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Photochemical Reactions of Nitroanthracene Derivatives in Fluid Solutions

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Abstract: The photochemical reaction of nitroanthracenes (9-cyano- or 9-benzoyl-10-nitroanthracene) is very simple, giving the final photoproducts (10-cyano-9-anthrol or its anion and 10-benzoyl-9-anthrol or its anion) under appropriate conditions. It is suggested that irradiation gives rise to the nitro to nitrite rearrangement at the higher excited triplet $n\pi^*$ states, followed by the cleavage of nitrites to anthryloxy radicals and nitrogen(II) oxide.

The photochemical reactions of aromatic nitro compounds have been studied by many investigators, and their reaction mechanisms are very complicated.[1-5] For example, Chapman et al.[4] studied photochemical reaction of 9-nitroanthracene as a reasonable selection for detailed study. In their study, irradiation of 9-nitroanthracene in acetone gave 10,10′-bianthrone, anthraquinone, and anthraquinone monooxime. They assumed that the reaction was initiated by a rearrangement of a nitro group to a nitrite, and that anthraquinone monooxime was formed via 9-nitrosoanthrone by combination of nitrogen(II) oxide and 9-anthryloxy radical.

Recently, we have reported[6] that the photochemical reaction of nitroanthracenes (9-cyano- or 9-benzoyl-10-nitroanthracene) in poly(methyl methacrylate) was significantly different from that of 9-nitroanthracene in the following ways: (1) The reaction was very simple, giving the final photoproducts (10-cyano-9-anthrol or its anion and 10-benzoyl-9-anthrol or its anion) under appropriate conditions. (2) Reaction intermediates which were essentially important in establishing reaction mechanisms were easily detected spectroscopically, and these intermediates were assumed to be 9-cyano- and 9-benzoyl-10-anthryloxy radicals.

We have also reported that the form of the final photoproducts was dependent on the basicity, polarity, and rigidity of medium as well as temperature.[7,8]

As an extension of our studies on the photophysics and photochemistry of nitroanthracenes, this paper deals with the photochemical reactions in fluid solutions in order to determine the intermediates involved, including the multiplicity of the reactive states of nitroanthracenes.

Experimental Section

Chemicals. The details of the methods of preparation and purification of 9-cyano-10-nitroanthracene ($CN\text{-}NO_2\text{-}A$) and 9-benzoyl-10-nitroanthracene ($Bz\text{-}NO_2\text{-}A$) have been given in our previous paper.[6] G. R.-grade triethylamine (Wako) was refluxed over calcium hydride and distilled under a nitrogen atmosphere. Uvasol diethyl ether (Merck) and all the other solvents (Wako, G. R. grade) were used without further purification. In the following, "basic solvent" means a solvent that contains 4 vol % triethylamine (TEA). The sample solution was degassed by several freeze–pump–thaw cycles.

Steady-State Photolysis. Irradiations were carried out using a 500-W super high-pressure mercury lamp (type USH-500D, Ushio Electric Inc.). Light of 366-nm monochromatic wavelength was selected by the combination of two-color glass filters (UV-35, UV-D35, Toshiba Chemical Industries Ltd.) and a filter solution ($CuSO_4\cdot5H_2O$, 100 g dm^{-3}, path length 3 cm). After completion of irradiation, absorption spectra were taken on a Hitachi 200-20 spectrophotometer. Phosphorescence and its excitation spectra were taken at 77 K in EPA using a Hitachi MPF-4 spectrophosphorometer with an HTV R928 photomultiplier whose spectral response extends up to 900 nm. The quantum yield of the reaction was determined by the Hatchard–Parker potassium ferrioxalate actinometry method.[9] The yield of the photoproduct was determined by measuring its absorbance. For the identification of organic radicals, electron spin resonance spectra were taken with a JEOL JES-ME-3X spectrometer.

Laser Flash Photolysis. The second harmonics (347.2 nm) from picosecond mode-locked and nanosecond Q-switched ruby lasers were used to excite the sample. The details of our picosecond transient absorption spectrometer have been given elsewhere.[10,11] The concentration of the sample was 2.5×10^{-3} M in a cell of 2-mm path length, and the sample solution was not deaerated. The transient absorption spectra were measured at room temperature.

