thermal parameters (Anisotropic for Si, O, C, Sb) led to convergence with $R_F = 4.7\%$, $R_{wF} = 5.3\%$, and GOF = 1.67 for 713 variables refined against those 8438 data with $|F_o| > 2.0\sigma|F_o|$. All other details regarding the crystal structure appear in the supplementary material.

Acknowledgment. These studies were supported by the National Science Foundation (CHE-9011593) and an NSF–Presidential Young Investigator Award (CHE-8657262). Acknowledgment is also made to the Chevron Research Co. and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Funds for the purchase of the X-ray diffraction equipment were made available from NSF Grant CHE-85-14495. F.J.F. gratefully acknowledges financial support from an Alfred P. Sloan Foundation Research Fellowship.

Supplementary Material Available: X-ray crystal data for **1b**, including experimental procedures, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, bond angles, and ORTEP figures (14 pages); tables of calculated and observed structure factors for **1b** (33 pages). Ordering information is given on any current masthead page.

Conformations, Spectroscopy, and Photochemistry of Methyl Phenanthrene-9-carboxylate, Phenanthrene-9-carboxamides, and Their Lewis Acid Complexes[1]

Frederick D. Lewis,* Steven V. Barancyk, and Eric L. Burch

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113.
Received September 25, 1991. Revised Manuscript Received December 31, 1991

Abstract: The spectroscopic properties and photochemical behavior of methyl phenanthrene-9-carboxylate and of a primary, secondary, and tertiary phenanthrene-9-carboxamides have been investigated in the absence and presence of strong Lewis acids. The ground-state conformations of the free and complexed molecules have been investigated by means of NMR and Gaussian 88 calculations. The dihedral angle between the phenanthrene and the carbonyl group is found to be dependent upon the bulk of the 9-substituent and upon Lewis acid complexation. Complexation also changes the secondary amide conformation from syn to anti. Both the phenanthrenes and their complexes are strongly fluorescent. Equilibrium constants for complex formation have been determined by means of fluorescence titrations. Rate constants for both radiative and nonradiative singlet-state decay increase upon complexation. The nonradiative rate constants for several boron halide complexes display a heavy-atom effect, which is larger for tertiary vs primary amides. Complexation results in an increase in both ester and amide singlet-state reactivity with simple alkenes.

Introduction

We have previously reported that Lewis acid complexation can result in marked changes in the conformation, spectroscopic properties, and photochemical behavior of cinnamic esters[2] and amides[3] and of their heterocyclic analogues, coumarin[4] and 2-quinolone.[1b] In the case of several cinnamic acids and amides, highly selective $E \rightarrow Z$ photoisomerization is observed in the presence of Lewis acids, as a consequence of selective ground-state complexation of the E isomer and Lewis acid-induced changes in the absorption spectra and photoisomerization quantum yields.[2a,3] Lewis acid-enhanced photodimerization and stereospecific cross-cycloaddition is observed for cinnamic esters,[2b] coumarin,[4] and 2-quinolones.[1b] These changes are attributed to increases in electrophilicity and singlet-state lifetimes for the complexed vs noncomplexed organic molecules. In the case of coumarin and quinolone, complexation on oxygen results in a change in the configuration of the lowest singlet state from n,π^* to π,π^*, resulting in a marked increase in singlet lifetime.[1b]

We report here the results of our investigation of the structure and photochemical behavior of methyl phenanthrene-9-carboxylate (PE), several related amides (1°PA, 2°PA, and 3°PA), and their Lewis acid complexes. Lewis acid complexation is found to have a pronounced effect on ground-state conformation, photophysical behavior, and photochemical reactivity. Of special significance is the decrease in singlet lifetime for boron halide complexes, which is attributed to a heavy-atom effect on the nonradiative-decay rate constant.

Results and Discussion

Ground-State Structures. ^{1}H NMR data for PE, the three amides, and their Lewis acid complexes are summarized in Table I along with literature data for phenanthrene and 9-acetylphenanthrene. The large downfield shift for H(8) and H(10) in the 9-carbonylphenanthrenes has been noted previously and attributed to a preferred s-trans conformation for the carbonyl and the C(9)–C(10) bond,[5] similar to that for the 1-carbonylnaphthalenes.[6] The downfield shifts for both H(8) and H(10) are significantly smaller for the amides vs the ester and decrease with increasing N-alkylation. The magnetic anisotropy diagrams of Jackman and Sternhell[7] for the carbonyl group indicate that an increase in the dihedral angle between the phenanthrene ring and the carbonyl group from 0° to 90° should result in an upfield shift of ca. 1.1 for H(8). Thus the observed changes are indicative of an increase in the dihedral angle from ca. 5° in the case of PE to ca. 90° for 3°PA, with intermediate values for 1°PA and 2°PA. The assignment of the upfield methyl signal to the syn methyl group in 3°PA is consistent with both previous assignments for

---

(1) (a) Lewis Acid Catalysis of Photochemical Reactions. 11. (b) Part 10: Lewis, F. D.; Reddy, G. D.; Elbert, J. E.; Tilberg, B. E.; Meltzer, J. A.; Kojima, M. *J. Org. Chem.* **1991**, *56*, 5311.

