J. Am. Chem. Soc. 1982, 104, 6793–6796

($-J \sim 1.5$ cm^{-1}),[9] suggesting that the heme group does not have a highly distorted structure.

The concept of orthogonal magnetic orbitals is currently enjoying considerable success in rationalizing *ferro*magnetic interactions.[21] What is surprising about the present results is the *lack* of experimental evidence for ferromagnetic interactions in symmetrical systems, despite the close proximity of spins. And yet, upon distortion, very strong *anti*ferromagnetic interactions can result. Continuing synthetic and structural investigations will test the generality of our observations. In particular, we are investigating $Co(TPP)(SbCl_6)$, whose properties (broad, low intensity, blue-shifted Soret (405 nm) relative to Co(TPP) and broad α,β bands (544 nm, 605, 645); diagnostic IR band at 1290 cm^{-1}) identify it as a cobalt(II) radical rather than a cobalt(III) complex as previously reported.[22] Like $[Cu(TPP\cdot)]^+$, it is paramagnetic in solution ($\mu_{corr}{}^{300} = 2.5\ \mu_B$) but diamagnetic in the solid state.

Acknowledgment. We are pleased to acknowledge and thank Dr. Jean-Claude Marchon for discussion of results prior to publication. This work was supported by The National Science Foundation (CHE 80-26812 to C.A.R.) and The National Institutes of Health (HL 15627 to W.R.S. and HL 16860 to G.L.).

Registry No. $[Cu^{II}(TPP)]^+$, 28206-02-2; $[Cu(TPP\cdot)][SbCl_3]$, 83435-78-3; $Fe^{III}(OClO_3)_2(TPP\cdot)$, 83435-87-4; $[Fe^{III}Cl(TPP\cdot)][SbCl_6]$, 78023-40-2; Cu(TPP), 14172-91-9; Cu(TTP), 19414-66-5; $[Cu(TTP\cdot)][ClO_4]$, 83435-80-7; tris(*p*-bromophenyl)ammonium hexachloroantimonate, 40927-19-3; thianthrenium perchlorate, 35787-71-4.

Supplementary Material Available: Table I, a summary of crystal data and intensity collection parameters for $[Cu(TPP\cdot)][SbCl_6]$; Table II, fractional atomic coordinates in the unit cell; Table III, anisotropic thermal parameters, and structure factor tables (20 pages). Ordering information is given on any current masthead page.

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Iron(III)–Porphyrin π-Cation Radical Complexes. Molecular Structures and Magnetic Properties

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Received June 28, 1982

Interest in the synthesis and structure of high-valent iron porphyrin complexes stems from the demonstrated or proposed involvement of species of this type in various biological processes mediated by peroxidases,[1] catalases,[2] or cytochromes P-450[3] and in model systems.[4] In this communication, we report on the full magnetic and structural characterization of two iron(III)–porphyrin cation radical complexes, and we suggest a qualitative explanation of the magnetic interactions observed in these compounds.

It was first reported a decade ago[5] that five-coordinate (tetraphenylporphyrinato)iron(III) complexes FeX(TPP) can be oxidized electrochemically to reversible one-electron oxidation products $FeX(TPP)^+$, but the latter have not been isolated, and their full characterization had to await the development of a better synthetic procedure. Recent work in these laboratories[6] showed that the hexachloroantimonate salt of phenoxathiin cation radical is a convenient stoichiometric one-electron oxidant which cleanly yields $FeCl(TPP)(SbCl_6)$, **1**, from FeCl(TPP). This product is isolable as black crystals. It has a magnetic moment of 4.9 μ_B, which is indicative of four unpaired electrons. Its Mössbauer spectral parameters ($\delta = 0.41$ mm/s, $\Delta E_Q = 0.56$ mm/s at 4.2 K) are in the range of those observed for high-spin iron(III) porphyrins,[6] and its ^1H NMR spectrum strongly suggests a singly occupied $d_{x^2-y^2}$ orbital and a large spin density on a porphyrin orbital of a_{2u} symmetry.[6,7] These data provide good evidence for a high-spin iron(III)–porphyrin cation radical configuration where the $S = {}^5/_2$ iron is spin-coupled to the $S = {}^1/_2$ porphyrin radical to give an overall $S = 2$ state. Further support to this assignment was brought recently by the detection of an infrared absorption band characteristic of porphyrin-centered oxidation.[8] It is therefore likely that the alternative high-spin iron(IV) formulation, previously proposed on the basis of some solution spectroscopic data,[5b,c] is erroneous.

