

CHEMISTRY OF EXCIPLEXES. PHOTOCYCLOADDITIONS OF ANTHRACENES TO CONJUGATED POLYENES.

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Abstract - The addition of polyenes to excited anthracenes may yield several novel adducts derivable from both concerted and stepwise pathways according to the Woodward-Hoffmann Rules. The role of exciplex intermediates in these photocycloadditions is discussed. The concerted pathway in these excited state reactions is found to be favored relative to stepwise pathway(s) by polar solvents. It is suggested that the key step responsible for the observed polar solvent effect is a potential surface crossing from the exciplex derived from the $^1B_{2u}(S_1)$ state of anthracene to a low lying doubly excited state.

INTRODUCTION

Our interest in the chemistry of exciplexes began in 1971 when Dr. Jacqueline Libman of Israel initiated a systematic investigation of the photocycloaddition of conjugated dienes to aromatic hydrocarbons. Many interesting additions were observed for the first time (1-5). In 1973, Dr. David M. Shold and Dr. Jeffrey K. McVey began a study of the detection and characterization of [arene*:diene] exciplexes (6), while Dr. B. Kim, Dr. W. Chiang and Dr. K. Srinivasachar continued our investigation of photocycloadditions (7). This report summarizes our recent investigation into the role of exciplexes in the photocycloaddition of conjugated polyenes to anthracenes.

Our work was stimulated by two reports given during the Second IUPAC Symposium on Photochemistry by Professor A. Weller (8) and by Professor G. S. Hammond (9), as well as by results from the Max Planck Institute of Radiation Chemistry in Mülheim, then under the direction of Professor G. O. Schenk (10). Their contributions indicated that photoexcited aromatic compounds may be deactivated by ground state molecules of comparatively low ionization potentials and that product formation may play a role in the deactivation.

Anthracene and its derivatives were chosen for our investigation because (a) they exhibit fluorescence with high quantum efficiencies (11), (b) they form well-characterized exciplexes with ground state donor molecules (8), and (c) they undergo photocycloadditions with dienes with high quantum efficiencies to produce well-characterized products (Table 1). Accordingly, it was expected that a study of the relationship between exciplex formation and photocycloaddition in such systems could lead to insights into the possible mechanism of excited state processes.

TABLE 1. Photocycloadditions of Anthracenes^a and Dienes^a

Arene ^b	Diene ^c	ϕ_{-A}^d
An	DMHD	0.46 ^e
An	CHD	0.34 ^e
An	<u>t,t</u> -2,4-hexadiene	0.27 ^e
An	2,3-dimethyl-1,3-butadiene	0.057 ^e
CNA	DMHD	0.56 ^f
CNA	CHD	0.45 ^f
CNA	<u>cis</u> -1,3-pentadiene	0.38 ^f

^aSee text for abbreviations. ^b 8×10^{-4} M. ^c1.0 M. ^dCorrected for incomplete light absorption. Errors $\pm 10\%$. ^eIn methylcyclohexane. ^fIn benzene.

EXCIPLEX FLUORESCENCE

The formation of fluorescent [arene*:diene] exciplexes had been reported independently by Taylor (12) and by Saltiel and Townsend (13). Using 2,5-dimethyl-2,4-hexadiene, DMHD, as a representative 1,3-diene, we have detected and characterized many exciplexes derived from anthracene and substituted anthracenes (6). Several of these exciplexes exhibit prominent fluorescence at -20°C . As in the case of [arene*:amine] exciplexes reported by Weller and his coworkers (14), [arene*:DMHD] exciplexes also exhibit charge-transfer character and their fluorescence maxima undergo red shifts when the polarity of the solvent is increased. Furthermore, for a given diene, e.g., DMHD, as the donor, the polarity of [arene*:DMHD] exciplexes is directly related to the IP of arenes in their ground state (6). The fluorescence maxima (λ_{max}) and the fluorescent quantum yields (ϕ_f) for the exciplexes derived from DMHD with either anthracene, [An*:DMHD], or 9-cyanoanthracene, [CNA*:DMHD], are summarized in Table 2. Using the formulation developed by Weller (14),

$$\bar{\nu}_{\text{CT}}^{\text{max}} = \bar{\nu}(0) - 2\mu^2/hca^3 [(\epsilon - 1/2\epsilon + 1) - (n^2 - 1/4n^2 + 2)] \quad (1)$$

and the data from Table 2, the dipole moment of the [CNA*:DMHD] exciplex is calculated to be 8.1 ± 1.0 debyes, corresponding to approximately 34+4% charge transfer, while the dipole moment of the [An*:DMHD] exciplex is estimated at 2.0 debyes, or less than 10% charge transfer. Although the [CNA*:DMHD] exciplex is considerably more polar than the [An*:DMHD] exciplex, it is still less polar than the exciplex derived from An and diethylaniline.