(2) (a) Lewis, F. D.; Oxman, J. D.; Gibson, L. L.; Hampsch, H. L.; Quillen, S. L. *J. Am. Chem. Soc.* **1986**, *108*, 3005. (b) Lewis, F. D.; Quillen, S. L.; Hale, P. D.; Oxman, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1261.

(3) Lewis, F. D.; Elbert, J. A.; Upthagrove, A. L.; Hale, P. D. *J. Org. Chem.* **1991**, *56*, 553.

(4) Lewis, F. D.; Barancyk, S. V. *J. Am. Chem. Soc.* **1989**, *111*, 8653.

(5) Bartle, K. D.; Smith, J. A. S. *Spectrochim. Acta* **1967**, *23A*, 1689.

(6) Smith, W. B.; Deavenport, D. L.; Ihrig, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 1959.

(7) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: Oxford, England, 1969.

0002-7863/92/1514-3866$03.00/0

Table I. ^{1}H NMR Data for Phenanthrene Derivatives and Their Lewis Acid Complexes

9-substituent	H(1)	H(4)	H(5)	H(8)	H(10)	N′-H	CH_3 syn	CH_3 anti
H	7.88	7.69	7.69	7.88	7.72			
$COCH_3$	7.90	8.65	8.67	8.83	8.15			
CO_2CH_3	7.92	8.68	8.70	9.07	8.50		4.04	
$CO_2CH_3{\cdot}EtAlCl_2$				8.60	8.92		4.50	
$CONH_2$	7.93	8.70	8.74	8.45	8.01	5.95, 6.14		
$CONH_2{\cdot}BF_3$	7.85	8.78	8.80	8.31	8.24			
$CONHCH_3$	7.91	8.69	8.73	8.34	7.68	6.11	3.16	
$CONHCH_3{\cdot}BF_3$	8.13	8.57	8.61	7.78	7.94	6.61		3.07
$CONH(CH_3)_2$	7.90	8.70	8.74	7.84	7.71		3.30	2.88
$CONH(CH_3)_2{\cdot}BF_3$	7.98	8.72	8.78	7.78	7.91		3.59	2.99

Table II. Absorption and Fluorescence Spectral Data for Phenanthrene Derivatives and Their Lewis Acid Complexes

9-substituent	abs, nm[a]	fl, nm	τ, ns	Φ_F	$10^{-7}k_f$, s^{-1}	$10^{-8}k_n$, s^{-1}	K_{eq}
H	294, 345	347	57.5	0.13	0.23	0.15	
CO_2CH_3	304, 357	366	9.7	0.15	1.5	0.88	
$CO_2CH_3{\cdot}BF_3$	306	456	6.9				<100
$CONH_2$	300, 350	360	11.7	0.08	0.68	0.79	
$CONH_2{\cdot}BF_3$	310	420	9.4	0.22	2.3	0.83	40000
$CONH_2{\cdot}BCl_3$	300	450	7.5	0.19	2.5	1.6	710
$CONH_2{\cdot}BBr_3$	324	433	5.0	0.12	2.4	2.3	1200
$CONHCH_3$	298, 350	361	16.4	0.08	0.49	0.56	
$CONHCH_3{\cdot}BF_3$	300	421	4.1	0.17	4.2	2.0	15000
$CON(CH_3)_2$	300, 350	352	6.7	0.04	0.59	1.4	
$CON(CH_3)_2{\cdot}BF_3$	300	404	0.4	0.01	2.5	25	40000
$CON(CH_3)_2{\cdot}BBr_3$	300			<0.001	2.4[b]	240	900

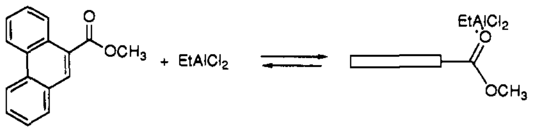
[a] Absorption maxima for the stronger ^1L_a and weaker ^1L_b band, respectively. [b] Calculated assuming all complexes have the same fluorescence rate constant.

aromatic amides and the effect of BF_3 complexation (vide infra).[8] The normal syn configuration for 2°PA[8,9] is supported by the similarity of its chemical shift to that for the syn methyl in 3°PA.

Further information about the ground-state conformations was obtained using Gaussian 88 calculations for the ester (STO-3G minimum basis set) and the primary and tertiary amide (AM1 basis set).[10] The dihedral angles in the energy-minimized structures were found to be 0° for PE, 58.5° for 1°PA, and 87.2° for 3°PA, in good qualitative agreement with the ^{1}H NMR results. The nonplanarity of the amides is a consequence of nonbonded repulsion between H(10) and the amine substituent anti to the carbonyl oxygen and is expected to decrease with decreasing bulk of the anti substituent (3°PA > 2°PA ~ 1°PA > PE).