An X-ray crystal structure of this complex was desirable to make a final decision on its electronic structure. Spin state–stereochemical relationships are well established for iron(II) and iron(III) porphyrins,[9] and it was expected that high-spin iron(III), having an occupied $d_{x^2-y^2}$ orbital, would show long Fe–N distances (ca. 2.05 Å). On the other hand, high-spin iron(IV), if present, would have an unoccupied $d_{x^2-y^2}$ orbital and therefore shorter Fe–N distances (<2.00 Å). Crystals of **1** suitable for X-ray studies were grown from 1,1,2,2-tetrachloroethane/*n*-hexane, but crystallographic difficulties forced us to abandon them. An analogous tetra-*p*-tolylporphyrin complex, **2**, was prepared in a similar way and gave large black crystals of a 1,1,2,2-tetrachloroethane solvate of moderate quality, which were subjected to crystal structure analysis.[10] The crystal lattice consists of discrete $FeCl(TTP)^+$

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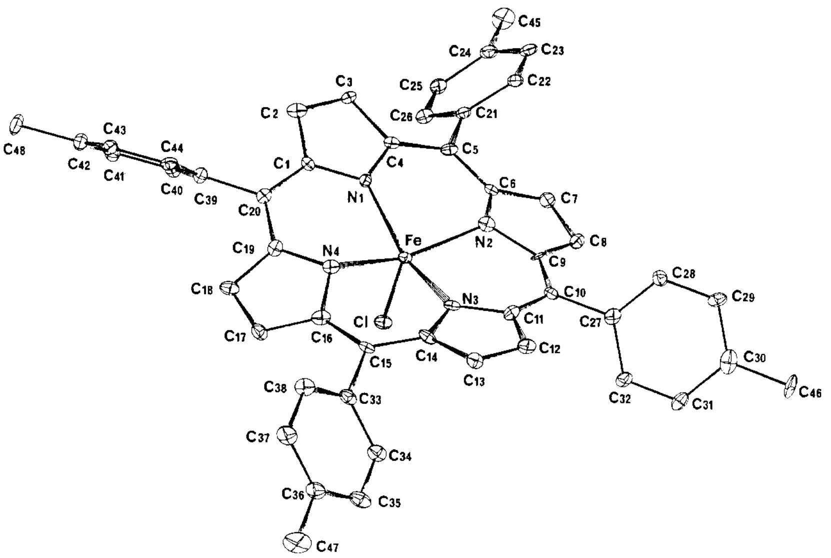

Figure 1. Perspective view and atom numbering scheme of the FeCl(TTP)$^+$ cation. Thermal ellipsoids are contoured at the 50% probability level (−140 °C).

and $SbCl_6^-$ ions with tetrachloroethane molecules (half of them on a well-defined site, the other half disordered over two sites sharing a common chlorine atom with a 0.55/0.45 occupancy ratio) occupying the holes resulting from the packing of the porphyrin complex and its counteranion. The most striking feature of this structure is the remarkable conformation of the porphyrin cation, in which nearly planar pyrrole rings tilt alternatively up and down to give rise to the saddle-shaped macrocycle illustrated in Figure 1. A similar distortion of the porphyrin core has been found in $Zn^{II}(ClO_4)(TPP\cdot)$[11] and $[Cu^{II}(TPP\cdot)][SbCl_6]$,[12] and it seems to be a structural feature of five- or four-coordinate complexes of tetraarylporphyrin cation radicals.[13] Bond distances in the coordination group closely parallel those of FeCl(TPP):[14] $Fe-N_1$, 2.09 (1); $Fe-N_2$, 2.08 (1); $Fe-N_3$, 2.05 (1); $Fe-N_4$, 2.05 (1) Å. The average value, 2.07 (1) Å, compared to 2.060 (3) Å in FeCl(TPP), falls within the range (2.060–2.087 Å) found for five-coordinate high-spin iron(III) porphyrins.[9] The Fe–Cl distance is 2.168 (5) vs. 2.193 (3) Å in FeCl(TPP); the slight contraction of this bond is consistent with the increased positive charge of the complex. This structural evidence is compelling for a high-spin iron(III) formulation, and it strongly argues against a high-spin iron(IV) configuration.

