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Charge-Transfer Photochemistry from the Donor–Acceptor Complexes of Anthracenes with Tetranitromethane

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The formation of electron donor–acceptor or EDA complexes of a series of 9-substituted and 9,10-disubstituted anthracenes with tetranitromethane (TNM) can be visually observed in dichloromethane solutions. The colors arise from charge-transfer (CT) transitions from the aromatic donor (An) to the tetranitromethane acceptor. Specific irradiation of the CT absorption band at $\lambda > 500$ nm leads to the rapid bleaching of the solution, and high yields of photoadducts 1 can be isolated especially from those anthracenes bearing electron-withdrawing substituents. X-ray crystallography establishes the photoadducts 1 to derive from an overall anti addition of the TNM fragments, $C(NO_2)_3$ and NO_2, across the meso positions of 9-bromo- and 9-phenylanthracene. The high quantum yields are associated with the efficient dissociative electron transfer accompanying the charge-transfer excitation of the 1:1 EDA complex. The subsequent multistep pathway by which the geminate species [$An^{+}\cdot$, $C(NO_2)_3^-$, NO_2] combine regiospecifically and stereospecifically to form the photoadduct 1 is described. The structural elucidation of the byproducts underscores the efficiency of ion-pair and radical-pair interactions following the CT excitation of EDA complexes.

Transient colors associated with charge-transfer (CT) absorptions are often observed during the course of many reactions between electron-rich organic or organometallic species and various electrophiles, and they are ascribed to the formation of electron donor–acceptor (EDA) complexes.[1] Charge-transfer interactions are also an important source of stabilization in chemical reactions—such that bond reorganizations leading to reactive intermediates and/or transition states are facilitated by the delocalization of incipient charge.[2,3] When electron donor–acceptor complexes are characterized as reaction intermediates, they exist as weakly bound species in which the donor component (D) and the acceptor moiety (A) are loosely associated to retain their individual identities,[5,6] i.e., eq 1. The association constant K for complex formation generally increases with the donor and acceptor strengths, as evaluated by the ionization potential and electron affinity, respectively.[5,7] Such complexes promote reactivity by bringing the reactants together and encouraging the orbital overlap required for electronic reorganization (including electron transfer.)

$$D + A \overset{K}{\rightleftharpoons} [D,A] \tag{1}$$

According to Mulliken,[6] the color of an EDA complex arises from a charge-transfer transition involving the promotion of an electron from an occupied molecular orbital primarily localized on the donor to an unoccupied orbital localized on the acceptor. Thus the CT excitation of a weakly bound EDA complex [D,A] populates an ionic state consisting of a radical–ion pair as summarized by eq 2. The ion pair generated by CT excitation in eq 2 has been observed by time-resolved spectroscopy and identified by the local absorptions characteristic of the individual donor cation ($D^{+}\cdot$) and the acceptor anion ($A^{-}\cdot$).[8,9]

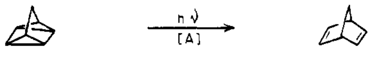
$$[D,A] \xrightarrow{h\nu_{CT}} [D^{+}\cdot, A^{-}\cdot] \tag{2}$$

The fate of the geminal ion pair depends on the properties of the component radical ions. For example, in a system consisting of a series of arene donors (An) and tetracyanoethylene (TCNE) as the acceptor, the irradiation of the CT band with a 25-ps laser pulse leads to the excited ion pair, i.e., eq 3, the picosecond spectrum of which is the same as the composite spectra of species generated independently by electrochemical oxidation and reduction of the arene donor and TCNE, respectively.[8] However, the back electron transfer to regenerate the original EDA complex is rapid, i.e., eq 4. Such a rate is sufficient to preclude the efficient chemical evolution of the ion pair. As a result, there is essentially no photochemistry attendant even upon the prolonged irradiation of the CT bands of these complexes.

$$[An,TCNE] \xrightarrow{h\nu_{CT}} [An^{+}\cdot, TCNE^{-}\cdot] \tag{3}$$

$$[An^{+}\cdot, TCNE^{-}\cdot] \xrightarrow{<50\ ps} [An,TCNE] \tag{4}$$

This situation is in marked contrast to the efficient charge-transfer photochemistry which has been reported for systems consisting of either a donor which yields an unstable cation,[11,12] e.g., eq 5–8,



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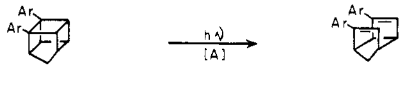

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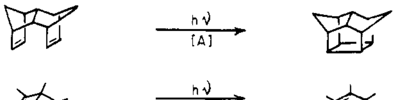

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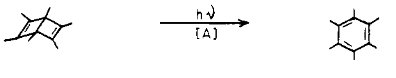

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[1] (a) Kosower, E. M. *Prog. Phys. Org. Chem.* **1965**, *3*, 81. (b) Colter, A. K.; Dack, M. R. J. *Mol. Complexes* **1973**, *1*, 301; **1974**, *2*, 1.

[2] For leading references, see: (a) Epiotis, N. D. *J. Am. Chem. Soc.* **1972**, *94*, 1924. (b) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57. (c) Houk, K. N. *J. Am. Chem. Soc.* **1973**, *95*, 4092. (d) Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761 and references therein.

[3] Thus the rates of many diverse types of reactions are found to correlate with measures of electron transfer such as CT transition energies and redox potentials.[4]

[4] (a) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 7240. (b) Fukuzumi, S.; Kochi, J. K. *Ibid.* **1982**, *104*, 7599.

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[8] (a) Hilinski, E. F.; Masnovi, J. M.; Amatore, C.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6167. (b) Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *Ibid.* **1984**, *106*, 8071.

[9] In some cases, the absorption spectra of ion pairs are slightly perturbed relative to those of the component ions.[10]

[10] Cf. Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 1441.

0022-3263/85/1950-5245$01.50/0

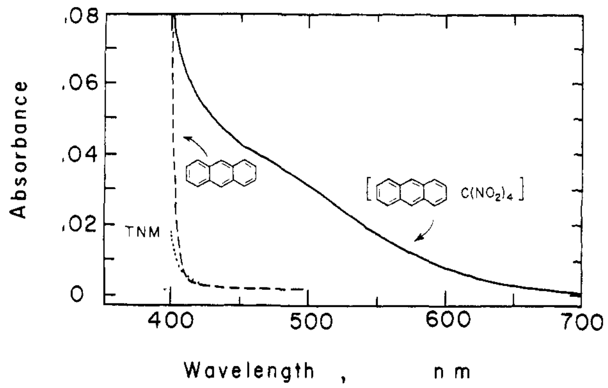
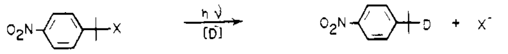


Figure 1. CT absorption spectrum of the EDA complex of 0.02 M anthracene and 0.02 M tetranitromethane (—) in dichloromethane solutions with a 1-cm optical path. The absorption spectrum of 0.02 M anthracene (---) and 0.02 M tetranitromethane (···) *alone in the same solvent.*

or an acceptor which yields an unstable anion,[13] e.g., eq 9.



(9)

Such photoinduced transformations are promoted by polar solvents and high concentrations of donors. The quantum yields exceed unity, indicative of chain processes. Thus the skeletal isomerization of the hydrocarbon donors in eq 5–8 results from the ready rearrangement of the cation radical, eq 10, which is coupled into the catalytic cycle via

$$D^{+\cdot} \longrightarrow D'^{+\cdot} \qquad (10)$$

an electron transfer step. Similarly the photostimulated substitution process in eq 9 represents a redox catalytic ($S_{RN}1$) process which is dependent on the lability of the acceptor anion radical, i.e., eq 11. In both systems, the

$$ArX^- \xrightarrow{-X^-} Ar\cdot \xrightarrow{D^-} ArD^{-}\cdot, \text{etc.} \qquad (11)$$

efficiency of the catalytic process is strongly influenced by the magnitude of the redox changes ($\Delta E°$) accompanying electron transfer.[14] Efficient propagation steps often obscure the nature of the CT excitation leading to the initiation of the chain process.

For this reason, we sought an electron donor–acceptor pair in which the CT interaction and its derived thermal and photochemical reactivity are not modulated by chain processes.[8,15] Tetranitromethane (TNM) is known to form aromatic complexes,[16,17] and photochemical reactions have been observed in these and related systems.[18] Our previous investigation of a series of 9-substituted and 9,10-disubstituted anthracenes with tetranitromethane by time-resolved (picosecond) spectroscopy established the photophysics of the CT transitions in this system as well as the temporal evolution of the reactive intermediates.[15,19] In this report, we focus on the charge-transfer photochemistry of the EDA complex and present details for the X-ray crystallography of the principal photoproducts.[20]

Table I. Quantum Yields for the Disappearance of the EDA Complex from Anthracenes with TNM and the Appearance of Photoadduct 1[a]

9-substituted anthracene	Φ_{-CT}	Φ_{-An}	Φ_P
Br	1.6	0.7	0.6
NO_2	1.5	0.7	0.6
H	1.62 0.73[b]	0.75	0.3
CHO	1.61		
C_6H_5	1.5	0.6	0.4
9-CH_3, 10-CH_3	~1.6[c]		

[a] In methylene chloride solution containing 0.050 M An and 0.050 M TNM at 25 °C. [b] With 0.050 M An and 0.50 M TNM. [c] Overlapping absorptions of the products interfere with this measurement.

Results

Mixing solutions of tetranitromethane and anthracene results immediately in the brown coloration of the electron donor–acceptor complex. The electronic absorption

(12)

spectrum appears as a broad tail which extends to beyond 700 nm, as shown in Figure 1.[15,21] Although the maximum of the CT band is hidden under the low energy edge of the localized transitions of the uncomplexed anthracene (and tetranitromethane), all the absorption beyond 450 nm clearly arises from the EDA complex. Similar CT bands are observed with 9-substituted and 9,10-disubstituted anthracenes, but in no case is the absorption maximum clearly resolved. Judging by the change in the CT absorbance with increasing amounts of either the anthracene donor or TNM, we conclude that the formation constant K in eq 12 is small ($K \sim 1$ M^{-1}).[14] Thus the anthracene complexes with TNM like those with TCNE are derived from weak ground-state interactions.

The EDA complexes of the anthracenes (An) and tetranitromethane persist unchanged for many hours if the solutions are carefully protected from light.[22] At prolonged times however some of the anthracenes, especially the electron-rich derivatives such as 9-methoxy- and 9,10-dimethylanthracene, undergo a slow thermal oxidation. All of our studies were therefore carried out on

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(11) Jones, G., II; Becker, W. G.; Chiang, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 1269. Jones, G., II; Becker, W. G. *Ibid.* **1983**, *105*, 1276.

(12) Mukai, T.; Sato, K.; Yamashita, Y. *J. Am. Chem. Soc.* **1981**, *103*, 670.