Addition of 1 equiv of $EtAlCl_2$ to PE or of $BF_3{\cdot}OEt_2$ to the amides (1×10^{-3} M in $CDCl_3$) is sufficient to effect quantitative formation of 1:1 complexes, as determined by ^{1}H NMR analysis.[11] Addition of less than 1 equiv of Lewis acid results in the observation of a single set of signals for the ester, but two sets of signals for the amides. Thus exchange of Lewis acid between complexed and noncomplexed PE is rapid on the NMR time scale, as previously observed for cinnamic esters and coumarin,[2,4] whereas exchange of the amides is slow, as previously observed for the cinnamamides and quinolone.[1b,3] These observations and the failure of PE to form a complex with 1 equiv of $BF_3{\cdot}OEt_2$ are indicative of the much greater Lewis basicity of the amides vs the ester. A quantitative indication of the greater basicity of the amides vs the ester is provided by the calculated Mulliken charges for their carbonyl oxygens (−0.267 for PE, −0.377 for 1°PA, and −0.364 for 3°PA).[10]

Addition of 1 equiv of $EtAlCl_2$ to PE results in large downfield shifts for CH_3 and H(10), similar to those observed for the methyl protons and H_β of (*E*)-methyl cinnamate.[2a] The only other significant Lewis acid-induced shift is the large upfield shift observed for H(8). Lewis acid complexes of several α,β-unsaturated acids and esters are reported to have lowest energy s-trans, syn-coordinated structures.[2b,12] Complexation of ethyl cinnamate with $SnCl_4$ is known to result in a change in enone conformation from s-cis to s-trans both in solution and in the solid state.[2b] Sn is located syn to the C_α,C_β bond and slightly out of the molecular plane. Loncharich et al.[12] have concluded, on the basis of ab initio calculations on the BH_3 complex of methyl acrylate, that the slight preference for the s-trans, syn-coordinated structure is largely steric in origin. In the case of the PE·$EtAlCl_2$ complex, rotation of the ester group out of the phenanthrene plane would be required in order for the complex to assume a similar geometry (eq 1). An increase in the phenanthrene–carbonyl dihedral angle would be expected to result in a decrease in the long-range deshielding of H(8) by the carbonyl group.[13]



(1)

Addition of 1 equiv of BF_3 to 3°PA results in a larger downfield shift for the syn vs anti methyl protons, as previously observed for benzamides[8b] and cinnamamides.[3] In contrast, addition of 1 equiv of BF_3 to 2°PA results in an upfield shift in the methyl signal to a value similar to that for the anti methyl in 3°PA, indicative of a change in amide configuration upon complexation (eq 2). Protonation of secondary amides has been reported previously to shift the configuration of several secondary amides from syn to anti.[14] This change is attributed to the increased effective size of the protonated vs unprotonated carbonyl oxygen. The amides 1°PA and 3°PA display smaller Lewis acid-induced upfield shifts

---

(8) (a) Spaargaren, K.; Korver, P. K.; van der Haak, P. J.; de Boer, T. J. *Org. Magn. Reson.* **1971**, *3*, 615. (b) Lewin, A. H.; Frucht, M. *Org. Magn. Reson.* **1975**, *7*, 206.

(9) Stewart, W. E.; Siddall, T. H. *Chem. Rev.* **1970**, *70*, 517.

(10) Gaussian 88: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA.

(11) Addition of >1 equiv of BF_3 results in the appearance of a new set of signals, assigned to 2°PA·$(BF_3)_2$. The large downfield shift for H_4 and H_5 suggests that the second BF_3 is coordinated to the phenanthrene ring.

(12) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14.

(13) The lanthanide-induced shifts for 9-carbonylphenanthrenes have been interpreted assuming the existence of rapidly equilibrating syn and anti planar conformations. However, a single nonplanar conformation was also considered. Benassi, R.; Iarossi, D.; Folli, U.; Schenetti, L.; Taddei, F. *J. Chem. Soc., Perkin Trans. 2* **1981**, 228.

(14) LaPlanche, L. A.; Roders, M. T. *J. Am. Chem. Soc.* **1964**, *86*, 337.