Moreover, the distorted structure of the macrocycle in **2** suggests a qualitative explanation of the antiferromagnetic coupling between unpaired spins on iron and porphyrin π-cation radical. In a saddle-shaped porphyrin complex, a significant overlap of the two pertinent magnetic orbitals $d_{x^2-y^2}$ and a_{2u} is possible,[15] resulting in a predominant antiferromagnetic contribution to the overall exchange interaction.[16]

Table I. Mössbauer Spectral Parameters of $Fe(ClO_4)_2(TPP)$

T, K	δ,[a] mm/s	ΔE_Q, mm/s	Γ_-,[b] mm/s	Γ_+,[b] mm/s
300	0.35	1.86	0.32	0.46
77	0.46	1.76	0.41	0.51
4.2	0.48	1.78	0.54	0.54
2	0.48	1.77	0.49	0.49

[a] Relative to Fe metal. [b] Line width at half-height. Indices − and + refer to the lower and higher energy lines, respectively.

Thus, five-coordination by an axial chlorine and four porphyrin nitrogens fails to stabilize the desired iron(IV) electronic structure. Reasoning that coordination by two axial oxygen atoms might provide a more favorable situation, we investigated the oxidation of six-coordinate high-spin iron(III) porphyrins of the type $[Fe(ROH)_2(TPP)][ClO_4]$, where ROH is water[17] or ethanol.[18] These complexes are easily prepared by a straightforward adaptation of the synthesis of $[Fe(C_2H_5OH)_2(TPP)][BF_4]$ that we have described earlier.[18] Preliminary electrochemical studies in dichloromethane revealed that one-electron oxidation of $[Fe(H_2O)_2(TPP)]^+$ leads to a stable species in a clean, reversible process ($E_{1/2}$ = 1.12 V vs. SCE, close to the values found for five-coordinate iron(III) tetraphenylporphyrins[7]). Isolation of the latter from the Bu_4NClO_4 background electrolyte was not attempted, and a synthesis by chemical oxidation was worked out. Stirring $[Fe(TPP)]_2O$ in dichloromethane with a 4-fold excess of $Fe(ClO_4)_3\cdot 9H_2O$ leads, after filtration and workup, to a purple crystalline solid of composition $Fe(ClO_4)_2(TPP)$, **3**, in 95% yield.[19]

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(10) Crystal structure information: $(C_{48}H_{36}N_4FeCl)(SbCl_6)\cdot 2C_2H_2Cl_4$, M_r 1430.3, monoclinic, space group $P2_1/c$; a = 10.98 (1) Å, b = 22.57 (1) Å, c = 23.65 (1) Å, β = 97.73 (5)°, V = 5808 Å^3, Z = 4. Enraf-Nonius CAD-4 diffractometer, niobium-filtered Mo Kα radiation, 7876 reflections collected at −140 °C. No absorption correction was applied. The structure was refined by full-matrix least-squares techniques: 4627 reflections with $F_o > 2\sigma(F_o)$, 666 variables (anisotropic thermal parameters for all non-hydrogen atoms, hydrogen atoms not included in the refinement); R = 0.088; R_w = 0.097.

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(15) Following Gouterman, we use D_{4h} nomenclature for labeling orbitals even though the nonplanarity of the porphyrin reduce the symmetry of the complex to C_{2v}. Specific features of the porphyrin a_{2u} orbital, which are to be contrasted with those of the a_{1u} orbital, are high spin densities at the meso positions, from which charge can overlap onto phenyl substituents, and significant spin densities on the four equivalent nitrogen atoms. A simple picture of the magnetic interactions in **2** can be drawn in which overlaps of the four nitrogen p_z orbitals (approximating the porphyrin a_{2u}) with the metal $d_{x^2-y^2}$ clearly indicate a pathway for antiferromagnetic coupling. Overlaps of d_{z^2} and d_{xy} with a_{2u} are assumed to be negligible. See: (a) Zerner, M.; Gouterman, M.; Kobayashi, H. *Theor. Chim. Acta* **1966**, *6*, 363. (b) Fajer, J.; Davis, M. S. *Porphyrins* **1979**, *4*, 198. (c) Tatsumi, K.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328.

