. In the spectrum of this figure, signals due to the ketyl and 2-propanol radicals became extremely weak and strong new signals with an E*/A phase pattern appeared. Almost all of the new signals can be explained by the stick diagram illustrated in Figure 2e. Also no signal due to the stannyl radical was observed.

The diagram in Figure 2e corresponds to a radical (radical I) with a g value of $2.0027_5 \pm 0.0001$ and hyperfine splittings consisting of one 43.6-G proton, one 13.0-G proton, two 9.0-G protons, and two 2.8-G protons. Here, this g-value was obtained from the shifts of the signals of radical I from those of the 2-propanol radical ($g = 2.00317^{19}$). The observed g-value and hfc constants of radical I are very similar to the corresponding values

⁽¹⁵⁾ Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. J. Chem. Phys. Lett. 1984, 110, 275.

⁽¹⁶⁾ Trifunac, A. D.; Thurnauer, M. C.; Norris, J. R. Chem. Phys. Lett. 1978, 57, 471.

⁽¹⁷⁾ Wilson, R. J. Chem. Soc. B **1968**, 84. (18) 1 G = 10^{-4} T.

⁽¹⁹⁾ Livingston, R.; Zeldes, H. J. Chem. Phys. 1966, 44, 1245.

⁽²⁰⁾ Wilson, R. J. Chem. Soc. B 1968, 1582.



Figure 3. Structures of cyclohexadienyl-type radicals expected to be produced from ACP (radicals I, O, M, and P) and the structure of one of the cyclohexadienyl-type radical produced from 2AN (radical R). Radicals II and III are proposed to be radicals O and R, respectively, as discussed in Appendix B.

of the cyclohexadienyl radical²¹ except that of the methylene protons as shown in Table I. Thus, radical I can safely be assigned to a cyclohexadienyl-type radical as shown in Figure 3. The position of the hydrogen abstraction of triplet ACP from Bu₃SnH is not the carbonyl oxygen but the ring carbon connecting with the acetyl group. Similar hydrogen abstraction that occurs at a ring carbon has already been found by us in the photoreduction of xanthone through its $\pi\pi^*$ triplet states.¹⁰⁻¹² Therefore, the reactivity of triplet ACP with Bu₃SnH in 2-propanol through the $\pi\pi^*$ character giving the cyclohexadienyl-type radical was proved to be much larger than that through the $n\pi^*$ character giving the ketyl radical.

We also carried out experiments on the solvent dependence of the present reaction. The CIDEP spectrum was measured with the benzene (*n*-heptane) solution containing 0.283 (0.312) mol dm⁻³ of ACP, but no CIDEP signal was observed beyond the sensitivity of the employed apparatus. Upon addition of 0.074 (0.134) mol dm⁻³ of Bu₃SnH to the benzene (*n*-heptane) solution of ACP, CIDEP signals appeared as shown by the spectrum in part a (b) of Figure 4. The stick diagram indicating the signal positions of radical I and the simulated absorption spectrum of the ACP ketyl radical are shown in part c (d) of Figures 4, respectively. From diagram c and spectrum d of Figure 4, the spectra shown in Figure 4a,b can be explained by combinations of the signals due to radical I and the ketyl radical with E/A* phase patterns. Typical peaks due to the ketyl radical are shown by the broken lines in Figure 4.

From the results obtained with the benzene and *n*-heptane solutions, the following facts were found: (1) The ketyl radical cannot be produced in the photoreduction of ACP with benzene and *n*-heptane. (2) Both ketyl and cyclohexadienyl-type radicals can be produced in the photoreduction of ACP with Bu₃SnH when benzene and *n*-heptane are used as solvents. This means that the reactivity through the $n\pi^*$ character of triplet ACP in benzene or *n*-heptane is larger than that in 2-propanol.

For an aromatic aldehyde or ketone having the nearly degenerate $n\pi^*$ and $\pi\pi^*$ triplet states, the solvent effect on the energy splitting between the $\pi\pi^*$ and $n\pi^*$ states has been believed to have the following order:¹¹ *n*-heptane > benzene \gg 2-propanol. According to the present experiments, the ratio of the yield of the ketyl radical to that of radical I in the photoreduction of ACP with Bu₃SnH was proved to have the same order. This is further support for the contribution of the $\pi\pi^*$ character in the formation of the cyclohexadienyl-type radical (radical I) from triplet ACP with Bu₃SnH.