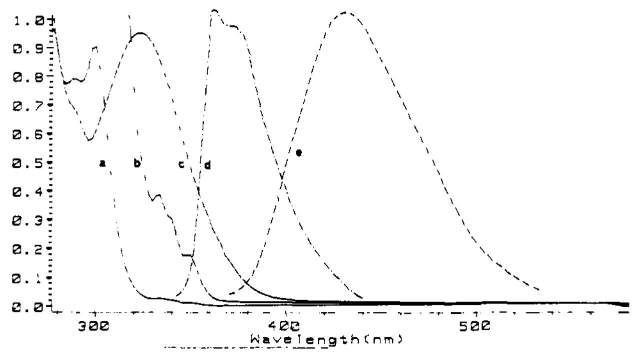


Figure 1. Electronic spectra of phenanthrene-9-carboxamide and its BBr_3 complex in dichloromethane solution. Absorption spectra: (a) the amide (9.05×10^{-5} M), (b) spectrum a × 15, and (c) the amide with 20 equiv of BBr_3. Fluorescence spectra: (d) the amide and (e) the amide with 20 equiv of BBr_3.

for H(8) and downfield shifts for H(10) than those observed for PE. Since the noncomplexed amides are nonplanar, complexation is expected to result in smaller changes in the phenanthrene–carbonyl dihedral angle (eq 2) than is the case for PE (eq 1).

(2)

Photophysical Properties. Absorption and fluorescence data for the phenanthrene derivatives and their Lewis acid complexes are summarized in Table II, and spectra for 1°PA and its BBr_3 complex are shown in Figure 1. Both the weak longest wavelength ^1L_b and the stronger ^1L_a band appear at longer wavelength than those for phenanthrene. Both bands are broadened, resulting in a loss of vibrational structure in the ^1L_b band. The fluorescence spectra of PE, 1°PA, and 2°PA are also much broader than that of phenanthrene, displaying a Stokes-shifted 0,0 band as a shoulder on an otherwise-structureless band. These observations are similar to those previously reported for 1-naphthoate[15] and 9-anthroate[16] esters, for which the lowest singlet state is proposed to be more planar than the ground state. A change in dihedral angle between the phenanthrene ring and the carbonyl group in the excited vs ground state could also account for the appearance of the fluorescence spectra of PE, 1°PA, and 2°PA. In contrast, 3°PA displays structured fluorescence and a small Stokes shift similar to that of phenanthrene as expected if the bulky tertiary amide group remains essentially orthogonal to the phenanthrene ring in the singlet state as well as the ground state.

The singlet lifetimes of the ester and amides are significantly shorter than that of phenanthrene,[17,18] as is generally the case for carboxyl-substituted aromatic hydrocarbons.[15,16] The fluorescence rate constants ($k_f = \Phi_f\tau^{-1}$) for the three amides are similar and somewhat smaller than the value for PE (Table II). The nonradiative rate constants ($k_n = (1 - \Phi_f)\tau^{-1}$) are significantly larger than that for phenanthrene, the values for PE, 1°PA, and 2°PA being somewhat smaller than that for 3°PA. The large nonradiative rate constants for the carboxyl-substituted phenanthrenes may result from mixing of the lowest π,π^* excited state with the higher energy n,π^* state of the ester or amide. Such mixing could lead to enhanced spin–orbit coupling, resulting in an increase in the rate constant for intersystem crossing and a decrease in the singlet lifetime. Alternatively, torsion about the amide C(O)–N bond might provide a pathway for singlet-state decay, as recently reported for *N*-methylacetamide.[19]

Lewis acid complexation of the ester or amides results in the appearance of a broad absorption band in the region of the phenanthrene ^1L_a band with a long-wavelength tail which extends beyond the lowest energy maximum in the phenanthrene ^1L_b band. The structureless fluorescence spectra of the Lewis acid complexes have an approximate mirror-image relationship to the absorption spectra, with emission maxima at significantly longer wavelengths than those of the noncomplexed ester or amides (Figure 1).[20] Fluorescence from an organic molecule and its Lewis acid complex has previously been reported in the case of the 2-quinolones for which a blue shift in both absorption and emission was observed upon complexation.[1b]

The observation of a large red shift in the fluorescence spectra of the three phenanthrene-9-carboxamides upon complexation permits the determination of the approximate equilibrium constants from the midpoints of fluorescence titration curves. Values of K_{eq} for 1°PA and 3°PA are similar and larger than that for 2°PA (Table II). Different orders have been reported for the Lewis basicity of cinnamamides (1° > 2° > 3°)[3] and for the Brønsted basicity of acetamides and benzamides (3° > 2° > 1°).[21] Values of K_{eq} for 1°PA with three boron halides are observed to decrease in the order $BF_3 > BBr_3 > BCl_3$. A different trend ($BCl_3 \sim BBr_3 > BF_3$) has been proposed by Laszlo and Teston[22] based upon correlations of NMR data for crotonaldehyde with MO calculations. Our observation that the least substituted amide and least bulky boron halide form the strongest complex leads us to conclude that steric effects must be considered in discussions of Lewis acid and base strength.