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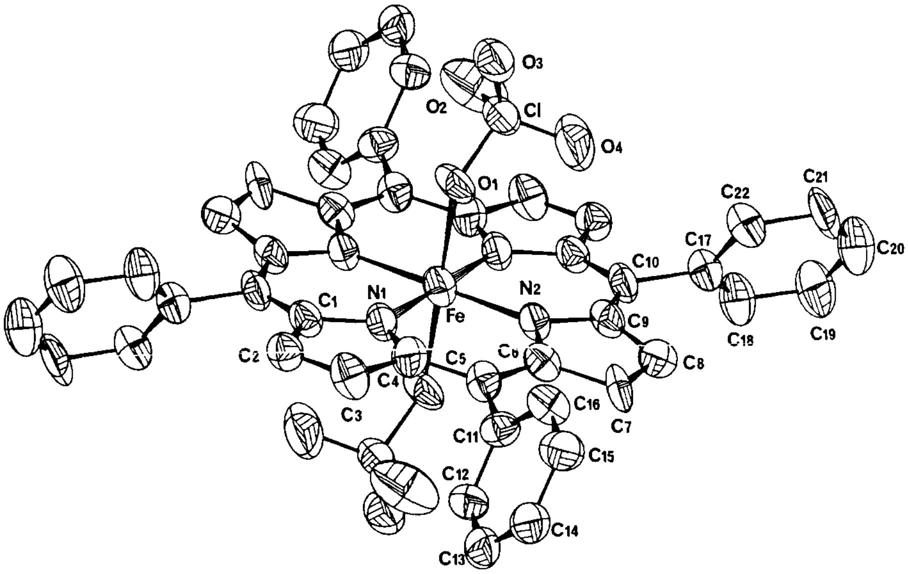

Figure 2. Perspective view and atom numbering scheme of $Fe(ClO_4)_2(TPP)$. Thermal ellipsoids are contoured at the 50% probability level (20 °C).

This complex has a visible spectrum in dichloromethane identical with that of the one-electron electrooxidation product of $[Fe(H_2O)_2(TPP)][ClO_4]$.[20] Incidentally, spectral changes during the synthesis of **3** indicate the intermediacy of the diaquo complex. Reduction of **3** by zinc under air gives $[Fe(TPP)]_2O$.

The infrared spectrum of $Fe(ClO_4)_2(TPP)$ in KBr pellet shows an intense absorption at 1280 cm^{-1}, indicative of porphyrin oxidation,[8] and multiple bands around 620, 900, and 1150 cm^{-1}, characteristic of perchlorate ligation.[21] Mössbauer spectral parameters recorded at several temperatures between 300 and 2 K (Table I) are in the range of those observed for six-coordinate high-spin iron(III) porphyrins (δ = 0.32–0.45 mm/s, ΔE_Q = 1.22–2.07 mm/s).[17,18,22] The temperature independence of ΔE_Q is consistent with a high-spin Fe(III) state.

A polycrystalline sample of **3** shows Curie–Weiss behavior over the range 5–300 K. The effective magnetic moment, corrected for diamagnetism ($\chi_{dia} = -764 \times 10^{-6}$ cgsu), is 6.5 ± 0.2 μ_B, slightly higher than the value expected for independent spins on the $S = {}^5/_2$ iron and the $S = {}^1/_2$ porphyrin radical ($\mu_{eff} = 6.17$ μ_B), and it is indicative of the presence of six unpaired spins in the molecule. Alternatively, ferromagnetic coupling between the metal and macrocycle spins would result in an $S = 3$ state and an effective magnetic moment $\mu_{eff} = 6.93$ μ_B. In any event, the observed value rules out an iron(IV) configuration, which would show at most a moment of 4.90 μ_B in its highest spin state.