TABLE 2. Fluorescence of [Anthracene:DMHD] and [9-Cyanoanthracene:DMHD] Exciplexes

Solvent (ϵ) ^a	Anthracene ^b		9-Cyanoanthracene ^{c,d}	
	λ_{max}	ϕ_f	λ_{max}	ϕ_f
Methylcyclohexane (2.02)	435 \pm 10 nm, 23000 cm ⁻¹	<0.001	490 \pm 5 nm, 20400 cm ⁻¹	0.0013
Ethyl acetate (6.0)	435 \pm 10 nm, 23000 cm ⁻¹	<0.001	555 \pm 5 nm, 18000 cm ⁻¹	0.003
Dichloromethane (9.1)	---	---	570 \pm 2 nm, 17500 cm ⁻¹	0.015
1,2-Dichloroethane (10.4)	445 \pm 5 nm, 22500 cm ⁻¹	0.004 ^d	---	---
Ethanol (24.3)	455 \pm 5 nm, 22000 cm ⁻¹	---	610 \pm 10 nm, 16400 cm ⁻¹	0.0015
Acetonitrile (36.2)	465 \pm 5 nm, 21500 cm ⁻¹	0.017 ^d	650 \pm 20 nm, ^e 15400 cm ⁻¹	< 0.001

^a Dielectric constant at 20° . ^b Parent emission, 378 nm (26500 cm⁻¹), $\phi_f = 0.36$.

^c Parent emission, 408 nm (24500 cm⁻¹), $\phi_f = 0.66$. ^d Measured at $-9 \pm 1^{\circ}$. ^e Estimated.

The data in Table 2 also indicate that exciplex fluorescence may intensify as the solvent becomes more polar. In the case of the [CNA*:DMHD] exciplex, the exciplex fluorescence efficiency reaches a maximum in solvents of moderate polarity (dichloromethane) and diminishes as the solvent becomes more polar. In a highly polar solvent such as acetonitrile, the principal mode of deactivation of excited CNA in the presence of DMHD is apparently the electron transfer process to yield radical ions. The chemical consequence is reminiscent of the deactivation of 9,10-dicyanoanthracene by unsaturated compounds, i.e., the quantum yield of CNA consumption is drastically reduced in polar solvents ($\phi_{\text{-CNA}}$ decreases from 0.56 in benzene to less than 0.01 in acetonitrile) and 9,10-dihydro-9-cyanoanthracene becomes a major product (15). As reported previously by Libman (16), it is apparent that photocycloaddition and electron transfer are competitive processes, and photocycloadditions occur at high efficiency only when electron transfer is energetically unfavorable.

THE EXCIPLEX AS THE INTERMEDIATE IN PHOTOCYCLOADDITION

Although we have detected a variety of [An*:DMHD] exciplexes, they, strictly speaking, may not be intermediates in photocycloadditions. In fact, compelling evidence for the role of exciplexes as the intermediates in photocycloaddition is rare. One characteristic feature

of exciplex systems is the reversibility of exciplex formation, indicative of the partial establishment of an equilibrium between the exciplex and the isolated components. In the case of the anthracene-DMHD system, this equilibrium is clearly revealed by a 68% increase in the Stern-Volmer quenching constant (K_{SV}) as the temperature is decreased from 50°C to -10°C (Table 3). Similar temperature dependence occurs for the quantum yield of the photocycloaddition of DMHD to anthracene. The quantum yield for this reaction increases by 83% from 50°C to -20°C. Thus, there is clearly a reversible step which precedes photocycloaddition.

TABLE 3. PHOTOCHEMICAL INTERACTION BETWEEN ANTHRACENE AND DMHD IN METHYLCYCLOHEXANE

Temp (°C)	$K_{SV} (M^{-1})^a$	ϕ^b	ϕ_{lim}^c
-20	---	0.33±0.01	---
-10	15.8±0.7	0.26±0.01	0.44
0	15.6±0.2	0.28±0.03	0.48
10	15.1±0.5	0.26±0.01	0.45
20	14.9±0.3	0.22±0.03	0.39
30	13.6±0.1	0.22±0.02	0.40
40	11.5±0.3	0.23±0.01	0.46
50	9.4±0.8	0.18±0.01	0.39

^aStern-Volmer quenching constant for the quenching of anthracene fluorescence by DMHD, measured with a Perkin-Elmer MP-4 Spectrofluorimeter.