The fluorescence decay of the Lewis acid complexes of PE, 1°PA, and 3°PA can be fit to a single exponential, providing the lifetime data reported in Table II along with calculated values for the fluorescence and the nonradiative-decay rate constants. In the case of 3°PA·BBr_3, for which no fluorescence is detected, the value of k_n is estimated, assuming a normal value of k_f. Values of k_f for the Lewis acid complexes are larger than for the noncomplexed amides, but are independent of N-alkylation or the choice of boron halide. In contrast, values of k_n are dependent upon both N-alkylation and boron halide, increasing with both N-alkylation and the atomic number of the boron halide. Both the magnitude of k_n and its dependence upon halide atomic number are larger for the complexes of 3°PA vs 1°PA.

The increase in k_n with increasing atomic number of the halide is attributed to a heavy-atom effect upon the nonradiative-decay rate constant for the boron halide complex.[23] Intramolecular heavy-atom effects on the naphthalene singlet lifetime have been observed for bromonaphthonorbornanes,[24] naphthylalkyl halides,[25] and substituted oligopeptides.[26] In all three cases, the decrease in singlet lifetime was attributed to an increase in the intersystem-crossing rate constant resulting from heavy-atom enhanced spin–orbit coupling. The magnitude of the heavy-atom effect is dependent upon both the distance between the naphthalene and heavy atom and their relative orientation.

A difference in the relative orientation of the amide and boron halide may be responsible for the larger effect of Lewis acids on the nonradiative decay of 3°PA vs 1°PA (Table II). The preferred geometry for both hydrogen bonding[27] and binding of small

---

(15) Lui, Y. H.; McGlynn, S. P. *J. Mol. Spectrosc.* **1974**, *49*, 214.

(16) Werner, T. C.; Hoffman, R. M. *J. Phys. Chem.* **1973**, *77*, 1611.

(17) Berlman, I. B. *Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971.

(18) Dichloromethane is the solvent of choice in studies of the spectroscopy and photochemistry of Lewis acid complexes.[1-4] Somewhat longer lifetimes are obtained for the phenanthrene derivatives in nonhalogenated solvents. For example, the lifetime of 3°PA in acetonitrile solution is 10.1 ns.

(19) (a) Wang, Y.; Purrello, R.; Spiro, T. G. *J. Am. Chem. Soc.* **1989**, *111*, 8274. (b) Song, S.; Asher, S. A.; Krimm, S.; Shaw, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 1155. (c) Li, Y.; Garrell, R. L.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5895.

(20) Addition of >1 equiv of BF_3 to 2°PA results in a further red shift in its fluorescence maxima and dual exponential fluorescence decay, attributed to emission from both 2°PA·BF_3 and 2°PA·$(BF_3)_2$.[11]

(21) Arnett, E. M. In *Progress in Physical Organic Chemistry*; Cohen, S. G., Streitwieser, A., Jr., Taft, R. W., Eds.; Wiley: New York, 1963; Vol. 1, pp 339–342.

(22) Laszlo, P.; Teston, M. *J. Am. Chem. Soc.* **1990**, *112*, 8750.

(23) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1969.

(24) Kavarnos, G.; Cole, T.; Scribe, P.; Dalton, J. C.; Turro, N. J. *J. Am. Chem. Soc.* **1971**, *93*, 1032.

(25) Davidson, R. S.; Bonneau, R.; Joussot-Dubien, J.; Trethewey, K. R. *Chem. Phys. Lett.* **1980**, *74*, 318.

(26) Basu, G.; Kubasik, M.; Anglos, D.; Secor, B.; Kuki, A. *J. Am. Chem. Soc.* **1990**, *112*, 9410.

Table III. Fluorescence Quenching by 2,3-Dimethyl-2-butene

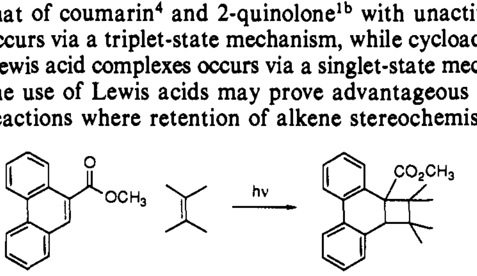
9-substituent	$k_q\tau$, M^{-1}	$10^{-8}k_q$, M^{-1} s^{-1}
CO_2CH_3	0.1	0.1
$CO_2CH_3·EtAlCl_2$	39	57.0[a]
$CONH_2$	0.7	0.6
$CONH_2·BF_3$	70	74.0

[a] Calculated assuming a singlet lifetime equal to that of the BF_3 complex.

cations[28] to *N*-methylacetamide is known to be in the amide plane, anti to nitrogen. However, the steric demand of either the amide or the cation can result in changes in this geometry. Both the bulk of the phenanthrene group and the change in 2°PA configuration upon complexation (eq 2) argue in favor of syn coordination for both 2°PA and 1°PA. The similar values of k_n for their BF_3 complexes is consistent with a similar relative orientation of the Lewis acid and phenanthrene chromophore in these complexes. In comparison, syn coordination for 3°PA would be subject to nonbonded repulsion between the Lewis acid and the syn methyl group. Either an anti or a linear coordination geometry would place the Lewis acid closer to the phenanthrene π-orbitals and thus provide a plausible explanation for the much larger values of k_n for the Lewis acid complexes of 3°PA vs 1°PA.