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(14) Note in eq 5–8 the oxidation potential of the reactant is less positive than that of the product. Similarly the reduction potential of the product in eq 9 is more negative than that of the reactant.

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(19) Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. *J. Am. Chem. Soc.*, in press.

(20) Preliminary results are included in ref 15.

(21) The broad CT absorption bands observed in TNM complexes may result from geometrically less defined structures arising from the poor orbital overlap of this quasi-spherical acceptor with the planar π-HOMO of anthracene.

(22) Tetranitromethane decomposes thermally ≳50 °C. See: Marshall, H. P.; Borgardt, F. G.; Noble, P., Jr. *J. Phys. Chem.* **1968**, *72*, 1513. Nazin, G. M.; Nechiporenko, G. N.; Sokolov, D. N.; Manelis, G. B.; Dubovitskii, F. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 315.

Table II. Yields of the Photoadduct 1 from the CT Excitation of Anthracene–TNM Complexes[a]

	9-substituted anthracene	yield,[b] %		9-substituted anthracene	yield, %
a	NO_2	85 (47)	**g**	Br	86 (72)
b	CN	40[c] (34)[c]	**h**	H	16 (8)[f]
c	CHO	69[d] (63)[e]	**i**	Ph	60[g] (61)[f]
d	CO_2CH_3	89	**j**	OCH_3	*h*
e	$COCH_3$	86 (84)	**k**	$OCOCH_3$	58[i]
f	Cl	93 (75)	**l**	CH_3	*j*

[a] In methylene chloride solutions at 10 °C containing 0.1 M An and 0.1 M TNM, irradiated through 500-nm cut-off filters unless indicated otherwise. [b] Yield based on ^{1}H NMR integration with an internal standard. Isolated yields in parentheses. [c] May be mixture of stereoisomers. [d] In addition to 14% of 9-formyl-10-(trinitromethyl)-9,10-dihydroanthracene (**3**). [e] Mixture of **1** and **3**. [f] From saturated cyclohexane solution. [g] In addition to 22% of 9-phenyl-9-hydroxy-10-(trinitromethyl)-9,10-dihydroanthracene (**4**). [h] 40% of 9-(trinitromethyl)anthrone (**5**). [i] In addition to 6% **5**. [j] Complex mixture, including reaction on the substituent.

freshly prepared solutions at <25 °C under conditions in which the thermal reactions were negligible.

Photochemical irradiation with light of wavelength greater than 500 nm selectively excites only the EDA complex. The results in Figure 1 preclude the possibility of the adventitious excitation of either the uncomplexed anthracene and/or tetranitromethane. The brief irradiation (<30 min) of the EDA complexes derived from 0.1 M anthracene and 0.1 M TNM in dichloromethane at 0 °C was performed with a focused beam from a 500-W xenon lamp or a 100-W mercury lamp passed through a sharp cut-off filter [Corning 3-69 (500 nm) or 2-63 (560 nm)]. The course of photochemistry was followed by either the bleaching of the CT absorption band or the disappearance of the anthracene absorptions at 350–400 nm. Qualitatively, the rate of the photochemical reaction was slower when the longer wavelength cut-off filters were used. However, we observed no significant difference in the distribution of photochemical products (vide infra), provided care was exercized to prevent the uncomplexed chromophores from absorbing the light.[23]

The 1:1 stoichiometry of the CT photochemistry from TNM and the anthracene donor is reflected in the determination of the quantum yields by two methods. Thus the consumption of the anthracene was monitored by the disappearance of the local transitions between 350–400 nm (after appropriate dilution) and is reported as $\Phi_{\text{-An}}$ in Table I. The consumption of the EDA complex was followed by the disappearance of the CT band at λ 500 nm, and the quantum yield is reported as $\Phi_{\text{-CT}}$. The relationship between the two values, $\Phi_{\text{-An}}$ and $\Phi_{\text{-CT}}$, is dependent on the concentrations. When the concentration of the anthracene and TNM are equal, $\Phi_{\text{-CT}} \simeq 2\Phi_{\text{-An}}$; but in the presence of a 10-fold excess of TNM, $\Phi_{\text{-CT}} = \Phi_{\text{-An}}$, as listed in Table I. Despite our inability to monitor the disappearance of TNM directly, the concentration dependence of the quantum yield demonstrates that only one anthracene donor and TNM are responsible for the CT photochemistry,[25] i.e., eq 13.

$$\text{An} + \text{TNM} \xrightarrow{h\nu_{\text{CT}}} \text{photoproducts} \qquad (13)$$

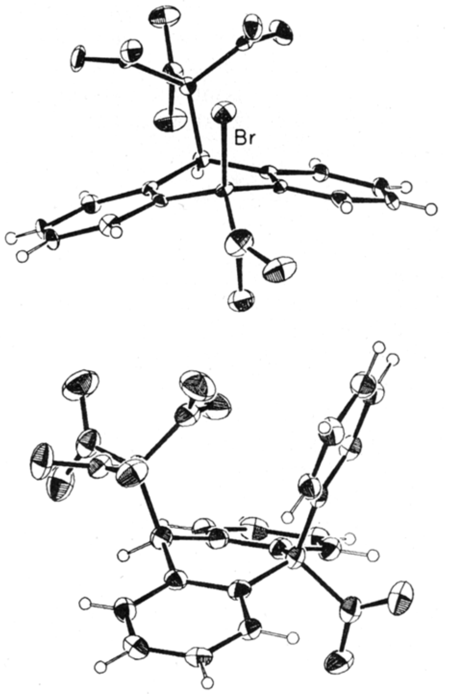
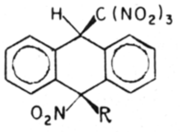


Figure 2. ORTEP diagrams of the photoadducts **1g** and **1i** derived from TNM with 9-bromoanthracene (top) and 9-phenylanthracene (bottom), respectively, by CT irradiation of the EDA complexes.

Examination of the ^{1}H NMR spectrum of the photolyzed solution confirmed the disappearance of the anthracene resonances, and it revealed the presence of new resonances at higher field, particularly an unusually broadened singlet at δ 6.0–6.7. Since the latter coincided with the bleaching of the characteristic anthracene chromophore in the region between λ 350–400 nm,[7] we concluded that photoproducts related to 9,10-dihydroanthracene were formed. Indeed the principal product isolated from the reaction mixture is the meso adduct 1 derived by the addition of the elements of TNM to the 9,10-positions of anthracene.

1 

With most anthracenes, the photochemical reaction mixtures were relatively clean, and the photoadduct 1 could be isolated in good yield simply by fractional crystallization (Table II). These highly nitrated photoadducts exhibited varying degrees of thermal stability—often undergoing an autocatalytic decomposition in solution and sometimes even in the crystalline state at room temperature. Those derived from anthracene with bulky or electron-donating meso substituents, such as phenyl, were generally the least stable. With such labile derivatives, alkanes were used as cosolvents together with excess TNM to promote the direct separation of the photoadduct im-

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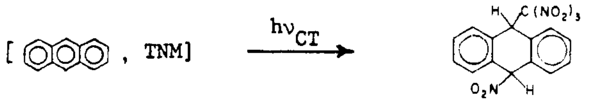
[23] Excitation at wavelengths <430 nm resulted in copious gas evolution accompanied by the heating of the sample and the generation of acid. Homolytic cleavage of the $O_2N–C(NO_2)_3$ bond upon irradiation of TNM under these conditions may be responsible.[24]

[24] (a) Frank, A. J.; Graetzel, M.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 593. (b) Isaacs, N. S.; Abed, O. H. *Tetrahedron Lett.* **1982**, *23*, 2799.

[25] See the derivation in the Experimental Section.

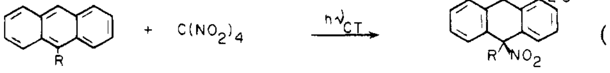
mediately during irradiation.

The structures of the photoproducts were confirmed by X-ray crystallography of the derivatives from 9-phenyl- and 9-bromoanthracene. The ORTEP diagrams of the photoproducts 1 shown in Figure 2 correspond to 1:1 adducts in which the TNM fragments, $C(NO_2)_3$ and NO_2, have added across the meso or 9,10-positions of the anthracene. Figure 2 also shows that the trinitromethyl group is attached regiospecifically at the unsubstituted 10-positions of 9-bromo- and 9-phenylanthracene. The broadened singlet resonance at δ 6.38 and 6.41 in the ^1H NMR spectra of these adducts is assigned to the proton at the 10-position. The reversible sharpening of this resonance with temperature variation is attributed to the restricted conformational and rotational (torsional) motions related to the globular bulkiness of the trinitromethyl substituent. The latter is observed even in the crystalline state, as shown by an X-ray crystallographic determination of a single crystal of the photoadduct **1h** derived from anthracene and TNM.[26] Analysis of the diffraction pattern obtained at room temperature indicates a massive site disorder in the molecule. In particular, the oxygen and the nitrogen atoms of the trinitromethyl portion of the structure could not be refined under conditions in which most of the remaining atoms were fairly well located (see Experimental Section.) The *selected* site disorder in photoadduct **1h** is undoubtedly due to the shallow energy minima associated with the molecular motions of the trinitromethyl group since the problem is clearly absent in the structure of the photoadducts **1g** and **1i** for the more hindered 9-bromo and 9-phenyl derivatives, respectively, in Figure 2.[27]



(14)

The assignment of the broadened singlet resonance in the ^1H NMR spectrum to the 10-proton is also supported by two series of related observations. For example the ^1H NMR spectra of the photoadducts 1 derived from *all* the 9-substituted anthracenes in Table II, showed this characteristic signal to be present in the rather narrow region between δ 6.0–6.7, with one outstanding exception. Thus the photoadduct **1h** of the parent anthracene with TNM shows *two* singlet resonances at δ 6.26 and 6.41, which exhibit different temperature-dependent behavior. As illustrated in Figure 3, the broadened singlet at δ 6.26 undergoes a (reversible) sharpening as the temperature is decreased from 40 to −64 °C, whereas the amplitude of the sharp singlet at δ 6.41 remains unchanged. The broadened singlet at δ 6.26 is thus the same as the other singlets observed in the photoadducts 1 derived from the various 9-substituted anthracenes. The sharp singlet at δ 6.41, unique to the anthracene adduct, must therefore be associated with the proton or carbon 9 bearing the nitro group. We thus conclude that the regiochemistry always directs the trinitromethyl group to the 10-position in 9-substituted anthracenes, i.e., eq 15. Time-resolved spectroscopic studies[15] have identified a hydranthryl radical **2** as the key intermediate in the formation of the photoadduct 1 (vide infra).