The E and A phase patterns in the E^*/A and E/A^* patterns of the observed spectra shown in Figures 2 and 4 can be interpreted



Figure 4. CIDEP spectra observed with (a) the benzene solution containing ACP (0.283 mol dm⁻³) and Bu₃SnH (0.074 mol dm⁻³) (microwave power, 10 mW) and (b) the *n*-heptane solution containing ACP (0.312 mol dm⁻³) and Bu₃SnH (0.134 mol dm⁻³) (microwave power, 20 mW). Diagram c and spectrum d represent the signal positions of radical I and the simulated absorption spectrum of the ACP ketyl radical (see text), respectively.



Figure 5. Mixing between the low-lying $n\pi^*$ and $\pi\pi^*$ triplet states of aromatic ketones for case a $(E_0(n) \ll E_0(\pi))$, case b $(E_0(n) < E_0(\pi))$, case c $(E_0(n) > E_0(\pi))$, and case d $(E_0(n) \gg E_0(\pi))$ (see Appendix B). The degrees of the populating rate constants are represented by the areas of circles. The polarization patterns (E and A) of the CIDEP spectra through the triplet mechanism from the triplet states are also shown.

in terms of the mixing^{22,23} between the low-lying $n\pi^*$ and $\pi\pi^*$ triplet states as illustrated in Figure 5. The details to get the results shown in Figure 5 are described in Appendix A. The A (E) polarization of the ketyl and 2-propanol radicals (radical I) in the spectrum of part a (d) of Figure 2, which was measured in 2-propanol, can be explained by the A (E) polarization of the $n\pi^*$ ($\pi\pi^*$) triplet state of case c in Figure 5.

The A polarization of radical I (the ketyl radical) observed in benzene and *n*-heptane as shown by the spectra of Figure 4a,b can be explained by the A polarization of the $\pi\pi^*$ ($n\pi^*$) triplet state of case b (case c). That is, when the ketyl radical is produced from triplet ACP and Bu₃SnH, the $\pi\pi^*$ triplet state is considered to become lower in energy than the $n\pi^*$ one through a hydrogen bond between C=O and H-Sn. This hydrogen bond has been believed to lower the $\pi\pi^*$ triplet states of aldehydes and ketones.² On the other hand, no such hydrogen bond may be considered when the cyclohexadienyl-type radical is produced. In the latter

⁽²²⁾ Hayashi, H.; Nagakura, S. Mol. Phys. 1972, 24, 801; 1974, 27, 969.
(23) Cheng, T. H.; Hirota, N. Mol. Phys. 1974, 27, 281.

⁽²¹⁾ Fessenden, R. W.; Schuler, R. H. J. Chem. Phys. 1963, 39, 2147.



Figure 6. CIDEP spectrum observed on the lower and higher field sides of radical I with the 2-propanol solution of ACP and Bu₃SnH (microwave power, 20 mW). Diagram a represents the signal positions of radical I (full lines) and the 2-propanol radical (broken lines). Diagram b represents the signal position of a new radical (radical II).



Figure 7. (a) CIDEP spectrum observed with the 2-propanol solution containing 2AN (0.018 mol dm⁻³) and Bu_3SnH (0.083 mol dm⁻³) (microwave power, 20 mW). Diagram b shows the signal positions of a new radical (radical III).

reaction, the $\pi\pi^*$ triplet state is considered to become higher than in the former one as shown by case b of Figure 5. The above interpretations for the observed phase patterns are consistent with the formation mechanism of the cyclohexadienyl-type radical (radical I).

By a careful examination of the spectrum of Figure 2d, weak signals on the lower and higher field sides of radical I were obtained. With increasing microwave power, these weak signals became clearer as shown in Figure 6. In this figure, the signal positions of radical I and the 2-propanol radical are represented by the full and broken lines in stick diagram a, respectively. The other weak signals can be explained by stick diagram b of Figure 6. Diagram b corresponds to a radical (radical II) with a g value of $2.0037_3 \pm 0.0001$ and hyperfine splittings consisting of two 42-G protons (or one 84-G proton), one 8-G proton, one 7-G proton, two 2-G protons, and three 1-G protons.