Photochemical Consequences. The observation of fluorescence from both the phenanthrene derivatives and their Lewis acid complexes permits comparison of the rate constants for fluorescence quenching by electron-donor alkenes. The rate constants obtained using 2,3-dimethyl-2-butene as the quencher are 2 orders of magnitude greater for complexed vs noncomplexed PE and 1°PA (Table III). The low rate constant for quenching of PE or 1°PA by 2,3-dimethyl-2-butene is presumably the result of unfavorable electron transfer from the alkene to the singlet phenanthrene. Quenching of singlet PE by the strong electron donor *trans*-anethole is reported to occur with a rate constant of ca. 5×10^9 M^{-1} s^{-1} and to be accompanied by exciplex emission.[29] An analogous increase in the rate constant for quenching of complexed vs noncomplexed 2-quinolones has been attributed to an increase in the excited-state electrophilicity upon complexation.[1b]

Preparative irradiation of PE with 2,3-dimethyl-2-butene either in the absence or presence of $EtAlCl_2$ results in the formation of a (2 + 2) cycloadduct as the major product (eq 3). The structure of the cycloadduct is analogous to that previously reported for the reaction of singlet phenanthrene-9-carbonitrile with 2,3-dimethyl-2-butene.[30] In the absence of a Lewis acid, a second unidentified adduct and the photodimer are observed. Since the photodimer is formed reversibly,[31] prolonged irradiation favors the stable cross adduct. In the presence of Lewis acid, neither the second adduct nor the photodimer is detected; however, the preparative yield of cross dimer is inferior to that obtained in the absence of Lewis acid. Other unactivated alkenes including cyclopentene and 2-methyl-2-pentene were observed to form adducts with PE and its $EtAlCl_2$ complex; however, these products were not fully characterized. In view of the fluorescence quenching results (Table III), it seems likely that cycloaddition of PE, like that of coumarin[4] and 2-quinolone[1b] with unactivated alkenes, occurs via a triplet-state mechanism, while cycloaddition of their Lewis acid complexes occurs via a singlet-state mechanism. Thus the use of Lewis acids may prove advantageous in preparative reactions where retention of alkene stereochemistry is desired.



(3)

The phenanthrene-9-carboxamides fail to undergo photodimerization[28] or cross-cycloaddition with simple alkenes either in the presence or in the absence of Lewis acids. This failure is somewhat surprising in view of the similar singlet lifetimes of the amides and the ester and their Lewis acid complexes (Table II) and the observation of larger values for the rate constant of fluorescence quenching by 2,3-dimethyl-2-butene for 1°PA vs PE (Table III). A plausible explanation for the nonreactivity of the phenanthrene-9-carboxamides is provided by the nonplanarity of these molecules. Assuming that the amide functional group is twisted out of the phenanthrene plane in the singlet state as in the ground state, nonbonded repulsion would disfavor the formation of a sandwich-type singlet excimer or exciplex involving the phenanthrene C(9)–C(10) bond.

Experimental Section

General Methods. Melting points were taken on a Fisher-Johns apparatus and are uncorrected. ^{1}H NMR spectra were recorded on an EM390 spectrometer with TMS as an internal standard or on a Varian XLA 400 spectrometer with TMS as internal standard. UV–visible absorption spectra were measured with a Hewlett-Packard 8452 A diode array spectrophotometer. Fluorescence spectra of degassed solutions were recorded with either a Perkin-Elmer MPF-44A spectrophotometer or a PTI LS-1 single photon counting instrument with a high-pressure Xe lamp and steady-state software. Fluorescence quantum yields were determined relative to equi-absorbing solutions of phenanthrene (noncomplexed phenanthrenes) or anthracene (complexed phenanthrenes).[17] Fluorescence lifetimes were measured with a PTI LS-1 single photon counting instrument with a gated hydrogen arc lamp (time resolution ca. 0.5 ns). All lifetimes reported for solutions were obtained from a single-exponential fit to the fluorescence decay ($\chi^2 < 1.2$), except for that of 2°PA·BF_3, for which the decay was fit to a biexponential. Samples containing Lewis acids were prepared under nitrogen either in a Vacuum Atmospheres drybox or using a gas-tight microliter syringe.