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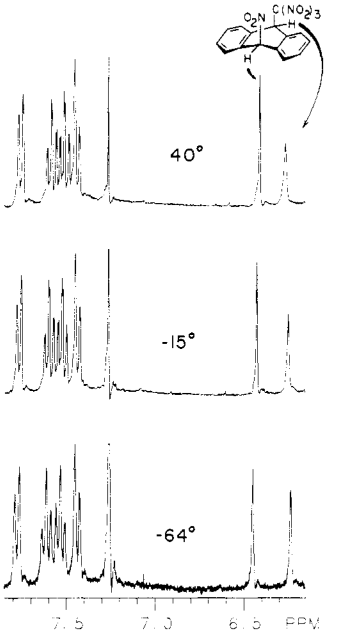

Figure 3. The ^1H NMR spectrum (300 MHz) of 9-nitro-10-(trinitromethyl)-9,10-dihydroanthracene (**1h**) in $CDCl_3$ at 40, −15, and −64 °C.

The CT photochemistry of the anthracene–TNM complexes is not highly sensitive to the presence of dioxygen, since rigorous degassing of the solution prior to photolysis did not materially affect either the distribution of photoproducts or the kinetics at room temperature.[28] The addition of small quantities of weak nucleophiles such as water, alcohol, or the hindered base 2,6-di-*tert*-butylpyridine had little effect, as long as the bulk properties of the solvent were not substantially changed. In this regard the formation of products other than the photoadduct 1 deserves comment. Those anthracenes bearing electron-withdrawing substituents such as nitro, halo, and carbonyl groups afforded consistently high yields of the photoadducts **1a** and **1d–g** as listed in Table II. In addition to 5–10% of the residual starting material, we also isolated small amounts of products which we infer to be substituted anthracenes, as judged by the presence of the characteristic anthracene chromophore in the electronic absorption spectrum. Such products of rearomatization are derived from the photoadduct 1 by either elimination of nitrous acid, HR (where R is such 9-substituents as chloro, bromo, etc.), or nitroform. It is conceivable that these processes may be occurring to a minor extent during the irradiation. With 9-anthraldehyde, the TNM adduct **1c** is formed in 70% yield, together with 14% of the reduced product 9-formyl-10-(trinitromethyl)dihydroanthracene **3**.

Those anthracenes having electron-donating substituents such as methoxy, methyl, and phenyl generally afford lower yields of the photoadducts 1. Thus only 60% of **1i** together with 20% of the 9-hydroxy analogue is formed from 9-phenylanthracene. For confirmation of the NMR analysis, the structure of **4** was established by X-ray crystallography and the ORTEP diagram is presented in Figure 4.

The electron-rich donor 9-methoxyanthracene gave a mixture of products of which only the 10-(trinitro-

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[26] For details (including the structural ambiguities), see the Experimental Section.

[27] Note that the X-ray crystallography for the bromo and phenyl derivatives in Figure 2 was carried out at −160 °C. The X-ray diffraction data of the parent anthracene adduct was collected at ambient temperatures.

[28] Masnovi, J. M.; Levine, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *106*, 4356.

Table III. Solvent Dependence of the Yields of Photoproducts from the CT Excitation of Anthracene–TNM Complexes[a]

		solvent (% yield of products)[b]				
substituent	product	alkane	benzene	cumene	CH_2Cl_2	MeCN[c,d]
H	**1h**	37[e]	23	25	15 (19)[f]	5
	6h	0[e]	2	2	4 (10)[f]	10
9-Br	**1g**			86	80 (40)[f]	65
	5g			0	3 (20)[f,g]	3
	6g			6	12 (15)[f]	*h*
9-C_6H_5[c]	**1i**	84[i]	70		64 (36)[f]	21
	4i	7[i]	14		24 (45)[f]	14
	6i	2[i]	3		10 (20)[f]	*h*
9-CH_3, 10-CH_3	**1m**	43[j]			15	
	7	5[j]			20	

[a] At room temperature, starting with 0.05 M anthracene and 0.1 M TNM at 25 °C irradiated 10 min through Corning 3-72 (430 nm) filter. [b] Determined by ^{1}H NMR analysis. Isolated yields in parentheses. [c] At 4 °C in an ice–water bath. [d] Saturated anthracene solution. [e] Cyclohexane solvents. [f] At −70 °C in CD_2Cl_2. [g] 40% yield at −95 °C in CD_2Cl_2. [h] Not determined due to incomplete conversion of starting material. [i] Methycyclohexane solvent. [j] Pentane solvent.

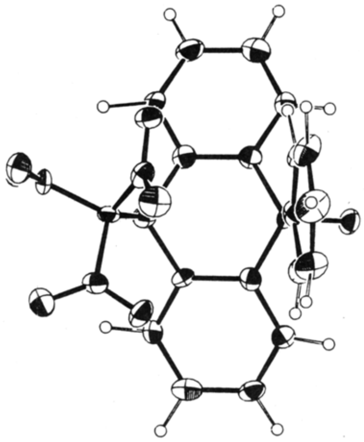


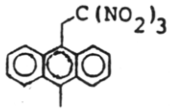
Figure 4. Top view of the ORTEP diagram of 9-phenyl-9-hydroxy-10-(trinitromethyl)-9,10 dihydroanthracene **4** obtained from the CT irradiation of 9-phenylanthracene and TNM.

methyl)anthrone (**5**) could be identified in major amounts (40%). [It is interesting to note that **5** is also obtained as a minor byproduct (6%) from the photoreaction of 9-anthryl acetate.] Since the repetition of the experiment at low temperatures gave essentially the same results, we conclude that the photoadduct **1j** from 9-methoxyanthracene is not an important product, if formed at all. The photoreaction mixture derived from 9-methylanthracene and TNM consisted of a number of components. Attempts to isolate pure products were unsuccessful, owing to their temperature sensitivity. However, an analysis of the ^{1}H NMR spectrum of the crude reaction mixture indicated that the 9-methyl substituent had undergone partial substitution (vide infra).

The solvent dependence of the CT photochemistry generally follows the polarity—the best yields of the photoadduct being obtained in hydrocarbon solvents when the solubility of the anthracene permits. The yields of photoadduct **1** from electron-rich anthracenes also appear to be more sensitive to solvent polarity than those derived from the electron-deficient anthracenes, as shown by the results in Table III. For example in dichloromethane as solvent, 9-phenylanthracene yields 60% of the photoadduct **1i** together with 20% of the 9-hydroxy analogue **4**, but in methylcyclohexane as solvent, it produces more than 85% of the photoadduct **1i** and only 7% of **4**.

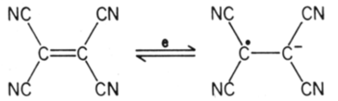
The meso disubstituted anthracenes also react with TNM qualitatively as well as the 9-substituted derivatives, although the quantum yields were not established. However, 9,10-diphenylanthracene, 9,10-dibromoanthracene, 9,10-dimethoxyanthracene, and 9,10-dimethylanthracene all form little, if any, of the photoadduct **1** in polar solvents. The photoproducts by and large have not been characterized, largely owing to their thermal instability. For example, 9,10-dimethylanthracene forms a highly unstable adduct which decomposes in the crystalline state even at −20 °C. It can be isolated in good yield when the CT irradiation is carried out in cyclohexane as the solvent. We tentatively assign to it the structure **1** similar to that of the other photoadducts. In the more polar dichloromethane, another product **7** is observed, which preliminary studies indicate to be derived by side chain substitution.

7



Discussion

The efficient photochemistry which results from the CT excitation of the EDA complexes of anthracene and tetranitromethane stands in strong contrast to the photoresistant behavior previously observed in the corresponding tetracyanoethylene complexes.[8] Since the excited ion pair is formed upon CT irradiation in both systems,[8,15] the difference must lie in the nature of acceptor anion. Indeed TCNE is known to undergo reversible electron transfer,[29]



(16)

whereas the anion radical of TNM is unstable and fragments to trinitromethide and NO_2 on the picosecond time scale,[30,31] i.e., eq 17. The rapid fragmentation of $TNM^{-\cdot}$

$$C(NO_2)_4 \xrightarrow{e} C(NO_2)_3^- + NO_2\cdot \qquad (17)$$

competes with the energy-wasting back electron transfer, which is the dominant pathway for deexcitation of the CT excited state of the TCNE complex (see eq 4). Therefore the efficient photochemical reactivity of the EDA complexes of TNM can be ascribed to the dissociative nature of electron capture by TNM. Accordingly the CT excitation of the TNM complex *effectively* results in electron transfer to afford the donor radical cation and the frag-

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(29) (a) Webster, O. W.; Mahler, W.; Benson, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3678. (b) Itoh, M. *Ibid.* **1970**, *92*, 886; *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1947.

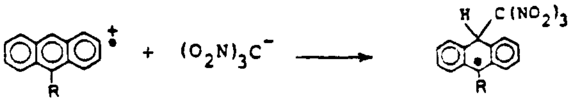
(30) (a) Rabani, J.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem.* **1965**, *69*, 53. (b) Chaudhri, S. A.; Asmus, K. D. *Ibid.* **1972**, *76*, 26.

(31) See also the time-resolved spectroscopic studies in ref 19.

mentation products of the acceptor, i.e., eq 18. Indeed

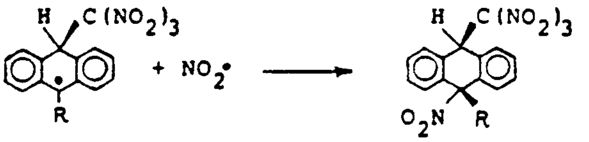
$$[\mathrm{An,TNM}] \underset{k_{-1}}{\overset{h\nu_{\mathrm{CT}}}{\rightleftharpoons}} [\mathrm{An^+,TNM^-\cdot}] \xrightarrow{k_2} [\mathrm{An^+,C(NO_2)_3^-,NO_2}] \quad (18)$$

the measured quantum yields of ~0.7 in Table I indicate that the CT excited ion pairs fragment to the geminate species in eq 18 roughly twice as fast as they undergo back electron transfer to regenerate the original EDA complex, i.e., $k_2/k_{-1} \sim 2.3$. Since the oxidation potential of trinitromethide ($E° = 1.95$ V)[32] is more positive than that of An ($E° < 1.7$ V),[7] the driving force for the back electron transfer from the geminate pair (i.e., $[\mathrm{An^{+}\cdot,C(NO_2)_3^-} \rightarrow \mathrm{An,\cdot C(NO_2)_3}]$, etc.) is endergonic.[33] Consequently the fragmentation of TNM upon CT excitation assures the *irreversible* destruction of the EDA complex, and it is reflected in the high quantum yields. The subsequent chemistry of the ions and radicals can be understood by considering the nature of the principal photoadduct **1** and the byproducts. Thus the attachment of the trinitromethyl group to the 10-position of anthracene irrespective of the polar character of the 9-substituent (viz., electron donating or electron attracting) is consistent with the collapse of the ion pair to form the more stable hydranthryl radical **2**,[34-37] i.e., eq 19. Owing to the mutual annhilation of charge in such an ion-pair, the collapse is expected to be most rapid when the substituent R is electron-withdrawing and the solvent is nonpolar.[28] The higher yields of the photoadduct **1** isolated under these circumstances (see Tables II and III) are in accord with this expectation. The presence of the hydranthryl radical **2** as an intermediate is confirmed by its transient absorption spectrum with $\lambda_{\max}$ 550 nm in the time-resolved spectroscopic study of the CT irradiation of the anthracene–TNM complexes.[19,28]