Since one 84-G proton cannot be considered for any generated radical from ACP, two 42-G protons can safely be assigned to the methylene protons of a cyclohexadienyl-type radical. The three 1-G protons are probably due to the methyl group. The larger g value obtained for radical II than for radical I and the appearance of the methyl hyperfine structure can be interpreted by delocalization of the odd electron to the carbonyl group. However, the position of the hydrogen abstraction cannot definitely be determined only from the results of the present CIDEP experiments. The structure of radical II is considered in Appendix B, where the most probable structure is proposed to be radical O shown in Figure 3. The photoreduction of xanthone with Bu_3SnH also gave two cyclohexadienyl-type radicals,¹² but the formation of one of the radicals was proved to be dominant as was the case in the photoreduction of ACP.

3. CIDEP Studies of 2-Acetonaphthone. The CIDEP spectrum was measured with the 2-propanol solution of 2AN (0.018 mol dm⁻³, but no signal was observed. Upon addition of Bu_3SnH (0.083 mol dm⁻³) to this solution, weak and broad CIDEP signals with an E*/A phase pattern were obtained as shown by the spectrum of Figure 7a. The signals of this spectrum can be explained by the stick diagram of Figure 7b. This diagram corresponds to a radical (radical III) with hyperfine splittings consisting of two 30-G protons and one 11-G proton. No further hyperfine structure of radical III could be resolved.

However, radical III can safely be assigned to a cyclohexadienyl-type radical from the appearance to two 30-G protons, which can be considered as the methylene ones. The position of the hydrogen abstraction is also considered in Appendix B, where the most probable structure for radical III is proposed to be radical R shown in Figure 3. CIDEP signals due to radical III were also obtained with each of the benzene and *n*-heptane solutions of 2AN in the presence of Bu₃SnH, but no signal was obtained without Bu₃SnH. The present results of the CIDEP studies of the photoreduction of 2AN correspond well with the fact that the lowest triplet state of 2AN is $\pi\pi^*$ in character irrespective of solvents.^{2,3}

4. Conclusion. In the present CIDEP studies of the photoreduction of BP, ACP, and 2AN with Bu_3SnH , the following results were obtained: (1) Cyclohexadienyl-type radicals were found to be produced in the reactions of ACP and 2AN in 2propanol, benzene, and *n*-heptane. (2) Ketyl radicals were found to be produced in the reaction of BP in 2-propanol and ACP in benzene and *n*-heptane.

The above results together with those obtained in the photoreduction of xanthone¹⁰⁻¹² seem to give the following facts for the photoreduction of aromatic ketones (and probably aldehydes) with hydrogen donors having such bonds as B-H, Ge-H, and Sn-H: (1) Photoreduction through the low-lying triplet states of $n\pi^*$ character occurs at the carbonyl oxygen and gives the corresponding ketyl radical as has been believed with other hydrogen donors such as alcohols and amines. (2) Photoreduction through the low-lying triplet states of $\pi\pi^*$ character occurs at the aromatic ring and gives such new radicals as cyclohexadienyl-type ones. This type of photoreduction had not been imagined until we recently discovered the formation of the cyclohexadienyl-type radical of xanthone.¹⁰ (3) The order and energy splitting between the low-lying $n\pi^*$ and $\pi\pi^*$ triplet states determine which type of photoreduction can occur in actual systems.

The hydrogen donors that can bring about the photoreduction of aromatic ketones at their aromatic rings should have bonds such as B-H, Ge-H, and Sn-H, which are to be abstracted. From the electronegativity of atoms,²⁴ these bonds have $M^{\delta+}-H^{\delta-}$ polarization. On the other hand, the C-H bonds of usual hydrogen donors have $C^{\delta-}-H^{\delta+}$ polarization.²⁴ Therefore, the M-H bond of the former donors is considered to be less favorable for approaching the carbonyl oxygen than the C-H one of the latter donors. This may be the reason for the photoreduction at the aromatic rings. Further theoretical studies on reaction mechanisms and experimental studies on reaction products are expected to be carried out for these new types of photoreduction of aromatic ketones.