^bQuantum yield of anthracene consumption in degassed solutions at 365 nm, measured at 0.0008 M anthracene and 0.09 M DMHD with a conventional merry-go-round apparatus. A correction factor has been applied to account for incomplete light absorption. ^cSee text.

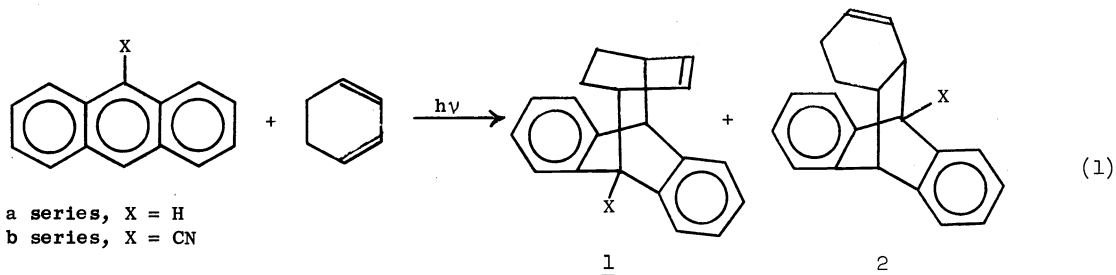
Under the conditions in which the quantum yields were measured, it is possible to determine the fraction of the excited anthracene which is quenched by DMHD. Therefore, one can calculate the limiting quantum yield, which is the fraction of the quenched excited anthracene which results in product formation:

$$\phi_{lim} = \phi [1 + (K_{SV}(\text{DMHD}))^{-1}] \quad (2)$$

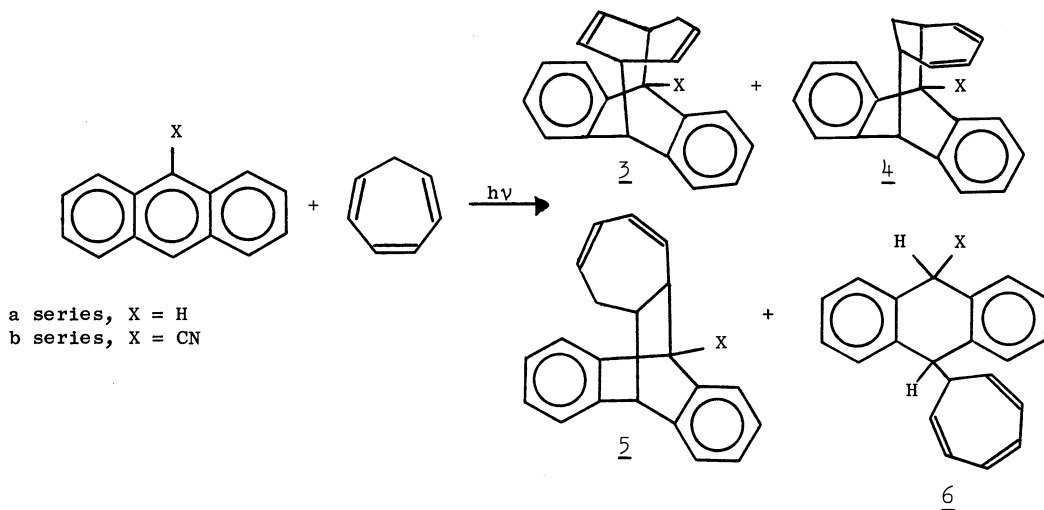
The significant result, shown in Table 3, is that the limiting quantum yield is constant with temperature, 0.44±0.04. The fact that both the quantum yield of cycloaddition and K_{SV} increase at decreasing temperatures rules out any mechanism which does not involve a reversible step prior to product formation. Furthermore, the absence of any change in limiting quantum yields implies that the exciplex is the precursor to quenching, exciplex fluorescence and product formation.