Materials. Dichloromethane (Aldrich, spectrograde) was distilled over calcium hydride prior to use. Methyl phenanthrene-9-carboxylate was prepared via esterification of the acid chloride of phenanthrene-9-carboxylic acid:[32] mp 115 °C (lit.[33] 118–119 °C). Phenanthrene-9-carboxamide was prepared via reaction of the acid chloride with ammonium chloride: mp 240 °C (lit.[34] 224–226 °C). *N*-Methylphenanthrene-9-carboxamide was prepared via reaction of the acid chloride with methylamine hydrochloride: mp 191–192 °C. *N,N*-Dimethylphenanthrene-9-carboxamide was prepared via reaction of the acid chloride with dimethylamine hydrochloride: mp 184–186 °C (lit.[35] 182.5–183 °C). ^{1}H NMR spectral data are reported in Table I.

Cycloaddition of Methyl Phenanthrene-9-carboxylate and 2,3-Dimethyl-2-butene. A solution of methyl phenanthrene-9-carboxylate (0.24 g, 0.001 mol) and 2,3-dimethyl-2-butene (2.37 mL, 0.02 mol) in 0.05 L of dichloromethane was purged with nitrogen and irradiated for 17 h with 350-nm light (Rayonet reactor with RUL 350 lamps). Removal of the solvent by rotary evaporation afforded a white solid, which upon recrystallization from hexane yielded 0.23 g (72%) of white crystals: mp 120–122 °C; ^{1}H NMR ($CDCl_3$) δ 0.50 (s, 3 H), 0.94 (s, 3 H), 1.03 (s, 3 H), 1.35 (s, 3 H), 3.57 (s, 1 H), 6.97–8.03 (m, 8 H, aromatic); IR ($CHCl_3$) λ_{max} 1730, 1490, 1460, 1445, 1405, 1380, 1245, 1220, 1180, 1165, 1130, 1040 cm^{-1}.

Acknowledgment. Financial support for this research has been provided by the National Science Foundation (Research Grant CHE-8922835 and Equipment Grant CBT-8908046). S.V.B. was the recipient of an Eastman Kodak graduate fellowship awarded by the Organic Chemistry Division of the American Chemical Society.

Registry No. Methyl phenanthrene-9-carboxylate, 1217-49-8; 2,3-dimethyl-2-butene, 563-79-1; methyl phenanthrene-9-carboxylate/2,3-dimethyl-2-butene cycloadduct, 139871-22-0; phenanthrene-9-carbonyl chloride, 16331-54-7; phenanthrene-9-carboxamide, 2510-60-3; *N*-methylphenanthrene-9-carboxamide, 139871-23-1; *N,N*-dimethylphenanthrene-9-carboxamide, 93315-43-6; ammonium chloride, 12125-02-9; methylamine hydrochloride, 593-51-1; dimethylamine hydrochloride, 506-59-2; 9-acetylphenanthrene, 2039-77-2; phenanthrene, 85-

---

(27) Novoa, J. J.; Whangbo, M.-H. *J. Am. Chem. Soc.* **1991**, *113*, 9017.

(28) Lewinski, K.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 3693.

(29) Sakuragi, H.; Tokumaru, K.; Itoh, H.; Terakawa, K.; Kikuchi, K.; Caldwell, R. A.; Hsu, C. C. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1049.

(30) Mizuno, K.; Pac, C.; Sakuri, H. *J. Am. Chem. Soc.* **1974**, *96*, 2993.

(31) Lewis, F. D.; Barancyk, S. V.; Burch, E. L. *J. Phys. Chem.*, in press.

(32) Bachmann, W. E. *J. Am. Chem. Soc.* **1934**, *56*, 1363.

(33) Harvey, R. G.; Fu, P. P.; Rabideau, P. W. *J. Org. Chem.* **1976**, *41*, 3722.

(34) Dewar, M. J. S.; Sampson, R. J. *J. Chem. Soc.* **1956**, 2789.

(35) van der Kamp, J.; Burger, A.; Mosettig, E. *J. Am. Chem. Soc.* **1938**, *60*, 1321.

01-8; methyl phenanthrene-9-carboxylate/ethyl dichloroaluminum complex, 139871-24-2; phenanthrene-9-carboxamide/boron trifluoride complex, 139871-25-3; *N*-methylphenanthrene-9-carboxamide/boron trifluoride complex, 139871-26-4; *N,N*-dimethylphenanthrene-9-carboxamide/boron trifluoride complex, 139871-27-5; phenanthrene-9-carboxamide/boron trichloride complex, 139871-28-6; phenanthrene-9-carboxamide/boron tribromide complex, 139871-29-7; *N,N*-dimethylphenanthrene-9-carboxamide/boron tribromide complex, 139871-30-0.