The Q-switched ruby laser used for nanosecond photolysis was constructed in this laboratory.[12] The half-peak duration of the second harmonic was 22 ns. The monitoring-light pulse was obtained from a Xe-flash lamp (Nikon SD-X). The transient absorptions and decay times at various wavelengths were observed by using an HTV R666 photomultiplier and a Tektronix 475A oscilloscope. The concentrations of the deaerated sample solutions in a cell of 10-mm path length were 6.1×10^{-4} M for $CN\text{-}NO_2\text{-}A$ and 4.2×10^{-4} M for $Bz\text{-}NO_2\text{-}A$.

Results

Steady-State Irradiation. The absorption spectral change of $CN\text{-}NO_2\text{-}A$ in basic ethanol at room temperature is shown in Figure 1. Upon irradiation, the absorption peaks of $CN\text{-}NO_2\text{-}A$ around 380 nm decreased and those of the product around 470 and 360 nm built up, accompanied with isosbestic points at 418 and 368 nm. The photoproduct was identified as 9-cyano-10-anthryloxy anion (CAO^-) from the comparison of the absorption spectrum with that of the authentic sample, i.e., 10-cyano-9-anthrol (CAOH) in basic ethanol. The same result was also obtained in benzene, cyclohexane, ether, isopentane, or EPA (ether/isopentane/ethanol = 5:5:2 in volume ratio), each containing TEA. The quantum yields of the formation of CAO^- were 0.74 in deaerated basic ethanol and 0.10 in an aerated sample.

Replacement of TEA by potassium hydroxide (KOH) in ethanol did not affect the general feature of the reaction. In the absence of TEA in ethanol, CAOH was obtained as a final photoproduct, though it was found that CAOH decomposes partly by the irradiation. By the addition of TEA, CAOH changed to CAO^-. Moreover, no spectral change of $CN\text{-}NO_2\text{-}A$ was observed by the addition of TEA. Thus it can be reasonably concluded that there is no complex formation between TEA and $CN\text{-}NO_2\text{-}A$ and that TEA or KOH merely works as a basic additive to dissociate CAOH to CAO^-.

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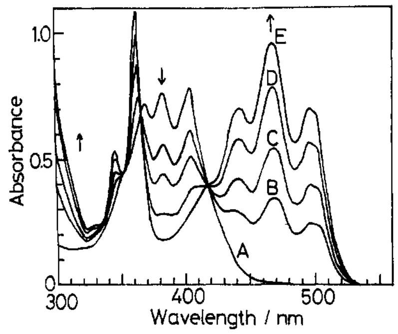


Figure 1. Absorption spectral change of CN-NO_2-A in basic ethanol upon irradiation at room temperature. A, 0; B, 0.5; C, 1.0; D, 2.0; E, 4.0 min.

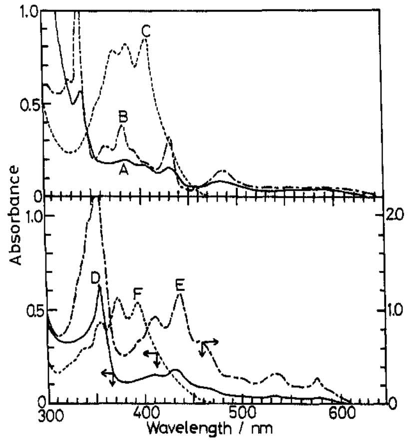


Figure 2. Absorption spectra of intermediates I (A, B) and II (D, E). A and D, in benzene at room temperature; B and E, in basic EPA at 77 K. Spectra C and F are the absorption spectra of CN-NO_2-A and Bz-NO_2-A in benzene at room temperature, respectively.

In benzene without TEA, the observed spectrum was a little different from that due to CAOH or CAO^- as shown in Figure 2 (spectrum A). We may call the species that gives spectrum A intermediate I hereafter. By the addition of TEA in the deaerated system, intermediate I changed to CAO^-. Nearly the same absorption spectrum was obtained by the photolysis of CN-NO_2-A in EPA at 77 K (spectrum B). (Comparison of spectrum A with spectrum B and that obtained in poly(methyl methacrylate) at room temperature[6] led us to the conclusion that the absorptions of spectrum A below 330 nm may be due to some byproducts.) Spectrum B was observed irrespective of the presence and absence of TEA. In the presence of TEA, intermediate I changed to the final product (CAO^-) as soon as the temperature was raised. In the absence of TEA, it changed to CAOH as the temperature was raised to room temperature.