ON THE MECHANISMS OF CONCERTED AND STEPWISE PHOTOCYCLOADDITIONS OF ANTHRACENES TO CONJUGATED POLYENES

Although excited anthracenes react with common 1,3-dienes to yield predominantly the $4\pi_s + 4\pi_s$ adduct (1-5), Kaupp reported that the $4\pi_s + 2\pi_s$ adduct was also formed as a minor product in the photocycloaddition of anthracene (An) to 1,3-cyclohexadiene (CHD) (reaction 1) (17).



a series, X = H
b series, X = CN



Sasaki, Kanematsu and Hayakawa reported that both the $4\pi_s+4\pi_s$ and $4\pi_s+6\pi_s$ adducts were formed in the photocycloaddition of anthracene to 1,3,5-cycloheptatriene (CHT) (reaction 2) (18). We subsequently showed that the $4\pi_s+4\pi_s$ adduct and the $4\pi_s+2\pi_s$ adduct were formed from divergent pathways in the photocycloaddition of 9-cyanoanthracene (CNA) to 1,3,5-cycloheptatriene (19). Therefore, adducts derivable from either concerted or stepwise pathways according to the Woodward-Hoffmann Rules may be formed simultaneously in these additions (20). We have now investigated the factors which may control the relative efficiencies of divergent pathways and found that the nature of the solvent has a distinct effect upon the relative yields of concerted and stepwise adducts. The results are summarized in Table 4.

TABLE 4. EFFECT OF SOLVENT ON PHOTOCYCLOADDITION PRODUCT COMPOSITION

Reaction ^a	Solvent (ϵ) ^b	Product Composition ^c					
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
1a, An+CHD	benzene (2.3)	85.0±1.0	15.0±1.0				
	ethanol (24.3)	87.6±1.0	12.4±1.0				
	MeCN (36.2)	89.5±1.0	10.5±1.0				
	ØH:MeI (5.1)	2.8±1.0	97.2±1.0				
	MeCN:MeI (22.9)	5.5±1.0	94.5±1.0				
1b, CNA+CHD ^d	benzene (2.3)	100.0±1.5	0±1.5				
2a, An+CHT	benzene (2.3)			28±1	46±2	8±1	18±1
	ethanol (24.3)			38±2	43±2	8±1	11±1
	MeCN (36.2)			40±2	40±2	7±1	13±1
	ØH:MeI (5.1)			6±1	48±2	40±2	6±1
	MeCN:MeI (22.9)			25±2	32±2	36±2	7±1
2b, CNA+CHT ^d	benzene (2.3)			33±2	14±1	38±2	16±1
	CH ₂ Cl ₂ (8.9)			37±2	13±1	34±2	15±2
	ethanol (24.3)			41±2	12±1	33±1	13±1
	MeCN (36.2)			51±2	11±1	25±1	12±1

^aAll reactions were carried out with a solution of the given solvent containing 1.4×10^{-2} M of the anthracene and 0.95 M of the polyene. ^bDielectric constants (ϵ)

for solvents at 20° are obtained from the "Landolt-Börnstein Zahlenwerte Funktionen", II Band, 6 Teil, pp. 618-656. ^cAll adducts exhibited satisfactory analyses and spectral properties. ^dIodomethane has no apparent effect on the adduct composition of these reaction.

The results clearly indicate that relative yields of all $4\pi_s+4\pi_s$ concerted adducts increase with the polarity of the solvent. Furthermore, with either diene, the relative yield of the $4\pi_s+4\pi_s$ adduct is increased with respect to the other adducts when the arene is changed from An to CNA. In the photoaddition of CHT to anthracene, we have isolated the $4\pi_s+2\pi_s$ adduct 5 as well as the formal "ene" type product 6 in addition to the $4\pi_s+4\pi_s$ and $4\pi_s+6\pi_s$ adducts reported in the literature (18). In mixed solvents containing 50% by volume of iodomethane, the quantum efficiency of adduct formation from anthracene is appreciably reduced ($\phi_{-An} < 0.01$) but the $4\pi_s+2\pi_s$ adduct (2 or 5) becomes a major product of the reaction. However, iodomethane apparently has no heavy atom effect on the adduct composition from cyanoanthracene, suggesting that the stepwise adducts 2, 4 and 5 may also arise via a singlet biradicaloid pathway (21).