A Study of Norrish Type II Reactions of Aryl Alkyl Ketones Included within Zeolites

V. Ramamurthy,[*,†] **D. R. Corbin,**[†] **and L. J. Johnston**[*,‡]

Contribution from Central Research and Development, Experimental Station, The Du Pont Company,[§] *Wilmington, Delaware 19880-0328, and Steacie Institute for Molecular Sciences, National Research Council of Canada,*[‖] *Ottawa, Ontario K1A 0R6, Canada.*
Received September 27, 1991. Revised Manuscript Received January 10, 1992

Abstract: The photochemical and photophysical behavior of a large number of phenyl alkanones included in zeolites has been investigated. The interior size and shape of the zeolites control the behavior of the triplet ketone as well as that of the 1,4-diradical generated by Norrish type II γ-hydrogen abstraction. A relationship between the size and shape of the reaction cavity and the extent of the restrictions on the triplet ketone and the diradical intermediate has been observed. A model based on the "reaction cavity" concept has been valuable in understanding the unique influence of the zeolite on the reaction course of the type II process.

Introduction

The Norrish type II reaction is a mechanistically well understood reaction and has been extensively studied in both isotropic[1] and anisotropic media.[2] The efficiency of product formation from the excited triplet state via type II hydrogen abstraction, the ratio of elimination to cyclization products, and the ratio of *cis*- to *trans*-cyclobutanols from the type II 1,4-diradical are sensitive to the environment. We envisioned that a study of the Norrish type II reactions of aryl alkyl ketones within various zeolites would yield information concerning the restriction provided by the internal structure of the zeolite on the reaction course. This, in conjunction with further studies for these and other systems, would aid in the long-range prediction of the photophysical and photochemical behavior of guest molecules included within zeolites.[3] In this context, we have utilized a large number of zeolites as hosts to carry out phototransformations of several aryl alkyl ketones (Scheme I). A comprehensive photochemical investigation of **1** has also been conducted within faujasite zeolites (X and Y). This includes alteration of the characteristics of the cage by cation exchange (Li, Na, K, Rb, and Cs) and by inclusion of a cohost such as solvent hexane. The dramatic difference in product distribution observed between faujasite and pentasil zeolites as hosts led us to undertake a flash photolysis investigation of valerophenone in these zeolites. Results of such studies, as well as those from a steady-state photophysical investigation, are presented herein.

Zeolites may be regarded as open structures of silica in which aluminum has been substituted in a fraction of the tetrahedral sites.[4] The frameworks thus obtained contain pores, channels, and cages. The substitution of trivalent aluminum ions for a fraction of the tetravalent silicon ions at lattice positions results in a network that bears a net negative charge, which must be compensated by other counterions. The latter are mobile and may occupy various exchange sites depending on their radius, charge, and degree of hydration. They can be replaced, to varying degrees, by exchange with other cations. If zeolite water is removed, many other organic and inorganic molecules can be accommodated in the intracrystalline cavities.

A brief description of the structure of the zeolites used in this study is appropriate.[4] The topological structure of X- and Y-type zeolites consists of an interconnected three-dimensional network of relatively large spherical cavities, termed supercages (diameter of about 13 Å, Figure 1). Each supercage is connected tetrahedrally to four other supercages through 8-Å windows or pores. The interiors of zeolites X and Y also contain, in addition to supercages, smaller sodalite cages. The windows to the sodalite cages are too small to allow organic molecules access to these cages. Charge-compensating cations present in the internal structure are known to occupy three different positions (Figure 1) in zeolites X and Y. Only cations of sites II and III are expected to be readily accessible to the adsorbed organic molecule.

Among the medium-pore-sized zeolites, perhaps the most studied are the pentasil zeolites, ZSM-5 and ZSM-11 (Figure 1). These zeolites also have three-dimensional pore structures; a major difference between the pentasil pore structures and the faujasites described above is the fact that the pentasil pores do not link cage structures as such. Instead, the pentasils are composed of two intersecting channel systems. For ZSM-5, one system consists of straight channels with a free diameter of about 5.4 × 5.6 Å and the other consists of sinusoidal channels with a free diameter

---

[†] The Du Pont Company.

[‡] National Research Council of Canada.

[§] Contribution No. 5994.

[‖] NRCC No. 33262.

(1) Wagner, P. J.; Park, B. S. *Org. Photochem.* **1991**, *11*, 227. Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. Turro, N. J.; Dalton, J. C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92. Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252.

(2) Weiss, R. G. *Tetrahedron* **1988**, *44*, 3413. Scheffer, J. R. In *Organic Solid State Chemistry*; Desiraju, G., Ed.; Elsevier: Amsterdam, 1987; p 1. Ramamurthy, V.; Eaton, D. F. *Acc. Chem. Res.* **1988**, *21*, 300.

(3) Turro, N. J.; Garcia-Garibay, M. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; p 1. Ramamurthy, V. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; p 429.

(4) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*, 2nd revised ed.; Butterworths: Cambridge, 1987. Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry, and Use*; John Wiley and Sons: New York, 1974. Dyer, A. *An Introduction to Zeolite Molecular Sieves*; John Wiley and Sons: Bath, 1988. van Bekkum, H., Flanigen, E. M., Jansen, J. C., Eds. *Introduction to Zeolite Science and Practice*; Elsevier: Amsterdam, 1991.

0002-7863/92/1514-3870$03.00/0