Irradiation of Bz-NO_2-A in basic ethanol at room temperature gave 9-benzoyl-10-anthryloxy anion (BAO^-). The quantum yields of the formation of BAO^- were 0.14 in deaerated basic ethanol and 0.04 in an aerated sample. In the absence of TEA, 10-benzoyl-9-anthrol (BAOH) was obtained, which changed to BAO^- by the addition of TEA. Although CAO^- was obtained upon the photolysis of CN-NO_2-A in any solvents containing TEA, BAOH was obtained upon the photolysis of Bz-NO_2-A in EPA, benzene, ether, cyclohexane, or isopentane even in the presence of TEA. This solvent effect on the stability of BAOH was explained in terms of the relatively large pK_a value of BAOH; that is, the measured pK_a values were 5.5 for CAOH[8] and 8.8 for BAOH[7] in 30 mol % ethanol–water mixed solvent. Nearly 100% yield of base form (BAO^-) was obtained in such basic solvents as acetone, ethanol, benzonitrile, methanol, *N,N*-dimethylformamide, acetonitrile, and dimethyl sulfoxide, all of which have dielectric constants greater than 20.[7]

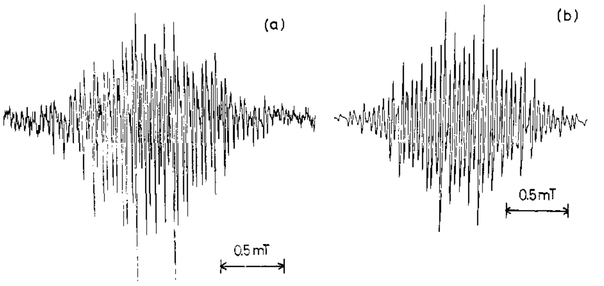


Figure 3. ESR spectrum of intermediate I (a) and simulated spectrum of 9-cyano-10-anthryloxy radical (b).

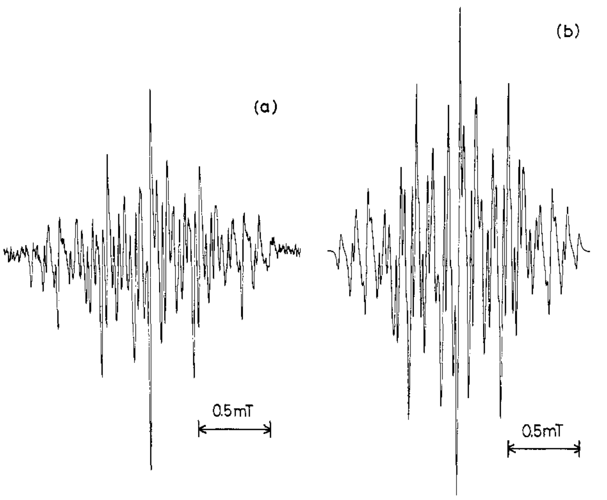
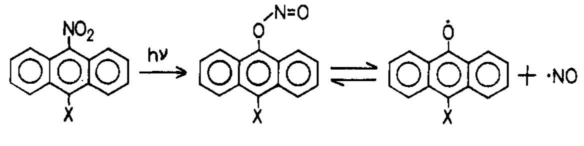


Figure 4. ESR spectrum of intermediate II (a) and simulated spectrum of 9-benzoyl-10-anthryloxy radical (b).

Scheme I



The photolysis of Bz-NO_2-A in benzene at room temperature without TEA gave rise to the similar result as that for CN-NO_2-A; that is, spectrum D in Figure 2 resembled that obtained for CN-NO_2-A. This spectrum changed to that of BAOH by the addition of TEA in the deaerated system. (The species that gives spectrum D may be called Intermediate II hereafter.) The same absorption spectrum was also obtained by the photolysis of Bz-NO_2-A in EPA at 77 K (spectrum E). In the absence of TEA, intermediate II changed to BAOH as the temperature was raised to room temperature. In the presence of TEA, intermediate II changed to BAO^- and then to BAOH as the temperature was raised to room temperature. This temperature effect on the stability of BAO^- was explained in terms of a negative enthalpy change of −14.6 kJ mol^{-1} for the equilibrium between BAOH and BAO^-.[7] All the results so far obtained indicate that intermediate II is essentially the same kind as intermediate I.

Chapman et al.[4] have proposed that the irradiation of 9-nitroanthracene gives rise to the nitro to nitrite rearrangement, followed by the cleavage of 9-anthryl nitrite to 9-anthryloxy radical and nitrogen(II) oxide as shown by Scheme I. Since the absorption spectra of intermediates I and II disappeared by the introduction of air and there were no formation of CAO^- and BAOH by the addition of TEA after that, it seems quite reasonable that 9-substituted-10-anthryloxy radicals are produced upon irradiation of CN-NO_2-A and Bz-NO_2-A.