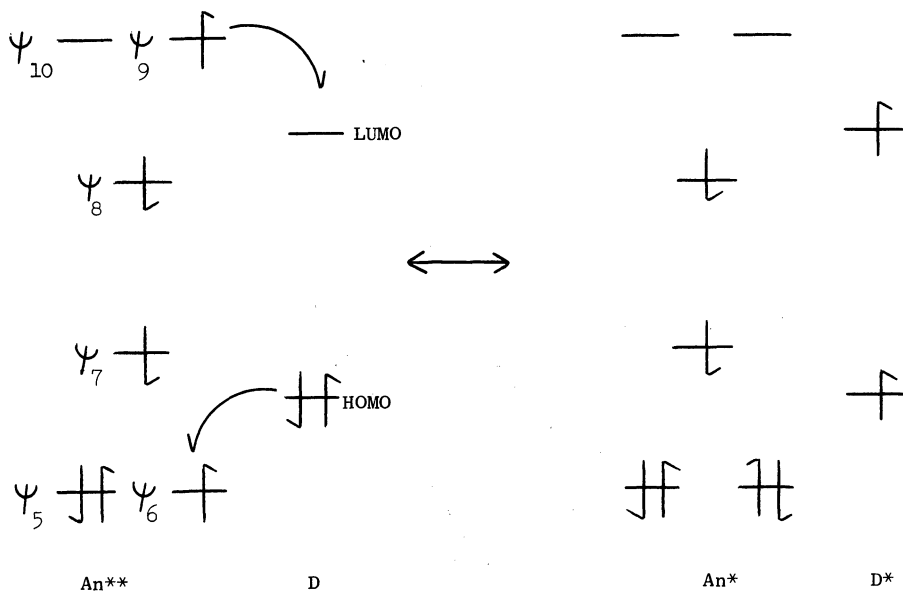
According to simple orbital symmetry considerations, concerted photochemical reactions are characterized by the correlation of the singly excited states of the substrate(s) and product, the correlation of the ground state product and the doubly excited substrate(s), as well as the correlation of the ground state substrates with the doubly excited product (20). The formation of the concerted ground state adduct from the singly excited substrate(s) may then be viewed as the result of the avoided crossing from the singly to the doubly excited potential energy surfaces followed by decay to the ground state (22-25). Since both the substrates and the products in our reactions contain relatively simple aromatic chromophores, the singly excited levels of these compounds will not vary appreciably with solvent. Therefore, if concerted product formation were the result of an avoided crossing in which the height of the barrier in the rate determining step was dependent only upon the singly excited surface, its efficiency, relative to other excited state processes, should not be affected by the solvent polarity as we have observed.

Encounter of excited aromatic compounds with the ground state of olefinic compounds may lead to the formation of exciplexes (6,12,13). Although polar solvents will stabilize the exciplex more than the uncomplexed excited aromatic compound, polar solvents will have virtually no effect on the energy level of singly excited products formed in the photocycloaddition. Hence, inclusion of solvent effect on the exciplex alone will not account for the observed solvent effect on the product composition.

So far we have examined possible effects of the solvent on the singly excited state surface. However, as we stated above, the surface crossing from a singly excited state to a doubly excited state may be the key step in concerted excited state reactions. Consequently, a more detailed examination of the role of the doubly excited state is warranted. As in the singlet state (*vide infra*), an exciplex derived from the doubly excited state of anthracene and ground state diene [An**:D] may be formed. An approximate wavefunction can be written as follows:

$$\begin{aligned} \Phi_{[An^{**}:D]} \approx & C_1\phi_{[An^{**}:D]} + C_2\phi_{[An:D^{**}]} + C_3\phi_{[An^*:D^*]} + C_4\phi_{[An^{\cdot-}:D^{\cdot+}]} + C_5\phi_{[An^{+\cdot}:D^{\cdot-}]} \\ & + C_6\phi_{[An^{++}:D^{\cdot-}]} + C_7\phi_{[An^{\cdot-}:D^{++}]} \end{aligned} \quad (3)$$

In the semiempirical formulation of the lowest doubly excited state of anthracene, $^1B_{1g}$, the anthracene MO's Ψ_6 (energetically degenerate with Ψ_5), Ψ_7 , Ψ_8 and Ψ_9 (degenerate with Ψ_{10}) become populated. The third term of equation [3], [An*:D*], can be viewed as resulting from two one-electron transfers between the doubly excited anthracene and the ground state diene as illustrated below:



This interaction is more favorable energetically than the corresponding exciton resonance interaction in the singly excited state, i.e., doubly excited anthracene is simultaneously a better electron donor and acceptor than is singly excited An. The implication of such an interaction is that delocalization of excitation energy from the An moiety into the D moiety is increased. The diene molecule may thereby undergo molecular deformations which ultimately will allow the rehybridization of the appropriate molecular orbitals necessary for product formation.