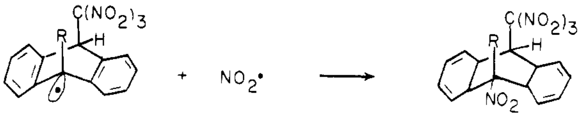


(19)

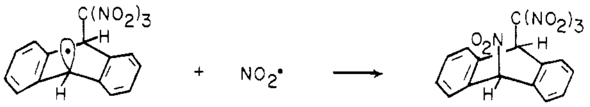
The subsequent coupling of the hydranthryl radical **2** with NO_2 represents the last stage in the formation of the photoadduct **1**. The molecular structure of the adducts in Figure 2 indicate that the NO_2 adds to the hydranthryl radical stereoselectively from the face opposite the bulky trinitromethyl group. This corresponds to an overall antiaddition of the TNM elements, $C(NO_2)_3$ and NO_2, to the meso positions of the anthracenes. Steric interactions are known to play an important role in the disposition of groups in the dihydroanthracene conformations.[38] Thus bulky substituents at the 9- and 10-positions prefer pseudoaxial orientations.[39] Indeed the X-ray crystal structures illustrated in Figures 2 and 4 all show the trinitromethyl groups occupying pseudoaxial positions in the photoproducts. This orientation is also likely to be maintained in the hydranthryl radical **2**. Consequently, the reaction of this conformation with NO_2 would lead to photoadducts with overall anti stereochemistry,[40] i.e., eq 21. A smaller substituent such as R = H at the 9-position might easily occupy a pseudoequatorial position, as in the hydranthryl radical **2i**. Reaction of this conformation with NO_2 accounts for the syn addition observed with anthracene,[26] i.e., eq 22. The isolation of an isomeric mixture of photoadducts **1b** from 9-cyanoanthracene[42] suggests that there may be a conformational ambiguity in the hydranthryl radical **2** when it contains a small, linear cyano substituent.



(20)

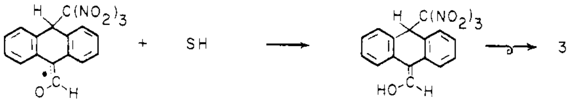


(21)



(22)

The formation of the photoadducts **1** in good yields with high regio- and stereoselectivity is impressive—especially if one considers the number and types of reactive intermediates generated during the CT photochemistry. No doubt much of the success of such a complex pathway derives from the favorable combination of rate constants for ion pair and radical pair interactions in eq 19 and 20, respectively.[28] The diversion of these reactive intermediates accounts for the byproducts of the CT photochemistry. For example, the formation of the reduced product **3** in relatively high yields from 9-anthraldehyde can arise from hydrogen atom transfer to the delocalized hydranthryl radical,[43] e.g., eq 23. Moreover the hydranthryl



(23)

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[32] Measured in acetonitrile vs. SCE: Kokorakina, V. A.; Foektistov, L. G.; Shevelev, S. A.; Fianzil'berg, A. A. *Elektrokhimiya* **1970**, *6*, 1849.

[33] For a relationship between the rate and driving force for outer-sphere electron transfer, see: Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 4186.

[34] Anthracene cation radicals are known to react at the meso positions.[35]

[35] Hammerich, O.; Parker, V. D. "Electrooxidation in Organic Chemistry"; Yoshida, K., Ed.; Wiley: New York, 1984; pp 66 ff. See also: Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 243.

[36] Most substituents stabilize benzylic radicals irrespective of their electron-withdrawing or -attracting properties. See: O'Neal, H. E.; Benson, S. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York 1973; Vol. II, pp 275 ff.

[37] The propensity of anthracene and its radical cation to react at the meso positions is in accord with kinetics and thermodynamic considerations. See: Brown, R. D. *J. Chem. Soc.* **1950**, *691*, 3249; **1951**, *1612*, 3129. Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. Hess, B. A.; Schaad, L. J. *Ibid.* **1971**, *93*, 305, 2413. Herndon, W. C. *Ibid.* **1973**, *95*, 2404. Herndon, W. C.; Ellzey, M. L. *Ibid.* **1974**, *96*, 6631. Fukui, K. *Fortschr. Chem. Forsch.* **1970**, *15*, 1.

[38] Daney, M.; Lapouyade, R.; Bouas-Laurent, H. *J. Org. Chem.* **1983**, *48*, 5055.

[39] (a) Cam, W.; Bock, H. *Chem. Ber.* **1978**, *111*, 3585; (b) Dalling, D. K.; Zilm, K. W.; Grant, D. M., Heeschen, W. A.; Horton, W. J.; Pugmire, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 4817.

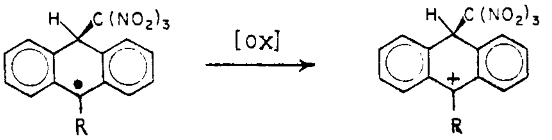
[40] The anti addition could also result from a delocalized hydranthryl radical in which the trinitromethyl group serves to bridge the 9- and 10-positions. Attack by NO_2 concomitant with ring opening could lead to overall antiaddition.[41] However, the observation of the syn adduct with R = H does not support this rationalization of the stereochemistry.

[41] Similar arguments have been employed in the stereochemistry of homolytic bromine additions to alkenes via bridged β-bromoalkyl radicals. Kaplan, L. "Bridged Free Radicals"; Marcel Dekker: New York, 1972.

[42] See the comments in the Experimental Section.

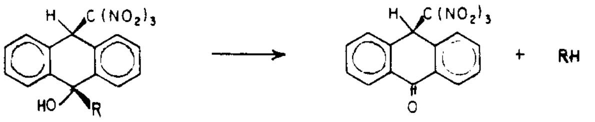
[43] The possibility of **3** being formed from a photochemical addition of nitroform to 9-anthraldehyde can be ruled out. However the absorption of light by anthraldehyde (Pyrex filter) did result in the formation of an unidentified substituted 9,10-dihydroanthraldehyde product. This product [^{1}H NMR δ 6.06 (s, 1 H), 7.25–7.5 (m, 8 H), 10.90 (s, 1 H)] was neither **3** nor the photodimer of anthraldehyde [δ 5.51 (s, 1 H), 6.64 (d, 2 H, J = 7.3 Hz), 6.86 (td, 2 H, J = 7.4, 1.3 Hz), 6.92 (td, 2 H, J = 7.4, 1.1 Hz), 7.04 (dd, 2 H, J = 1.1, 7.3 Hz), 10.12 (s, 1 H)].

radicals **2** may be diverted by oxidation with TNM,[44] which occurs in competition with the trapping by NO_2. Such a side reaction is most likely to occur with substituents such as phenyl, methoxy, and acetoxy which are capable of stabilizing the derived benzylic cation, i.e., eq 24, where



(24)

R = Ph, OMe, OAc. Subsequent reaction with adventitious water accounts for the alcohol **4** and the anthrone **5** (R = OMe,OAc) observed as important byproducts especially from 9-phenylanthracene and 9-methoxyanthracene, respectively. The formation of **4** or **5** in yields



(25)

which increase with the variation of the substituent in the order R = OMe > Ph > OAc is consistent with the expected ease of oxidation of the corresponding hydranthryl radical **2**.[45] Finally, aromatization can occur from the benzylic cation by proton loss to afford the 10-trinitromethyl-substituted anthracene **6**.

Summary and Conclusion

Trinitromethane (TNM) forms photoreactive EDA complexes with a series of 9-substituted and 9,10-disubstituted anthracenes An. These complexes undergo efficient chemical reaction following charge-transfer excitation owing to the instability of the acceptor anion. Thus TNM$^{-}\cdot$ is formed concomitantly with An$^{+}\cdot$ upon irradiation, but it rapidly fragments to $C(NO_2)_3^-$ and NO_2. These fragmentation products are efficiently trapped as the meso adducts of the anthracene, the structures of which are established by X-ray crystallography. The CT photochemistry of anthracene–TNM complexes is akin to the photochemistry reported for anthracene with CCl_4,[46] which doubtlessly proceeds via an analogous EDA complex. With both acceptors, the quantum efficiency of CT photochemistry depends heavily on the ease of fragmentation of the anion radical, and the products are determined by the relative rates of the subsequent ion pair and radical pair interactions.

Experimental Section

Materials. Tetranitromethane[47] (Aldrich) was purified by the method of Bielski and Allen.[48] Anthracene, 9-cyanoanthracene, 9-acetylanthracene, and 9-chloroanthracene from Aldrich were each crystallized from ethanol.[49] 9-Phenylanthracene (Aldrich Gold Label), 9,10-diphenylanthracene, and 9,10-dimethylanthracene (Aldrich) were used as received. 9-Bromoanthracene and 9-anthraldehyde from Aldrich were each purified by repeated crystallizations from ethanol.[49] 9-Methoxyanthracene,[50] 9-nitroanthracene,[51] methyl 9-anthroate,[52] 9-anthryl acetate,[50] 9,10-dimethoxyanthracene,[53] and 9,10-dibromoanthracene were prepared according to the methods described in the literature. The solvents methylene chloride (Aldrich Gold Label), chloroform (Fisher), *n*-pentane (Matheson, Coleman and Bell), and cyclohexane (Matheson, Coleman and Bell) were each dried over molecular sieves (Linde, 5A) and distilled under argon prior to use. Nitroform was prepared by reduction of tetranitromethane.[54]

Photochemistry of the EDA Complexes. General Procedure for Product Isolation. A concentrated solution of the anthracene (saturated or >0.1 M) and 1.2 equiv of TNM in methylene chloride, *n*-pentane, or cyclohexane was maintained at 10–15 °C in a water-filled Pyrex Dewar flask. The solution was irradiated with light from either a xenon or mercury high-pressure lamp which was passed through a Corning 3-69 glass sharp cut-off filter until the CT absorptions of the EDA complex were bleached (2–15 min). Crystals of the photoproduct **1** sometimes formed spontaneously upon irradiation. Concentration of the reaction mixture in vacuo allowed the collection of the major products by filtration. Recrystallization from a mixture consisting of either methylene chloride and carbon tetrachloride or methylene chloride and hexane below room temperature afforded the pure products for characterization. Additional material was obtained by rapid removal of the solvent from the original filtrate, followed by fractional crystallization of the residue. Mechanical separation of the crystals of different morphology afforded additional **1** as well as small amounts of other products given in Table III. Generally, the photoadducts **1** were thermally unstable. They decomposed autocatalytically in solution with the release of acid and concomitant rearomatization to disubstituted anthracenes. Small amounts of these decomposition products were obtained following the isolation of the primary adducts. Some examples of the CT photochemistry for specific anthracenes are described below.