The ESR spectra of intermediates I and II in benzene at room temperature are shown in Figures 3a and 4a, respectively. (By the introduction of air, these ESR spectra disappeared.) Figures 3b and 4b show the simulated ESR spectra of 9-cyano- and 9-benzoyl-10-anthryloxy radicals assuming the following hyperfine couplings: $a_1(H) = 0.333$, $a_2(H) = 0.296$, $a_3(H) = 0.108$, $a_4(H) = 0.079$, and $a(N) = 0.151$ mT for 9-cyano-10-anthryloxy radical

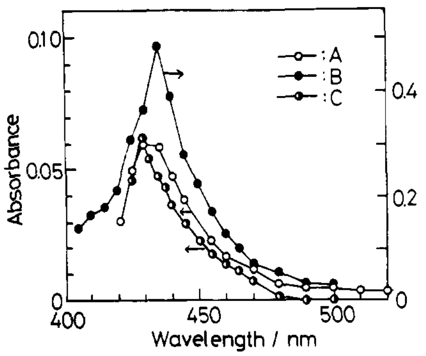


Figure 5. $T' \leftarrow T_1$ absorption spectra of Bz-NO_2-A (A, B) and CN-NO_2-A (C) in EPA at 77 K. A, by conventional flash photolysis; B and C, at 50-ns delay by nanosecond laser photolysis.

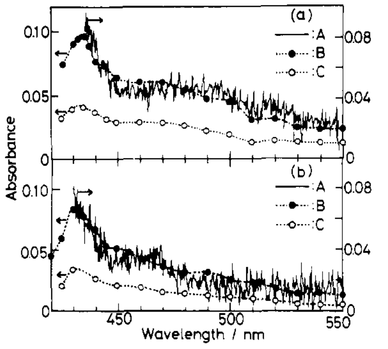
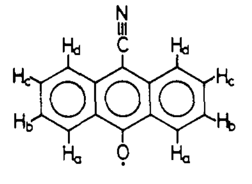


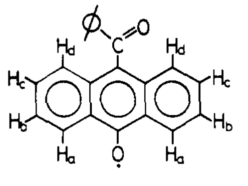
Figure 6. Time-resolved absorption spectra of CN-NO_2-A (a) and Bz-NO_2-A (b) in benzene at room temperature. A, at 460-ps delay by picosecond laser photolysis; B and C, at 50-ns and 10-μs delays by nanosecond laser photolysis, respectively.

and $a_1(H) = 0.333$, $a_2(H) = 0.302$, $a_3(H) = 0.104$, and $a_4(H) = 0.081$ mT for 9-benzoyl-10-anthryloxy radical.

Since the observed spectra are in essential agreement with the simulated spectra, intermediates I and II can be assigned to the following radicals, respectively. On the basis of the calculation of spin densities using McLachlan's method,[13] we have assigned to hyperfine couplings as follows: $a_1(H) \rightarrow a(H_d)$, $a_2(H) \rightarrow a(H_b)$, $a_3(H) \rightarrow a(H_c)$, and $a_4(H) \rightarrow a(H_a)$ for intermediate I and $a_1(H) \rightarrow a(H_d)$, $a_2(H) \rightarrow a(H_b)$, $a_3(H) \rightarrow a(H_c)$, and $a_4(H) \rightarrow a(H_a)$ for intermediate II.



I



II

Laser Flash Photolysis. Figure 5 shows the transient absorption spectra of CN-NO_2-A and Bz-NO_2-A obtained by a nanosecond laser photolysis and by a conventional flash photolysis at 77 K in EPA. All of the transient spectra show the characteristic absorption bands around 430 nm, and they are very similar to the $T' \leftarrow T_1$ absorptions of 9-acetylanthracene,[11,14] 9-nitroanthracene,[15] 9-benzoylanthracene,[16] and 9- and 9,10-dibromoanthracene.[17]

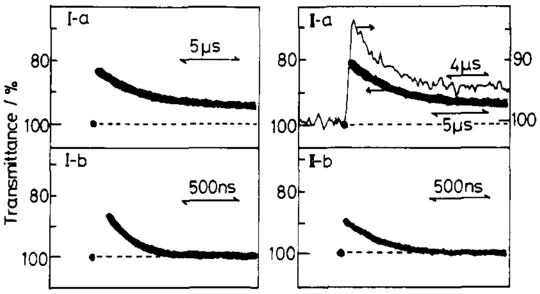


Figure 7. Decay curves of the transmittance of the transient absorptions of CN-NO_2-A (I) and Bz-NO_2-A (II) at 430 nm at room temperature in deaerated benzene (a) and the aerated case (b). Solid curve in part II-a was taken by using a Tektronix 390AD transient digitizer equipped with a graphic display computer system.