Although the delocalization of excitation energy from An** into D in the exciplex to give [An*:D*] may be highly unfavorable energetically with both An* and D* moieties in the singlet manifold, one possible formulation of this state involves the contribution of a [An*:D*] term with both An* and D* in the triplet manifold. The energy of this configuration can be estimated as the sum of the triplet energies of An and D. The total energy of the locally excited anthracene and a conjugated polyene each in its respective triplet state is approximately 90-100 Kcal (26), which is not appreciably different from that of the $^1B_{1g}$ state of anthracene as characterized by Jortner (95 Kcal) (27).

With the above discussion in mind, our results may be rationalized by reference to Figure 1. Encounter of anthracene in its $^1B_{2u}$ state with the ground state of the diene leads to the formation of an exciplex intermediate, [An*:D], which subsequently crosses over to the potential surface of the low lying doubly excited complex. Since photocycloaddition does not seem to be a reversible process, i.e., $\phi_{-An} > \phi_i$, it is reasonable to expect that the reaction complex cannot return to the singlet exciplex once it has crossed onto the doubly excited surface. Therefore, the ease of concerted photocycloaddition will be determined by the barrier of avoided crossing from the singly excited surface to the doubly excited surface. Since a polar solvent will stabilize the doubly excited exciplex more than the singly excited exciplex, the avoided crossing between them may occur at a lower point on the potential surface (see the insert in Figure 1). Thus, the concerted addition becomes relatively more favorable in polar solvents. This hypothesis is also supported by the increased relative yields of the $4\pi_s + 4\pi_s$ adducts with CNA, which forms a more polar exciplex than does An with dienes.

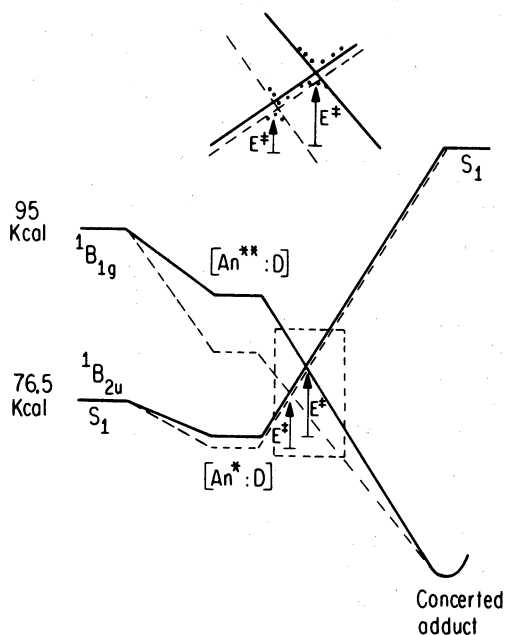


Figure 1. A schematic potential surface diagram for the photocycloaddition of anthracene to a conjugated polyene. The — line represents the reaction in a non-polar solvent and the ---- line represents the reaction in a polar solvent.

The mechanism(s) for the formation of the stepwise adducts, $4\pi_s + 2\pi_s$ and $4\pi_s + 6\pi_s$, is less clearly understood at this moment. The addition of a solvent containing a heavy atom, iodomethane, will promote the intersystem crossing of excited singlet species to the triplet manifold by spin-orbit coupling. The use of mixed solvents containing iodomethane has a dramatic effect on the relative ratio of the two types of adducts from anthracene (Table 4). The $4\pi_s + 2\pi_s$ adduct in particular becomes a major product in these reactions and the quantum yields of these photocycloadditions are drastically reduced. The results suggest that the stepwise adducts may be formed from the triplet manifold, in the case of An, and their formation will thus be relatively unaffected by the solvent. Since the stepwise adducts may also be derived from the singlet manifold, the possible mechanism of their formation will be discussed elsewhere (28).

CONCLUSION

We have shown that exciplexes are intermediates in the photocycloaddition of anthracenes to conjugated polyenes. Furthermore, it was found that the concerted pathway in these excited state reactions is favored relative to stepwise pathway(s) by polar solvents. We propose that the potential surface crossing from the exciplex derived from the $1B_{2u}(S_1)$ state of anthracene to the doubly excited state is the key step responsible for the observed polar solvent effect. The importance of doubly excited states in photochemistry is currently under investigation in our laboratory.

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