Appendix A

Here, we will consider the phase patterns of the CIDEP spectra of the radicals produced from triplet ketones. According to the CIDEP theories,⁶ the patterns can be explained by the radical-pair and triplet mechanisms (RPM and TM). E/A polarization patterns can arise from the geminate recombination of triplet radical pairs and from the random encounter of escaping radicals. Although the g value of Bu₃Sn[•] was obtained to be as large as 2.0158,²⁵ the Δg term of the RPM⁶ cannot explain the E/A^{*} and E^{*}/A patterns observed in the present study. Here, Δg is the difference between the g values of radicals in a radical pair. Thus, the remaining net polarization should be explained by the TM.

Let us consider the polarization patterns through the TM from a triplet precursor where its $n\pi^*$ and $\pi\pi^*$ triplet states lie close to each other. Here, the molecular axes z, x, and y are taken to be along the C=O bond of the carbonyl group, perpendicular to the molecular plane, and completing the right-handed Cartesian frame, respectively. The zeroth order energies of the $n\pi^*$ and $\pi\pi^*$ triplet states are represented by $E_0(n)$ and $E_0(\pi)$, respectively. When $E_0(n) \ll E_0(\pi)$ (case a) and $E_0(n) \gg E_0(\pi)$ (case d), the

⁽²⁴⁾ For example, see: Prichard, H. O.; Skinner, H. A. Chem. Rev. 1955, 55, 745.

⁽²⁵⁾ Lehnig, M.; Dören, K. J. Organomet. Chem. 1981, 210, 331.

| TABLE II: | Calculated S | pin Densities | (ρ_i) and hfc | Constants $(a_i)^a$ |
|-----------|--------------|---------------|--------------------|---------------------|
|-----------|--------------|---------------|--------------------|---------------------|

| | radical | | | | | |
|------------------|-----------------|----------------|---------------|---------------|----------------|--|
| | cyclohexadienyl | 0 | М | Р | R | |
| $\rho_i (a_i/G)$ | | | | | | |
| i = 1 | | 0.2479 | -0.085 5 | 0.238 4 | | |
| i = 2 | 0.3865 (11.0) | | 0.2339 (6.7) | -0.0350 (1.0) | 0.304 1 | |
| <i>i</i> = 3 | -0.1311(3.7) | 0.2214 (6.3) | | 0.237 5 (6.8) | -0.0681 (1.9) | |
| i = 4 | 0.4176 (11.9) | -0.0342 (1.0) | 0.4641 (13.2) | | 0.308 5 (8.8) | |
| i = 5 | -0.1311 (3.7) | 0.2384 (6.8) | -0.1451 (4.1) | 0.237 5 (6.8) | 0.0756 (2.2) | |
| i = 6 | 0.386 5 (11.0) | -0.041 9 (1.2) | 0.4781 (13.6) | -0.0350 (1.0) | -0.0229 (0.7) | |
| i = 7 | `` , | | | | 0.063 3 (1.8) | |
| i = 8 | | | | | -0.019 5 (0.6) | |

"The carbon positions are illustrated in Figure 3 and those of the cyclohexadienyl radical are numbered as those of radical I in this figure.

interactions between the two triplet states are so small that the energies after interaction (E_i) are considered to be similar to E_0 .

The lowest triplet state of BP is a typical example for a pure $n\pi^*$ triplet state, where the order of the energies of its three sublevels (X, Y, and Z) and that of the populating rate constants of the sublevels (P_i) were measured as follows:²⁶ $Z \gg Y > X$ and $P^n_x \gg P^n_x$, P^n_y . Thus, this situation can be used for a pure $n\pi^*$ triplet state as shown in Figure 5. Therefore, the polarization pattern due to the TM from a pure $n\pi^*$ triplet state is an E as shown in Figure 5. The lowest triplet state of benzene is a typical example for a pure $\pi\pi^*$ triplet state, where the following relations may hold:²⁶ $Y \sim Z \gg X$ and $P^n_i \ll P^n_z$. Thus, this situation can be used for a pure $\pi\pi^*$ triplet state as shown in Figure 5.