Thus, the observed spectra of the two compounds can be assigned to the $T' \leftarrow T_1$ absorptions which undoubtedly originate from the lowest triplet state $T_1(\pi\pi^*)$.

The time-resolved absorption spectra obtained by nanosecond laser photolyses of CN-NO_2-A and Bz-NO_2-A in benzene at room temperature are shown in Figure 6 (open and closed circles) The oscilloscope traces of the band maxima decayed with two components. Typical examples are shown in Figure 7. (Since transient absorptions were very weak, we also show a result for Bz-NO_2-A which was taken by using a Tektronix 390AD transient digitizer equipped with a graphic display computer system.) The short-lived components decayed following single exponential decay functions with lifetimes of 4.9 μs for CN-NO_2-A and 5.4 μs for Bz-NO_2-A. The absorption spectra of long-lived species (open circles in Figure 6) did not decay and the spectral profiles are similar to those of anthryloxy radicals (spectra A and D in Figure 2). In the presence of dissolved oxygen, the absorptions at the band maxima decayed with one component (Figure 7b) with the quenching rate constants of 3.1×10^9 M^{-1} s^{-1} for CN-NO_2-A and 2.9×10^9 M^{-1} s^{-1} for Bz-NO_2-A. On the basis of these results, the observed spectra at 50-ns delay (closed circles in Figure 6) can be interpreted in terms of a superposition of $T' \leftarrow T_1$ absorption on that of anthryloxy radical.

In our previous paper,[15] the transient absorption spectra on the picosecond time scale were taken by a photographic method. Although we assigned them to the $T' \leftarrow T_1$ absorptions of CN-NO_2-A and Bz-NO_2-A, spectral accuracy was not calibrated sufficiently at that time. Recently, we have improved our picosecond spectrometer using multichannel detectors of photodiode array, and the obtained spectra are shown by solid lines in Figure 6. (The absorptions below 435 nm could not be observed because of very weak intensity of the probe light.) The spectra are essentially identical with those obtained at 50-ns delay. Thus one can conclude that the observed transient spectra at 460-ps delay are not due to $T' \leftarrow T_1$ absorptions alone but due to the superposition of $T' \leftarrow T_1$ absorptions on that of anthryloxy radicals. Since there was no measurable change of the spectral shapes in the picosecond domain, the lowest triplet state $T_1(\pi\pi^*)$ and anthryloxy radical may build up simultaneously.

The conclusion that anthryloxy radicals are not produced via the lowest triplet states is strongly confirmed by the following experimental facts: (1) The $T' \leftarrow T_1$ absorptions of CN-NO_2-A and Bz-NO_2-A were quenched by the addition of ferrocene with the rate constant of $k_q \simeq 3.5 \times 10^9$ M^{-1} s^{-1}. (Although the absorption spectrum of 9-cyano-10-anthryloxy radical was not quenched by the addition of ferrocene, the absorption spectrum of 9-benzoyl-10-anthryloxy radical was slightly quenched by ferrocene.) (2) There was no essential change in the photochemistry of CN-NO_2-A and Bz-NO_2-A by the addition of ferrocene. Namely, the addition of ferrocene did not affect the decrease of reactants and the increase of products during the photolysis. No change in the decrease of reactants was observed

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[15] Hamanoue, K.; Hirayama, S.; Nakayama, T.; Teranishi, H. *J. Phys. Chem.* **1980**, *84*, 2074. The $T' \leftarrow T_1$ absorption of 9-nitroanthracene in benzene with $\lambda m_{ax} \simeq 440$ nm was taken by a photographic method and its spectral accuracy was not calibrated sufficiently. Using our improved picosecond spectrometer, we have confirmed that the $T' \leftarrow T_1$ absorption has an absorption maximum at 433 nm with a shoulder at 410 nm.

[16] Hamanoue, K.; Hirayama, S.; Okamoto, M.; Nakayama, T.; Teranishi, H. *Mem. Fac. Ind. Arts. Kyoto Tech. Univ., Sci. Technol.* **1978**, *27*, 69. Recently, we have confirmed that the $T' \leftarrow T_1$ absorption of 9-benzoylanthracene has two absorption maxima at 408 and 434 nm in benzene.