9-Nitroanthracene. A solution of 111 mg (0.50 mmol) of 9-nitroanthracene and 100 mg (0.51 mmol) of TNM dissolved in 5 mL of methylene chloride was irradiated for ~15 min. Colorless crystals of **1** (R = NO_2) formed during the irradiation. The solution was concentrated and filtered. The slightly yellow precipitate was taken up in ~15 mL CH_2Cl_2, and ~5 mL of CCl_4 was added. Colorless crystals of **1a** (R = NO_2) formed during the slow evaporation of the solvent. The crystals were collected by filtration, washed with several small portions of cold CCl_4, and air-dried to afford 135 mg (65%) of **1a** (R = NO_2). Recrystallization from a mixture of CH_2Cl_2 and CCl_4 afforded colorless crystals, which melted over a range from 129 to 240 °C accompanied by gas evolution, a series of color changes, and crystallization remelting:[55] ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.22 (br s, 1 H),

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[44] The oxidation of carbon-centered radicals such as α-aminoalkyl and α-alkoxyalkyl by TNM has been observed to occur at close to diffusion-controlled rates. See: Schuchmann; M. N., Steenken, S.; Wroblewski, J.; Von Sonntag, C. *Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med.* **1984**, *46*, 225. Frank, A. J.; Graetzel, M.; Henglein, A.; Janata, E. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 547. Hiller, K. O.; Asmus, K. D. *J. Phys. Chem.* **1983**, *87*, 3682; Broszkiewicz, R. K.; Soeylemez, T.; Schulte-Frohlinde, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 368. Vorob'eva, R. P., Kozlov, Yu. N.; Kokorin, A. I.; Petrov, A. N. *Khim. Fiz.* **1982**, 1518.

[45] (a) Alternatively, NO_2 is ambident and is known to react with organic radicals to form nitro and nitrite products. In the gas phase, the reaction at oxygen is favored kinetically, but the reaction at nitrogen seems to be favored thermodynamically, Park, J. Y.; Gutman, D. *J. Phys. Chem.* **1983**, *87*, 1844. Formation of **4** and **5** may result from the reaction of NO_2 with **2** to form the nitrites, followed by hydrolysis or loss of NO. (b) Radicals add to 9-nitroanthracene at the 10-position, and the resulting α-nitrohydranthryl may rearrange to nitrites which eliminate NO. Testaferri, L.; Tingoli, M.; Tiecco, M. *J. Chem. Soc., Perkin Trans. 2* **1983**, 543. (c) NO_2 itself may in some cases be able to promote the oxidation in eq 24, see, e.g.: Pryor, W. A.; Gleicher, G. J.; Cosgrove, J. P.; Church, D. F. *J. Org. Chem.* **1984**, *49*, 5189. (d) Adducts **1** appear to be primary products and are formed in high yields even at low temperature (Table III). At low temperature, however, the product yields were more sensitive to the presence of oxygen and nucleophiles.

[46] Vermeersh, G.; Marko, J.; Febvay-Garot, N.; Caplain, S.; Lablache-Combier, A. *Tetrahedron* **1978**, *34*, 1493.

[47] Liang, P. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. 3, p 803.

[48] Bielski, B. H. J.; Allen, A. O. *J. Phys. Chem.* **1967**, *71*, 4544.

[49] A small amount (~1%) of an anthracene impurity remained after this treatment.

[50] Meek, J. S.; Monroe, P. A.; Bouboulis, C. J. *J. Org. Chem.* **1983**, *48*, 2572.

[51] Braun, C. E.; Cook, C. D.; Merritt, C., Jr.; Rousseau, J. E. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. 4, p 711.

[52] Parish, R. C.; Stock, L. M. *J. Org. Chem.* **1965**, *30*, 927.

[53] Barnett, E. B.; Cook, J. W.; Mathews, M. A. *J. Chem. Soc.* **1923**, *123*, 1994.

[54] Homer, J.; Huck, P. J. *J. Chem. Soc. A* **1968**, 277.

7.56 (br d, 2 H, J = 8 Hz), 7.65 (td, 2 H, J = 1.5, 7.3 Hz), 7.69 (td, 2 H, J = 1.6, 7.3 Hz), 7.76 (dd, J = 1.6, 7.8 Hz); UV (log ϵ) 235 (5.01) sh, 280 (4.36) nm; IR (KBr or Nujol) 2942 (w), 2877 (w), 1625 (s), 1597 (vs), 1581 (vs), 1576 (vs), 1491 (m), 1452 (m), 1354 (m), 1308 (s), 1298 (s), 1171 (w), 961 (w), 845 (m), 823 (s), 807 (m), 795 (m), 769 (m), 733 (s), 677 (w), 652 (w), 612 (w), 581 (m), 378 (w), 361 (m) cm^{-1}. Anal. Calcd for $C_{15}H_9N_5O_{10}$: C, 42.97; H, 2.16; N, 16.71. Found: C, 42.76; H, 2.32; N, 16.60.

The crystals of **1a** (R = NO_2) decomposed violently without melting when heated slowly to 130 °C in a melting point capillary. The resultant slightly yellow powder was characterized as 10-(trinitromethyl)anthrone **5**[45b] from the ^{1}H NMR spectrum in $CDCl_3$ (Me_4Si): δ 6.02 (br s, 1 H), 7.59–7.66 (m, 4 H), 7.68 (dd, 2 H, J = 2.4, 6.2 Hz), 8.25 (dd, 2 H, J = 2.4, 6.8 Hz). After recrystallization from a mixture of CH_2Cl_2 and CCl_4 it afforded pale yellow crystals, which showed a complex melting behavior: UV (log ϵ) 236 (5.10) sh, 280 (4.50) sh nm; IR (KBr) 2944 (m), 1670 (vs), 1620 (vs), 1597 (vs), 1574 (vs), 1460 (m), 1400 (w), 1351 (w), 1322 (s), 1314 (s), 1296 (s), 1287 (s), 1169 (w), 1094 (w), 933 (m), 848 (w), 824 (w), 812 (s), 795 (s), 767 (w), 723 (m), 715 (w), 687 (m), 636 (w), 582 (w) cm^{-1}. Anal. Calcd for $C_{15}H_9N_3O_7$: C, 52.49; H, 2.64; N, 12.24. Found: C, 52.53; H, 290; N, 12.20.

9-Bromoanthracene. A solution of 128 mg (0.50 mmol) of 9-bromoanthracene and 100 mg of TNM (0.51 mmol TNM) dissolved in 5 mL of CH_2Cl_2 was irradiated for ~10 min. The solvent was evaporated to yield a yellow residue, which was taken up in ~3 mL of CH_2Cl_2, and ~1 mL of CCl_4 was added. Over a period of several hours, colorless crystals formed, which were collected by filtration, washed three times with small portions of cold CCl_4, and air-dried to afford 136 mg (60%) of **1g** (R = Br) as colorless plates. (The structure of **1g** (R = Br) was confirmed by X-ray crystallography.) Recrystallization again from a mixture of CH_2Cl_2 and CCl_4 afforded colorless plates of analytically pure material, which underwent a dramatic series of color changes, gas evolution, and partial melting–remelting between 112 and 200 °C:[55] ^{1}H NMR ($CDCl_3$ Me_4Si) δ 6.38 (br s, 1 H), 7.47 (m, 4 H), 7.57 (td, 2 H, J = 2.1, 7.2 Hz), 7.68 (d, 2 H, J = 8.1 Hz); UV (log ϵ) 236 (5.10) sh, 280 (4.50) sh nm; ^{13}C NMR ($CDCl_3$, $^{13}CDCl_3$ δ 77.00 at 75.46 MHz (C)) δ 47.4 (d, J = 144 Hz), 94.6 (s), 125.2 (s), 128.6 (d, J = 164 Hz), 129.1 (dd, J = 12, 164 Hz), 131.3 (d, J = 164 Hz), 131.6 (d, J = 170 Hz), 135.4 (s) [the trinitromethyl resonance was tentatively assigned to a very weak signal at δ 150.8[56]]; IR (KBr or Nujol) 2946 (w), 1626 (vs), 1592 (vs), 1582 (s), 1562 (vs), 1493 (w), 1449 (w), 1340 (m), 1293 (s), 991 (w), 837 (w), 810 (m), 793 (m), 766 (m), 717 (m), 582 (w) cm^{-1}. Anal. Calcd for $C_{15}H_9N_4O_8Br$: C, 39.76; H, 2.02; N, 12.36. Found: C, 39.73; H, 2.03; N, 12.32.

Slow heating of the crystals of **1g** (R = Br) in a melting point capillary to 118 °C caused the vigorous breakup of the crystals and formed the same product **5** [10-(trinitromethyl)anthrone],[45b] which was obtained by heating **1a** (R = NO_2) (vide supra). Fractional recrystallization of the filtrate afforded a small amount of additional **1g** (R = Br) (which was unstable in solution), and it was separated mechanically from another product (orange needles). The new product was derived from the thermal decomposition of **1g** (R = Br), and its spectral characteristics were consistent with it being an anthracene derivative.

9-Phenylanthracene. A solution of 127 mg (0.50 mmol) of 9-phenylanthracene and 100 mg (0.51 mmol) of TNM dissolved in 5 mL of CH_2Cl_2 was irradiated for 7 min. The solvent was removed, the residue was taken up in ~2 mL of CH_2Cl_2, and ~1 mL of CCl_4 was added. Crystallization occurred after a few hours, and the very pale yellow crystals were collected by filtration. After washing with a small amount of cold CCl_4, 61 mg (30%) of the alcohol **4** [9-phenyl-9-hydroxy-10-(trinitromethyl)-9,10-dihydroanthracene] was obtained. The structure of **4** was determined by X-ray crystallography: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.43 (s, 1 H), 6.32 (br s, 1 H), 7.23–7.32 (m, 7 H), 7.41 (t, 2 H, J = 7.6 Hz), 7.62 (t, 2 H, J = 7.6 Hz), 8.19 (d, 2 H, J = 7.8 Hz); UV (log ϵ) 220 (5.52) sh, 254 (4.75), 284 (4.52) sh nm; IR (KBr) 3058 (w), 2867 (w), 1605 (vs), 1595 (vs), 1578 (vs), 1549 (vs), 1493 (m), 1448 (m), 1385 (m), 1340 (s), 1295 (vs), 1217 (w), 839 (m), 812 (m), 809 (m), 795 (s), 776 (m), 767 (s), 752 (s), 737 (s), 697 (s), 689 (s), 648 (w), 640 (w), 579 (w) cm^{-1}.