When $E_0(n) < E_0(\pi)$ (case b) and $E_0(n) > E_0(\pi)$ (case c), the x (y) sublevel of the $n\pi^*$ triplet state and the y (x) one of the $\pi\pi^*$ triplet state mix with each other through the spin-orbit interaction,²² and their energies change as shown in Figure 5. There is another mixing between the $n\pi^*$ and $\pi\pi^*$ triplet states through the vibronic interaction. Because this mixing occurs between the sublevels with the same molecular axis, no energy change is expected for the triplet sublevels, but the z sublevel of the $\pi\pi^*$ triplet state is considered to borrow a populating rate from the z one of the $n\pi^*$ triplet state.²² Thus, the energy levels, populating rate constants, and the polarization patterns through the TM of the low-lying triplet states for cases b and c can be obtained qualitatively as shown in Figure 5.

Appendix B

Here, we will consider the structures of radicals II and III, using the molecular orbital calculations performed by the method of McLauchlan.²⁷ The bonding parameters used were those as given by Streitwieser,²⁸ but the methylene group (X) was considered as a heteroatom with $h_X = 2$ and $k_{CX} = 0.7$. The λ value was taken to be 1.2. These parameters gave better results for the cyclohexadienyl radical than those calculated by Leone and Koski.²⁹

The hfc constant (a_i) of an α proton connecting the *i*th sp² carbon atom with a π electron density (ρ_i) was obtained by using

(27) McLauchlan, A. D. Mol. Phys. 1960, 3, 233.

the familiar formula of McConnell,³⁰ $a_i = Q\rho_i$ with a value of 28.5 G for Q.²⁸ The calculated ρ_i and a_i values for the cyclohexadienyl radical and radicals O, M, P, and R are listed in Table II. Although the present calculations may only give qualitative results, the changes of the calculated values with radicals, O, M, P, and R from the values with the cyclohexadienyl radical can safely be compared with the changes of the observed values with radicals. II and III from the values with the cyclohexadienyl radical.

The a_i values of the ring protons of radical II were observed to be smaller than the corresponding values of the cyclohexadienyl radical as shown in Table I. For radical M, however, its a_4 and a_6 were calculated to be larger than a_4 of the cyclohexadienyl radical as shown in Table II. Therefore, radical M can clearly be eliminated for the assignment of radical II. For radical O (P), its a_3 and a_5 (a_3 and a_5) were calculated to be smaller than a_2 and a_6 of the cyclohexadienyl radical and its a_4 and a_6 (a_2 and a_6) to be smaller than a_3 and a_5 of the latter radical as shown in Table II. These tendencies of radicals O and P agree well with the observed differences in the a_i values of the ring protons between radical II and the cyclohexadienyl radical. However, the calculated a_5 and a_3 values of radical O seem to better explain the observed 8-G and 7-G protons of radical II than the calculated values of radical P, where a_3 and a_5 were calculated to be the same. Although a molecular distortion within radical P might explain the inequality of a_3 and a_5 , we propose that the most probable structure of radical II is radical O.

Similar calculations were also carried out for the cyclohexadienyl-type radicals produced from 2AN. The calculated results for radical R of Figure 3 are listed in Table II. Radical R can be considered the most probable structure for radical III for the following reasons: For radical R, its a_4 was calculated to be much larger than its a_3 , a_5 , a_6 , a_7 , and a_8 and to be smaller than a_4 of the cyclohexadienyl radical, as shown in Table II. These tendencies agree well with the observed ones in the a_i values of radical III and the cyclohexadienyl radical as shown in Table I. No calculation for any other cyclohexadienyl-type radical expected to be formed from 2AN could reproduce the observed tendencies from the cyclohexadienyl radical III.

Registry No. Benzophenone, 119-61-9; acetophenone, 98-86-2; 2acetonaphthone, 93-08-3; tri-*n*-butylstannane, 688-73-3; benzophenone ketyl, 16592-08-8; radical I, 103239-71-0; radical O, 103239-72-1; radical M, 103239-73-2; radical P, 103239-74-3; radical R, 103239-75-4.

(30) McConnell, H. M.; Chesnut, D. B. J. Chem. Phys. 1958, 28, 107.

⁽²⁶⁾ For review, see: Kinoshita, M.; Iwasaki, N.; Nishi, N. Appl. Spectrosc. Rev. 1981, 17, 1.

⁽²⁸⁾ Streitwieser, Jr., A. Molecular Orbital Theory for Organic Chemists; Wiley: New York, 1961; p 135.

⁽²⁹⁾ Leone, J. A.; Koski, W. S. J. Am. Chem. Soc. 1966, 88, 565.