[17] Hamanoue, K.; Tai, S.; Hidaka, T.; Nakayama, T.; Kimoto, M.; Teranishi, H. *J. Phys. Chem.*, in press.

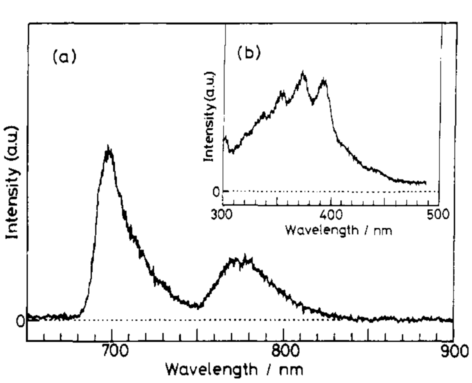

Figure 8. Phosphorescence (a) and its excitation (b) spectra of Bz-NO_2-A in EPA at 77 K.

during the irradiation by the introduction of air. (Although the yield of BAO^- decreased by the addition of ferrocene, it was confirmed that 9-benzoyl-10-anthryloxy radical reacted partly with ferrocene.)

For the sake of following discussion, we show the phosphorescence and its excitation spectra of Bz-NO_2-A in EPA in 77 K (Figure 8). Both spectra were measured with the band path of 4 nm and not corrected for the spectral response of the equipment.

Discussion

In conjunction with our measurements of $T' \leftarrow T_1$ absorption and its lifetime of 9-nitroanthracene (NO_2-A),[15] Snyder and Testa[18] recently observed that the intensity of phosphorescence due to anthraquinone increased during the irradiation of NO_2-A in ethanol at 77 K and concluded that what we measured are the $T' \leftarrow T_1$ absorption and its lifetimes of anthraquinone and not those of NO_2-A. On the basis of the following reasons, however, we still persist in our assignment that the observed spectrum is due to the $T' \leftarrow T_1$ absorption of NO_2-A: (1) The $T' \leftarrow T_1$ absorption ($\lambda_{max} = 430$ nm) and its lifetime ($\tau = 17.7$ ms) of NO_2-A in EPA at 77 K[15] are greatly different from those of anthraquinone, i.e., $\lambda_{max} = 365$ nm and $\tau = 3.4$ ms.[19] (2) The phosphorescence intensity due to anthraquinone did not increase during the repeated spectral measurements of NO_2-A in deaerated ethanol at 77 K, while it increased in the aerated case.[20] This indicates that anthraquinone may be present as an impurity in NO_2-A and that the primary photoproduct in the experiments of Snyder and Testa is not anthraquinone but a precursor that is converted to anthraquinone by a reaction with oxygen. (3) Upon the steady-state irradiation of NO_2-A in EPA at 77 K, spectral growth of a new absorption was observed.[20] Since this spectrum is very similar to that of 9-benzoyl-10-anthryloxy radical (spectrum E in Figure 2) and since the spin density of the benzoyl group of the radical is calculated to be zero, it is reasonable to conclude that the new absorption is assigned to 9-anthryloxy radical. This conclusion and the intensity increase of phosphorescence due to anthraquinone during the irradiation of NO_2-A in aerated ethanol at 77 K are consistent with the results of Chapman et al.,[4] who observed that anthraquinone was the major product upon the photolysis of acetone solution of NO_2-A in the presence of oxygen and speculated that photooxidation of NO_2-A to anthraquinone involves reaction of oxygen with 9-anthryloxy radical. (4) Although Snyder and Testa[18] concluded that NO_2-A does not phosphoresce, the phosphorescence spectrum due to NO_2-A was actually observed in ethanol at 77 K,[20] by using an HTV R928 photomultiplier whose spectral response extends to 900 nm. The spectrum has two band maxima at 685 and 760 nm and its lifetime is 14.3 ± 1.3 ms, which is compatible with that of $T' \leftarrow T_1$ absorption mentioned above. The phosphorescence intensity of NO_2-A was approximately one-half of that of anthracene. Thus, the choice of an IP21 photomultiplier made by Snyder and Testa[18,21] is most unfortunate, because its spectral response suddenly drops above 650 nm. (5) Although Hirayama[22] has already reported that the phosphorescence spectrum of Bz-NO_2-A has a band maxima at 695 nm in EPA at 77 K, we also show the spectrum in Figure 8a. The excitation spectrum (Figure 8b) is identical with the absorption spectrum of Bz-NO_2-A. Moreover the phosphorescence spectrum is very similar to that of NO_2-A.[20] (The very weak phosphorescence was also observed for CN-NO_2-A, however, it was difficult to take the excitation spectrum.)