Alternatively, a solution of 5 mg of 9-phenylanthracene and 8 μL (~3 equiv) of TNM in 1 mL of pentane was irradiated for 5 min. It resulted in the precipitation of colorless crystals of **1i** (R = C_6H_5). Concentration afforded a high yield (4.5 mg, 90%) of **1i** (R = C_6H_5) which was very unstable in solution, decomposing autocatalytically. It was however successfully recrystallized from cyclohexane to afford colorless plates, which showed the characteristically complex melting behavior typical of the photoadducts **1** from 85 to 200 °C. The structure of **1i** (R = C_6H_5) was established by X-ray crystallography: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.41 (br s, 1 H), 7.25 (dt, 2 H, J = 1.6, 7.5 Hz), 7.36 (t, 2 H, J = 7.6 Hz), 7.44 (m, 5 H), 7.52 (td, 2 H, J = 1.0, 7.6 Hz), 7.63 (td, 2 H, J = 1.0, 7.3 Hz); UV (log ϵ) 230 (5.14) sh, 258 (4.71), 283 (4.29 sh nm; IR (KBr) 3401 (m), 3264 (w), 3032 (w), 1614 (vs), 1599 (vs) 1578 (vs), 1493 (w) 1484 (w), 1450 (m), 1355 (m), 1292 (s), 1163 (w), 1036 (w) 1027 (m), 1016 (m), 1005 (m), 913 (w) 837 (m), 812 (m), 794 (s), 773 (s), 768 (s), 753 (s), 694 (s), 636 (m), 590 (m), 496 (m) cm^{-1}.

Anthracene. A solution of 93 mg (0.50 mmol) of anthracene and 100 mg (0.51 mmol) of TNM dissolved in 5 mL of CH_2Cl_2 was irradiated for ~10 min. The solvent was removed, the residue was taken up in ~3 mL of CH_2Cl_2, and ~1 mL of CCl_4 was added. Slow crystallization occurred over a period of several hours to give a low yield of a single colorless glassy crystal identified as **1h** (R = H). An improved yield of **1** resulted when a saturated solution of anthracene (1–2 mg) and 8 μL (~5 equiv) of TNM in 1 mL of pentane or CCl_4 was irradiated. Under these conditions, crystals of **1h** (R = H) formed during the irradiation, and they were collected by filtration. After washing with several small portions of cold CCl_4, **1h** (R = H) was obtained. Recrystallization of **1** from cyclohexane afforded colorless, thin plates, which melted at 160–161 °C with vigorous evolution of gas:[55] ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.26 (br s, 1 H), 6.41 (s, 1 H), 7.44 (dd, 2 H, J = 1.4, 7.6 Hz), 7.51 (td, 2 H, J = 1.4, 7.6 Hz), 7.58 (td, 2 H, J = 1.4, 7.6 Hz), 7.76 (dd, 2 H, J = 1.4, 7.6 Hz); UV (log ϵ) 227 (5.15) sh, 252 (4.68), 280 (4.32) sh nm; ^{13}C NMR spectrum ($CDCl_3$, $^{13}CDCl_3$ δ 77.00 at 75.46 M Hz (C)) δ 48.4 (d, J = 139 Hz), 85.3 (d, J = 149 Hz), 128.9 (s), 129.5 (d, J = 160 Hz), 130.0 (s), 130.3 (dd, J = 6.3, 170 Hz), 130.7 (dd, J = 8.3, 167 Hz), 133.1 (d, J = 172 Hz) [the $^{13}C(NO_2)_3$ resonance was not observed[56]]; IR (KBr) 2928 (w), 1624 (s), 1594 (vs), 1580 (vs), 1557 (vs), 1493 (m), 1452 (w), 1385 (w), 1353 (s), 1294 (s), 1257 (w), 864 (w), 852 (w), 824 (w) 814 (m), 793 (m) 781 (w) 769 (w), 762 (m), 722 (m), 633 (w), 579 (w) cm^{-1}. Anal. Calcd for $C_{15}H_{10}N_4O_8$: C, 48.14; H, 2.69; N, 14.97. Found: C, 48.27; H, 2.70; N, 14.87. ^{1}H NMR analysis of the filtrate indicated that it contained a mixture of products suggestive of symmetrically disubstituted meso derivatives of 9,10-dihydroanthracene.

Recrystallization of **1** from a 4:1 mixture of CH_2Cl_2 and p-xylene afforded large colorless plates suitable for an X-ray determination.

9-Anthraldehyde. A solution of 103 mg (0.5 mmol) of 9-anthraldehyde and 100 mg (0.51 mmol) of TNM dissolved in 5 mL of CH_2Cl_2 was irradiated for ~15 min. The solvent was removed in vacuo, the residue was taken up in ~2 mL of CH_2Cl_2, and 1 mL of CCl_4 was added. Slow crystallization afforded 60 mg (30%) of powdery pale yellow crystals of **1c** (R = CHO). Recrystallization from a mixture of CH_2Cl_2 and CCl_4 afforded colorless plates: ^{1}H NMR ($CDCl_3$ Me_4Si) δ 6.28 (br s, 1 H), 7.59 (m, 6 H), 7.65 (m, 2 H), 10.11 (s, 1 H); UV (log ϵ) 230 (5.19) sh, 250 (4.57) sh nm; IR (KBr) 2952 (w), 1744 (s), 1623 (vs), 1595 (vs), 1578 (vs), 1556 (vs), 1493 (w), 1450 (w), 1384 (w), 1334 (m), 1297 (s), 842 (m), 814 (m), 795 (s), 772 (m), 712 (w), 690 (w), 584 (w) cm^{-1}. Anal. Calcd for $C_{16}H_{10}N_4O_9$: C, 47.77; H, 2.51; N, 13.93. Found: C, 47.90; H, 2.54; N, 13.93. Fractional crystallization of the filtrate afforded two morphologically distinct crystalline forms, which were mechanically separated to give an additional 27 mg (13%) of **1c** (R = CHO) and 21 mg (12%) of **3**. Recrystallization from a mixture of CH_2Cl_2 and CCl_4 afforded colorless needles of **3**, which melted at 95–97 °C with gas evolution: ^{1}H NMR ($CDCl_3$,

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(55) 9-Nitro-9,10-dihydroanthracenes characteristically undergo dramatic and violent decomposition when heated, see ref 53.

(56) The ^{13}C NMR of tetranitromethane (neat with 1% C_6D_6 for locking) is a nonet nine lines due to coupling to four equivalent ^{14}N, δ 119.6 relative to C_6D_6, δ 128, J = 9.5 Hz). This indicates that the predominant species present is $C(NO_2)_4$ (rather than isomers such as trinitromethyl nitrite). The resonances of the trinitromethyl groups in the products might be difficult to observe because of their multiplicity, quadrupolar effects of the ^{14}N nuclei, and the absence of Overhauser enhancement.

Me_4Si) δ 6.58 (br s, 1 H), 5.50 (d, 1 H, J = 1.5 Hz), 7.43 (d, 4 H, J = 2.8 Hz), 7.53–7.60 (m, 4 H), 9.60 (d, 1 H, J = 1.5 Hz); IR (KBr) 2950 (w), 1740 (s), 1624 (vs), 1576 (vs), 1559 (vs), 1384 (s), 1332 (m), 1297 (s), 841 (m), 814 (m), 794 (s), 773 (m), 713 (m), 692 (m), 582 (m) cm^{-1}.

9-Anthryl Acetate, 9-Acetylanthracene, 9-Chloroanthracene, and Methyl 9-Anthroate. Irradiations of 0.50 mmol of these arenes with 100 mg (0.51 mmol) of TNM in CH_2Cl_2 for ~10 min proceeded in a manner described above to afford in good yields the adducts 1 (R = CO_2CH_3, $OCOCH_3$,$COCH_3$, and Cl) after evaporation of the solvent. The yields of the crude products were about 80% in each case. The spectroscopic data for these products, reported below, allow the identification of the products as the photoadducts 1. (However, the stereochemistry has not been established by X-ray crystallography.) **1d** (R = CO_2CH_3): ^1H NMR ($CDCl_3$, Me_4Si) δ 3.97 (s, 3 H), 6.19 (br s, 1 H), 7.4–7.55 (m, 6 H), 7.66 (br d, 2 H, 8.0 Hz); IR (KBr): 2957 (vw), 1676 (vs), 1661 (vs), 1626 (m), 1601 (vs), 1592 (vs), 1574 (w), 1543 (m), 1460 (m), 1435 (m), 1400 (w), 1385 (w), 1368 (w), 1330 (s), 1321 (vs), 1304 (s), 1285 (s), 1261 (s), 1240 (s), 1185 (m), 1173 (m), 1163 (m), 1130 (m), 1076 (m), 932 (m), 730 (m), 694 (m), 687 (m), 621 (w) cm^{-1}. **1k** (R = $OCOCH_3$): ^1H NMR ($CDCl_3$, Me_4Si) δ 2.17 (s, 3 H), 6.36 (br s, 1 H), 7.42–7.54 (m, 8 H). **1e** (R = $COCH_3$): ^1H NMR ($CDCl_3$, Me_4Si) δ 2.59 (s, 3 H), 6.26 (br s, 1 H), 7.48–7.54 (m, 6 H), 7.60 (m, 2 H); UV (log ε) 230 (4.91) sh, 260 (4.31) sh nm; IR (KBr) 2948 (w), 2880 (w), 1731 (s), 1633 (vs), 1631 (vs), 1588 (vs), 1585 (vs), 1558 (vs), 1490 (m), 1449 (w), 1419 (w), 1356 (s), 1347 (s), 1298 (s), 1162 (s), 840 (m), 817 (s), 796 (s), 768 (m), 738 (s), 601 (m), 586 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{12}N_4O_9$: C, 49.05; H, 2.91; N, 13.46. Found: C, 48.98; H, 2.93; N, 13.40. **1f** (R = Cl): ^1H NMR ($CDCl_3$, Me_4Si) δ 6.31 (br s, 1 H), 7.49–7.60 (m, 6 H), 7.65 (br d, 2 H, J = 8.1 Hz); IR (KBr) 2961 (m), 2889 (w), 1684 (m), 1676 (w), 1671 (w), 1653 (m), 1611 (vs), 1592 (vs), 1577 (vs), 1561 (s), 1489 (m), 1457 (w), 1450 (m), 1351 (m), 1332 (s), 1294 (s), 1282 (s), 1170 (w), 933 (s), 837 (m), 816 (m), 795 (s), 770 (m), 735 (s), 725 (s), 698 (m), 685 (m), 668 (m), 580 (m), 442 (m), 419 (m), 408 (m), 401 (m), 391 (m), 374 (m), 366 (s) cm^{-1}. Anal. Calcd for $C_{15}H_9N_4O_8Cl$: C, 44.08; H, 2.22, N, 13.71. Found: C, 44.66; H, 2.31; N, 13.66. **1k** (R = $OCOCH_3$): ^1H NMR ($CDCl_3$, Me_4Si) δ 2.15 (s, 3 H), 6.38 (br s, 1 H), 7.45–7.55 (m, 8 H); IR (KBr) 2942 (m), 1669 (vs), 1620 (s), 1597 (vs), 1574 (s), 1551 (m), 1460 (w), 1400 (w), 1353 (w), 1322 (s), 1314 (s), 1297 (s), 1286 (s), 933 (w), 812 (m), 795 (m), 775 (w), 724 (m), 695 (w), 687 (w), 635 (w) cm^{-1}.

9-Cyanoanthracene. A solution of 101 mg (0.50 mmol) of 9-cyanoanthracene and 100 mg (0.51 mmol) of TNM dissolved in ~5 mL of CH_2Cl_2 was irradiated for 15 min. The solvent was removed, the solid residue was taken up in ~3 mL CH_2Cl_2, and ~1 mL of CCl_4 was added. The crystals obtained by slow evaporation of the solvent contained approximately equal amounts of two compounds which could not be completely separated by repeated recrystallizations in this manner. These materials may be steriosomers of **1b** (R = CN).

9-Methoxyanthracene. A solution of 104 mg (0.50 mmol) of 9-methoxyanthracene and 100 mg (0.51 mmol) of TNM dissolved in ~5 mL of CH_2Cl_2 slowly decomposed thermally at room temperature. Therefore the irradiation was performed immediately after mixing the components at 0 °C. The major product initially formed, however, was determined to be the anthrone **5** and no adduct **1j** (R = OCH_3) was observed.

9-Methylanthracene. Irradiation of a solution of 0.073 M 9-methylanthracene and 1.0 M TNM in 1 mL of CH_2Cl_2 or $CDCl_3$ for 1.5 min. with light passed through a Corning 3-70 (500 nm) cut-off filter at 4 °C afforded a mixture of products. Immediate analysis of the crude reaction mixture by ^1H NMR spectroscopy indicated a complex mixture of products (at least 12 major products formed). These products include adducts such as **1** and **4**, as indicated by the broadened singlet resonances observed between δ 6.3–6.8: 6.43 (br s, 15%), 6.35 (br s, 5%), 6.47 (br s, 4%), 6.61 (br s, 4%), 6.80 (br s, 2%). For the substitution of the methyl group the partial assignments are δ 8.37 (d, 2 H, J = 8 Hz), 7.97 (dt, 2 H, J = 1.5, 7.5 Hz), 7.83 (dd, 2 H, J = 1.3, 7.8 Hz), 6.75 (s, 2 H) [~8%], 8.31 (d, 2 H, J = 8 Hz), 7.92 (d, 2 H, J = 7.5 Hz), 6.71 (s, 2 H) [~6%]. For other meso addition products the ^1H NMR spectrum in $CDCl_3$ (Me_4Si) shows the following: δ 6.90 (s, 12%), 5.62 (s, 7%), 6.89 (s, 4%), 6.55 (s, 4%), 7.13 (s, 2%), 7.15 (s, 1%), 5.86 (s, 1%), 5.76 (s, 1%), 5.71 (s, 1%), 5.86 (s, 1%), 5.63 (s, 1%). Associated with these signals are resonances for the methyl groups between δ 1.8 and 2.8: 2.48 (s, 15%), 2.42 (s, 9%), 2.37 (s, 9%), 1.86 (s, 6%), 2.26 (s, 4%), 1.83 (s, 3%), 2.15 (s, 3%), 2.10 (s, 3%), 2.03 (s, 3%), 2.69 (s, 2%), 2.27 (s, 2%), 2.78 (s, 1%), 2.74 (s, 1%), 2.68 (s, 1%), 2.66 (s, 1%) 2.32 (s, 1%), 2.30 (s, 1%), 2.29 (s, 1%), 2.27 (s, 1%).

9,10-Diphenylanthracene. A solution of ~ 0.05 M 9,10-diphenylanthracene and ~0.2 M TNM in 1 mL of CH_2Cl_2 or $CDCl_3$ was irradiated for 2 min by passing the light through a Corning 3-70 (500 nm) cut-off filter at 4 °C. Immediate analysis of the crude product by ^1H NMR spectroscopy indicated the formation of two principal products in a ratio of 7:3, and an overall yield of ~90%. The major product exhibited resonances at δ 4.25 (d, 1 H, J = 5.6 Hz), 5.30 (d, 1 H, J = 5.8 Hz), 5.77 (m, 1 H), 6.80 (t, 1 H, J = 1.3 Hz), 6.87 (dt, 1 H, J = 1.4, 9.9 Hz), 7.1–7.7 (m, 13 H) in $CDCl_3$ (Me_4Si). The minor product exhibited a similar NMR spectrum: δ 4.29 (d, 1 H, J = 5.6 Hz), 5.00 (br s, 1 H), 5.72 (m, 1 H), 5.87 (t, J = 1.3 Hz), 6.84 (dd, 1 H, incompletely resolved), 7.05 (br d, 1 H, J = 7.6 Hz), 7.1–7.7 (m, 12 H). The similarity of the NMR spectra of these products suggests they may be isomers. The cis/trans isomers of the TNM adducts to the terminal ring of the anthracene are consistent with the observed spectra. Such a formulation is reasonable if one considers that 9,10-diphenylanthracene is sufficiently hindered at the meso positions that it preferentially reacts in one of the terminal rings.[57]

9,10-Dimethylanthracene. Irradiation of a solution of 0.05 M 9,10-dimethylanthracene and 0.3 M TNM in 1 mL of CH_2Cl_2 or $CDCl_3$ at 4 °C [Corning 3-70 (500 nm) cut-off filters] for 2 min afforded **7** as the major product in 20% yield: ^1H NMR ($CDCl_3$, Me_4Si) δ 8.42 (d, 2 H, J = 8.8 Hz), 8.33 (d, 2 H, J = 8.8 Hz), 7.66 (m, 2 H), 7.58 (m, 2 H), 6.54 (s, 2 H), 3.17 (s, 3 H). Adduct **1** was observed in 15% yield: ^1H NMR ($CDCl_3$, Me_4Si) 7.40–7.55 (m, 8 H), 2.40 (s, 3 H), 2.12 (s, 3 H).

9,10-Dibromoanthracene and 9,10-Dimethoxyanthracene. The reactions of these arenes with TNM gave complex mixtures of products. For example, with 9,10-dibromoanthracene, end-ring adducts similar to those observed with 9,10-diphenylanthracene appeared to be the major primary products. With 9,10-dimethoxyanthracene these and other (demethoxylated) products were observed. Hydrolysis leading to loss of the meso substituent and the formation of anthraquinone was especially facile for both of these arene derivatives.

General Procedure for the Determination of Product Yields. The yields of the principal photoproducts were obtained upon the irradiation of an equimolar (0.1 M) solution of the arene and TNM in a Pyrex cuvette. The light from a 500-W xenon lamp was focused through a heat filter (water) and a Corning glass filter (cut off λ >480 nm). Irradiation for a brief period (50–300 s) was followed immediately by ^1H NMR analysis of the photolysate after the solvent (either CH_2Cl_2 or $CHCl_3$) was removed in vacuo below room temperature and the residue taken up in $CDCl_3$. Glass filters with different vis cut offs were also employed. At constant irradiation times, the photochemical conversion times were found to be lower with filters with longer wavelength cut offs. However, the relative distribution of the products were unchanged with CH_2Cl_2 and CH_3COCH_3 as the internal standards. The yields of products determined in this manner at 90–95% conversions are reported in Tables II and III.

Irradiations at low temperatures were performed in sealed NMR tubes which were either air saturated or thoroughly degassed by four successive freeze–pump–thaw cycles at <0.05 torr. A constant external temperature could be maintained as low as 77 K with a transparent Pyrex Dewar flask. The irradiated samples were stored at 77 K and analyzed by ^1H NMR spectroscopy at either −65 ($CDCl_3$ bath) or −95 °C (CD_2Cl_2 bath). Although small amounts of thermally unstable species were sometimes observed, none was found to afford **1**. This photoadduct was isolated as the principal (or exclusive) product irrespective of whether the irradiations were carried out at room temperature or at −65 °C.

Determination of Quantum Yields. Quantum yields were measured with a 500-W xenon lamp focused through aqueous and IR heat filters, followed by a 480-nm interference filter (10-nm

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(57) Cook, J. W.; Hunter, L. *J. Chem. Soc.* **1953**, 4109.

band-pass) used as monochromator. Samples containing 0.050 M of the anthracene and either 0.050 M or 0.50 M TNM in 1.0 mL of deareated CH_2Cl_2 were irradiated for periods of 0.5–5.0 min. at room temperature (~22 °C). The CT absorptions of the EDA complexes were monitored periodically by UV spectroscopy. The decrease in the intensity of the arene absorptions between 350–400 nm also could be monitored after appropriate (250-fold) dilution. Conversions were kept to less than 10%. Potassium ferrioxalate and Reinecke's salt were used as actinometers.[58] The decrease in the CT absorptions of the EDA complexes were about twice the decrease in the absorptions of the arenes. The consumption of TNM thus was approximately the same as the consumption of the anthracenes listed in Table II.

For the dependence of the quantum yield on concentration, consider the CT equilibrium in eq 1, then

$$K = [\mathrm{D,A}](\mathrm{D}_0 - [\mathrm{D,A}])^{-1}(\mathrm{A}_0 - [\mathrm{D,A}])^{-1}$$

where the subscript zero refers to the initial concentration.

A. For $\mathrm{D}_0 = \mathrm{A}_0 < 0.06/K$, then $[\mathrm{D,A}] < 0.05\ \mathrm{D}_0$. It follows that the change in the concentration of the EDA complex is

$$\Delta[\mathrm{D,A}] \sim K[2\mathrm{D}_0(\Delta\mathrm{D}) - (\Delta\mathrm{D})^2]$$

Therefore for $\Delta\mathrm{D} = \Delta\mathrm{A} \ll \mathrm{D}_0 = \mathrm{A}_0$, then

$$\Delta[\mathrm{D,A}]/[\mathrm{D,A}] \simeq 2\Delta\mathrm{D}/\mathrm{D}_0 = 2\Delta\mathrm{A}/\mathrm{A}_0$$

B. For $\mathrm{A}_0 \gg \mathrm{D}_0$, a similar treatment yields

$$\Delta[\mathrm{D,A}] = K\mathrm{A}_0(\Delta\mathrm{D} - \Delta[\mathrm{D,A}])$$

Then for $\mathrm{A}_0 < (19K)^{-1}$, $[\mathrm{D,A}] < 0.05\mathrm{D}_0$ and it follows that

$$\Delta[\mathrm{D,A}]/[\mathrm{D,A}] \simeq \Delta\mathrm{D}/\mathrm{D}_0$$

In the anthracene–TNM system, the foregoing conditions are satisfied by $K < 1$,[19] $\mathrm{D}_0 = \mathrm{A}_0 \leq 0.1$, and photochemical conversions $\lesssim 5\%$.