All the results obtained so far indicate that the transient absorption spectra at 77 K in EPA[15] are actually due to the $T' \leftarrow T_1$ absorptions of nitroanthracenes. Thus our present assignment that the spectra taken at 460-ps and 50-ns delays (Figure 6) are due to the superposition of $T' \leftarrow T_1$ absorption on that of anthryloxy radical is reasonable.

The role of a carbonyl or a nitro group is so dramatic in enhancing a radiationless process that neither carbonyl-nor nitro-substituted anthracene has been known to be fluorescent at room temperature. As discussed in our previous paper,[15] we ascribed the lack of fluorescence in nitroanthracenes to the efficient intersystem crossing (isc) from the lowest excited $\pi\pi^*$ singlet state, $S_1(\pi\pi^*)$, to the higher triplet $n\pi^*$ state, $T_n(n\pi^*)$, which is located near or very slightly below the lowest excited singlet state. The rate of isc may be very rapid because of a favorable spin–orbit coupling and large Franck–Condon factor, and we have estimated its rate constant to be greater than 10^{11} s^{-1}. The existence of such a $T_n(n\pi^*)$ is also suggested by Mikula et al.[23] for 1- and 2-nitronaphthalene.

It is concluded, therefore, that the previously observed buildup times of the transient absorptions of nitroanthracenes, i.e., 72–86 ps,[15] should correspond to the lifetimes of $T_n(n\pi^*)$ states. Since the large S_1–T_1 splitting makes it likely that there is a second or third triplet state between S_1 and T_1, the internal conversion from $T_n(n\pi^*)$ to T_1 may well pass through these states. Since vibronic interaction between the two electronic states depends on the overlap integral[24] and it is small between $n\pi^*$ and $\pi\pi^*$ states, the vibronic interaction between these states is expected to be much weaker than those in anthracene, 9-methylanthracene, 9-phenylanthracene, 9,10-dichloroanthracene, and 9,10-dibromoanthracene. The rate constants of $T_n(\pi\pi^*) \rightarrow T_1$ internal conversion in these compounds have been estimated to be $\approx 10^{11}$ s^{-1} by Kokubun et al.[25]

Since Chapman et al.[4] have suggested that the reactive state of 9-nitroanthracene is an $n\pi^*$ excited state, it seems quite reasonable that the nitro to nitrite rearrangement arises from the $T_n(n\pi^*)$ state. This conclusion is consistent with our observation that the absorption spectra of $T' \leftarrow T_1$ transition and anthryloxy radicals build up simultaneously.

Assuming that the rate constant (k_r) for the rearrangement of a nitro group to a nitrite is much smaller than that for the cleavage of nitrite to anthryloxy radical and that the efficiency of the formation of anthryloxy anion from nitrite is unity, the quantum yield (Φ) of the formation of anthryloxy anion is given by $\Phi = k_r\tau$. Where τ is the lifetime of the $T_n(n\pi^*)$ state, that is, the inverse of the sum of k_r and the rate constant (k_{ic}) for the internal conversion from the $T_n(n\pi^*)$ to $T_1(\pi\pi^*)$ states. The choice of parameter of Φ, and $\tau \simeq 77$ ps, which is the average value of the lifetimes of the $T_n(n\pi^*)$ states in various solvents,[15] gives $k_r = 9.6 \times 10^9$ s^{-1} and $k_{ic} = 3.4 \times 10^9$ s^{-1} for CN-NO_2-A and $k_r = 1.8 \times 10^9$ s^{-1} and $k_{ic} = 11.2 \times 10^9$ s^{-1} for Bz-NO_2-A. At present, we cannot analyze the differences in the calculated values for CN-NO_2-A and Bz-NO_2-A quantitatively. One possible reason for this discrepancy might be attributed to the decomposition of BAO^-, because we have observed its decomposition by the further prolonged irradiation. Moreover, the observed transient absorptions on the picosecond time scale are very weak. Thus, the

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value of τ for CN-NO_2-A might be different from that for Bz-NO_2-A. We are now planning to measure the $T_n(n\pi^*)$ lifetimes using a picosecond mode-locked Nd^{3+}:YAG laser or Nd^{3+}:glass laser.

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Registry No. CN-NO_2-A, 14789-43-6; Bz-NO_2-A, 40933-02-6; CAOH, 14789-46-9; BAOH, 75532-21-7.

Optical Activity due to Isotopic Substitution. Synthesis, Stereochemistry, and Circular Dichroism of (+)- and (−)-[2,7,12-$^2H_3$]Cyclotribenzylene

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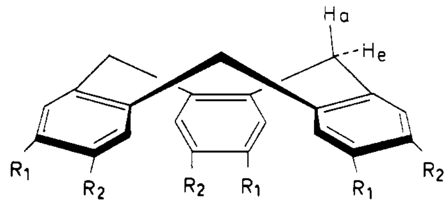
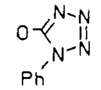
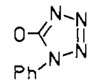
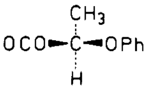
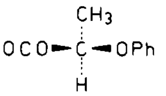
Abstract: The enantiomers of [2.7.12-$^2H_3$]cyclotribenzylene (**3**), whose chirality is due to isotopic substitution, were synthesized from cyclotriguaiacylene (**2**), and their absolute configuration was established as *M*-(−) or *P*-(+). The phenolic groups in the starting compound **2** were removed by hydrogenolysis of the corresponding tris(2-phenyl-1-tetrazolyl) ether **8**, and the resulting cyclotrianisylene (**4**) was demethylated into cyclotriphenolene (**5**). Optical resolution of **5** followed by deuteriolysis of the phenolic groups then provided the desired (+)- and (−)-**3** with a high isotopic purity. The energy barrier for crown inversion in **3** was calculated from the racemization rates to be $\Delta G^{\ddagger}$ = 112.5 kJ/mol (298 K). The circular dichroism of (*M*)-(−)-**3** consisted of a well-resolved sequence of positive and negative bands centered at 265 nm with $\Delta\epsilon$ ca. +0.01 to −0.06 from high to low energy. Interpretation in terms of vibronic rotation of the B_{2u} transition moment, induced by the deuterium atoms perturbing the breathing mode of each phenyl ring, was qualitatively consistent with the observed spectrum.

There is a continuous interest in the chiroptical properties of molecules optically active by isotopic substitution.[1] The isotope acting as an electronically neutral perturber, originates weak Cotton effects which in turn may reveal some intrinsical electronic, vibrational, or conformational properties of the substrate. So far, most of the work in this area has been concerned with the n → π* transition of ketones chiral by deuterium substitution.[2] Recently, the number of chromophores studied has, however, increased, including substrates having thioketone,[3] alkene and diene,[4] quinone,[5,6] carboxylic acid,[7] anhydride, imide, and nitrosamine structures.[6,8] On the other hand, as yet there have been very few reports dealing with the aromatic chromophore.[9-11]

In previous papers,[11,12] we described the synthesis and circular dichroism (CD) of (*M*)-(−)-[$^2H_9$]cyclotriveratrylene (**1**) in which the chirality arises from the selective replacement, on the aromatic rings, of three OCH_3 by three OCD_3 substituents. This compound exhibited a strong isotopically engendered exciton CD connected with the aromatic B_{2u} transition, the origin of which was ascribed to a difference in the rotamer populations of Ar–O–CH_3 vs. Ar–O–CD_3. Recently we have obtained the enantiomers of an analogous, simpler compound, [2,7,12-$^2H_3$]-cyclotribenzylene ((+)- and (−)-**3**), in which no such conformational changes can occur since the deuterium atoms responsible for the chirality are bound directly to the aromatic rings.[13] We now report the full synthetic details and the chiroptical properties of **3**. This compound actually displays a comparatively strong CD, which therefore can be solely ascribed to a "primary effect" of a deuterium atom on the properties of the benzene chromophore. There is only one previous example in which such a "primary effect" of an isotope was observed: (*S*)-(−)-[4-^{2}H]-[2.2]paracyclophane (**12**);[9] however, the CD of this compound was substantially weaker than that of **3**.



	R1	R2	
1	OCH_3	OCD_3	*M*-(−)
2	OCH_3	OH	*P*-(−)
3	D	H	*P*-(+)
4	OCH_3	H	*P*-(−)
5	OH	H	*P*-(−)
6	$OCOCH_3$	H	*P*-(−)
7	H	H	
8	OCH_3		*M*-(−)
9		H	*P*-(−)
10	 $OCO\text{—}\overset{CH_3}{\underset{H}{C}}\text{—}OPh$	H	*P*-(−)
11	H	 $OCO\text{—}\overset{CH_3}{\underset{H}{C}}\text{—}OPh$	*M*-(+)

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