Instrumentation. A Hewlett-Packard HP 8450A diode-array spectrometer was used to obtain the UV–vis spectra in cyclohexane (sh = shoulder). NMR spectra were taken on a Nicolet NT 360 (360 MHz) spectrometer in the FT mode (1-s delay between pulses) using dilute solutions in chloroform-*d*, dichloromethane-d_2, or acetonitrile-d_3. Chemical shifts are reported in ppm upfield from Me_4Si vs. internal chloroform (δ 7.26) in the following form: chemical shift (multiplicity, integration, apparent coupling constants in Hz), where s = singlet, d = doublet, t = triplet, m = unresolved multiplet, and br = broadened. A Perkin-Elmer Model 298 spectrophotometer was used to obtain IR spectra of Nujol mulls. (Identical spectra were obtained in KBr pellets on a Nicolet 10DX FTIR spectrometer.) Melting points were taken in capillary tubes using a Mel-Temp (Laboratory Devices) apparatus. The presence of paramagnetic species was probed on a Varian E110 EPR spectrometer. Photochemical irradiations were performed with a focused beam from a 500-W xenon lamp which was passed through a Corning glass sharp cut-off filter [either a 3-69 (500 nm), 3-72 (430 nm), or 2-63 (560 nm)] or an Edmund interference filter [which transmitted at 480 ± 10 nm] to assure the selective and specific CT excitation of the EDA complexes.

X-ray Crystallography of the Photoproducts. General. A single crystal of either **1g**, **1i**, or **4** was mounted on a glass fiber with the aid of silicone grease and placed in a locally interfaced Picker goniostat equipped with a graphite monochromator to collect the continuous θ–2θ at −160 °C. The general procedures and a description of the equipment and data reduction techniques have been described elsewhere in detail.[59] The structure was generally solved by direct methods (MULTAN 78) and Fourier techniques and the structure refined by full-matrix least squares. All atoms, including the hydrogens were located and refined. Information pertinent to the collection and refinement of the crystal data, as well as the final cell constants are enumerated separately.

A. Photoadduct 1g: empirical formula, $C_{15}H_9N_4O_8Br$; crystal dimension, 0.12 × 0.24 × 0.24 mm; space group $P2_1/a$; cell dimensions at −160 °C (30 reflections), a = 17.486 (6) Å, b = 13.443 (4) Å, c = 7.838 (2) Å, β = 118.02 (1)°; Z (molecules per unit cell) = 4; volume, 1626.46 Å^3; calculated density, 1.851 g cm^{-3}; wavelength, 0.71069 Å; molecular weight, 453.16; linear absorption coefficient 25.557 cm^{-1}; collection range, $6° < 2\theta < 50°$; scan width and speed, 2.0 + dispersion at 4.0° min^{-1}; single background time at extremes of scan, 10 s; total reflections collected 3524, number of unique intensities, 2884; number with $F > 0$, 2699; number with $F > \sigma(F)$, 2583; number with $F > 2.33\sigma(F)$, 2427; final residuals, $R(F) = 0.0562$, $R_w(F) = 0.0588$. A final difference Fourier was featureless, the largest peak being 0.45 e Å^{-3}.

B. Photoadduct 1i: empirical formula, $C_{21}H_{14}N_4O_8$; crystal dimensions, 0.08 × 0.17 × 0.23 mm; space group $P2_1/m$; cell dimensions at −162 °C (34 reflections), a = 9.119 (4) Å, b = 13.211 (6) Å, c = 16.037 (7) Å, β = 101.12 (2)°; Z = 4; volume, 1895.78 Å^3, calculated density, 1.578 g cm^{-3}; radiation (Mo Kα), 0.71069; molecular weight, 450.3 6; linear absorption coefficient, 1.160 cm^{-1}; collection range, $6° < 2\theta < 45°$; scan width and speed, 2.0 + dispersion at 4.0° min^{-1}; total reflections collected, 2742; number of unique intensities, 2489; number with $F > 3.00\ \sigma(F)$, 1983; final residuals, $R(F) = 0.0465$, $R_w(F) = 0.0487$. A difference Fourier was essentially featureless, the largest peak being 0.19 e Å^{-3}.

C. Hydroxy photoadduct 4: empirical formula, $C_{21}H_{15}N_3O_7{\cdot}{}^1/_2CH_2Cl_2$; crystal dimensions, 0.21 × 0.18 × 0.17 mm; space group, $P\bar{1}$; cell dimensions at −160 °C (26 reflections), a = 14.530 (4) Å, b = 14.793 (5) Å, c = 10.486 (3) Å, α = 110.45 (1)°, β = 95.90 (1)°, γ = 102.85 (1)°; Z = 4; volume, 2018.42 Å^3; calculated density, 1.523 g cm^{-3}; radiation (Mo Kα), 0.71069; molecular weight, 467.83; linear absorption coefficient, 2.363 cm^{-1}; collection range, $6° < 2\theta < 45°$; scan width and speed, 2.0 + dispersion at 4.0° min^{-1}; total reflections, 6003; number of unique intensities, 5289; number with $F > 0$, 5042; number with $F > \sigma(F)$, 4873; number with $F > 2.33\sigma(F)$, 4631; final residuals, $R(F)$ = 0.0834, $R_w(F)$ = 0.0884. The structure was solved with minor difficulty owing to two independent molecules that were located in the asymmetric cell as well as a disordered solvent molecule. There are four of the units which are hydrogen bonded to yield tetramers. Pertinent distances for the hydrogen bonds are O(1)–O(1′) = 2.738 Å and O(1′)–O(1′) = 2.699 Å. The two independent molecules in the cell have slightly different conformations, and other than torsional difference they have essentially identical distances and angles. All hydrogens with the exception of the 2OH hydrogens were located and refined isotropically. A final difference Fourier was featureless, the largest peak being 0.43 e Å^{-3}.

The X-ray crystallographic determination of the photoadduct **1h** was carried out at ambient temperatures on an Enraf-Nonius CAD-4 diffractometer:[60] empirical formula, $C_{15}H_{10}N_4O_4$; crystal dimensions, 0.60 × 0.60 × 0.20 mm; space group, $P2_12_12_1$; cell dimensions at ~25 °C, a = 7.276 (1) Å, b = 10.410 (2) Å, c = 20.942 (2) Å; Z = 4; volume, 1586 Å^3; calculated density, 1.57 g cm^{-3}; radiation (Mo Kα), 0.71073 Å; molecular weight, 374.3; linear absorption coefficient, 1.22 cm^{-1}; collection range, $4° < 2\theta < 50°$; scan width, time, and speed range; 0.90 + 0.35 tan θ, 1205, 0.7–5.0 min^{-1}; total reflections, 1646; number of independent data with $I > 3\sigma(I)$, 851; total variables, 109; final residuals, $R(F)$ = 0.168; $R_w(F)$ = 0.164. The structure was solved by MULTAN,[61] which revealed the positions of 18 non-hydrogen atoms in the molecule, missing only the three nitro groups of the trinitromethane moiety. In subsequent difference Fourier syntheses, several small peaks of electron density appeared in the vicinity of the missing nitro groups, but when placed into least-squares refinement, they invariably took on unreasonably large thermal parameters and displayed nonmeaningful geometry. Even when the population factors were cut, based on the assumption of a severe disorder of this group, no chemically reasonable model could be obtained. Attempts to refine the nitro groups as rigid bodies with partial occupancies also failed, and we thus conclude that there is a massive disorder of the trinitromethyl group. Thus little can be ascertained regarding the identity of this portion of the molecule.

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Considering the magnitude of the missing group, the remaining atoms are quite well behaved if the remaining nitro group at C-9 is located in a pseudoaxial syn configuration. All calculations were made by using Molecular Structure Corporations TEXRAY 230 modification of the SDS-PLUS series of programs.

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Supplementary Material Available: Tables of the crystallographic data for the photoadducts including the fractional coordinates, thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

Reinvestigation of the Bicyclo[2.2.2]octane-1,4-diyl Dication[1]

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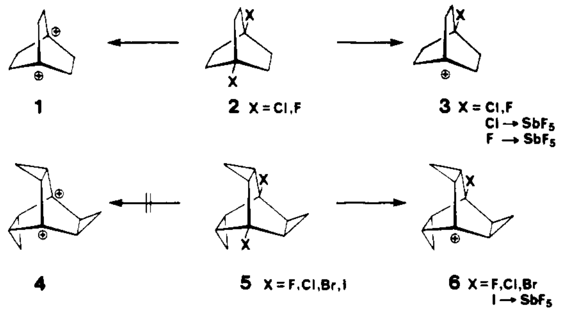
The reaction of 1,4-dihalobicyclo[2.2.2]octanes **2**-Cl and -F with SbF_5/SO_2ClF was reinvestigated and found by ^{13}C NMR spectroscopy and quenching experiments to yield only the 4-halo-1-bicyclo[2.2.2]octyl monocation mono-donor–acceptor complexes **3**-X–SbF_5 under any of the tested conditions. In SO_2-containing solutions disulfoxonium ion **7** formed, indicating that if dication **1** were intermediately formed it alkylates SO_2. **7** may, however, also be formed by stepwise alkylation. The previously reported stable 1,4-bicyclo[2.2.2]octanediyl dication **1** could not be detected. The results are consistent with the observation that the structurally similar 1,5-trishomobarrelenediyl dication **4**, which is expected to be more stable than **1**, could not be observed.



Previously Olah et al. reported[2a] that treatment of 1,4-dichlorobicyclo[2.2.2]octane (**2**-Cl) with SbF_5 in SO_2ClF gave the elusive 1,4-bicyclo[2.2.2]octanediyl dication **1** characterized by its ^1H and ^{13}C NMR spectra as well as its methanol quench product 1,4-dimethoxybicyclo[2.2.2]octane (**10**). The ^{13}C chemical shift additivity criterion was consistent with a carbodication.[3] The existence of **1** with two positive charges 1,4-disposed and separated by only two carbons in a bicyclo[2.2.2]octyl skeleton was rationalized with positive charge delocalization into a pseudo 2π aromatic like skeletal system on the basis of MINDO/3 theory.[2b] In contrast the related 1,5-trishomobarrelenyl dication **4** could not be observed by de Meijere et al., when 1,5-dihalotrishomobarrelenes **5** were treated with SbF_5/SO_2ClF.[4] Instead, halo monocations **6** were formed,[4,5] although MINDO/3 calculations predicted the same degree of stabilization. This was unexpected since cyclopropylcarbinyl cations in anellated bicyclooctyl systems are known to be stabilized.[6,7] Indeed, MINDO/3 calculations predicted a large degree of extra stabilization (14 kcal/mol) for the dication **4** over the parent **1** due to the three anellated cyclopropyl groups.[5,8] Experimentally, the 1-trishomobarrelenyl monocation is more stable than the 1-bicyclo[2.2.2]octyl bridgehead monocation.[9] The behavior of bridgehead dihalides similar to **5** with only one or two anellated cyclopropanes is analogous.[5,8] Hence, a thorough reinvestigation of the reaction of 1,4-dihalobicyclo[2.2.2]octanes **2** (X = Cl, F) with SbF_5–SO_2ClF was initiated. This has now been carried out independently in two of our laboratories and elsewhere.[10]

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