Crystals of $Fe(ClO_4)_2(TPP)$ marginally suitable for X-ray diffraction were obtained from dichloromethane/*n*-hexane.[23] The crystal lattice is composed of centrosymmetric $Fe(ClO_4)_2(TPP)$ molecules with a coordination geometry shown in Figure 2. The six-coordinate iron atom is bound to an oxygen atom of both axial perchlorates and to the four nitrogen atoms of the planar macrocycle, and it is required by symmetry to be in the porphyrin plane. The planarity of the Fe(TPP) core in **3** explains the peculiar magnetic behavior of this complex, very different from **1** where the metal and the porphyrin radical show strong antiferromagnetic coupling. In the diperchlorato complex, overlap integrals of the two pertinent magnetic orbitals $d_{x^2-y^2}$ and a_{2u} cancel out by symmetry,[24] and the antiferromagnetic exchange interaction is therefore nonexistent.

Pertinent bond lengths in the coordination unit of **3** are as follows: $Fe-N_1$, 2.04 (1); $Fe-N_2$, 2.05 (2); Fe–O 2.13 (1) Å. The equatorial bond lengths values are consistent with one-electron occupancy of the $d_{x^2-y^2}$ orbital, and therefore they confirm the Fe–O, Fe(III) state, while the axial bond elongation explains the large value of the quadrupole splitting. Bond lengths and angles in the planar porphyrin radical do not show any significant deviation, within experimental error, from those found in a six-coordinate high-spin iron(III) porphyrin like $[Fe(C_2H_5OH)_2(TPP)][BF_4]$, for example.[18]

In summary, the molecular structures of $[FeCl(TTP)][SbCl_6]$ and $Fe(ClO_4)_2(TPP)$ suggest a correlation between the macrocycle geometry and the metal–ligand magnetic interactions in high-spin iron(III)–porphyrin cation radical complexes. A saddle-shape distortion results in strong antiferromagnetic coupling between the $S = {}^5/_2$ iron and the $S = {}^1/_2$ porphyrin radical, while ring planarity allows no antiferromagnetic interaction. Finally, the presence of a hole in a porphyrin π orbital seems to have no significant effect on the macrocycle bond distances or on the Mössbauer parameters of the central high-spin iron(III) atom. It is tempting to speculate that the latter is true also for iron(IV)–porphyrin complexes. This would take into account the fact that horseradish peroxidase compounds I and II, which are described as iron(IV)–porphyrin cation radical and iron(IV)–porphyrin, respectively, have virtually identical Mössbauer spectral parameters.[1b]

Acknowledgment. This research was supported by a grant from CNRS (LA 321, Chimie et Physicochimie Moléculaires). We thank Dr. Francesco Arena, Dr. Jeanne Jordanov, and Michel Maeder for assistance and Dr. Jean-Marc Latour for fruitful discussions. We are pleased to acknowledge and thank Professor Christopher A. Reed for exchange of information prior to publication.

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(19) Anal. Calcd for $C_{44}H_{28}N_4O_8Cl_2Fe$: C, 60.90; H, 3.25; N, 6.46; Cl, 8.17; Fe, 6.44. Found: C, 59.73; H, 3.23; N, 6.25; Cl, 9.13; Fe, 6.41.

(20) λ_{max} (ϵ): 396 nm (110), 522 (13.5), 605 (11), 675 (6), 810 (3 L/(mol cm) × 10^3).

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(23) Crystal structure information: $C_{44}H_{28}N_4Fe(ClO_4)_2$, M_r 867.5, monoclinic, space group $P2_1/c$; a = 12.132 (1) Å, b = 14.622 (2) Å, c = 13.153 (1) Å, β = 127.84 (1)°, V = 1842 Å^3, Z = 2. Enraf-Nonius CAD-4 diffractometer, niobium-filtered Mo Kα radiation, 4001 reflections. No absorption correction was applied. The structure was refined by full-matrix least-squares techniques: 1448 reflections with $F_o > 3\sigma(F_o)$, 270 variables (anisotropic thermal parameters for all non-hydrogen atoms, hydrogen atoms not included in the refinement); $R = 0.116$; $R_w = 0.130$.

(24) The ^1H NMR spectrum of **3** in CD_2Cl_2 at 25 °C shows the following chemical shifts: *m*-H, −27; pyrrole H, −22.6; *p*-H, 20.6; *o*-H, 27.1 ppm relative to the corresponding resonance lines in diamagnetic Ni(TPP). See: La Mar, G. N.; Walker, F. A., *Porphyrins* **1979**, *4*, 61. Assignments were made by comparison with the methyl-substituted analogues in meta and para positions. The alternating sign pattern of phenyl protons indicates an A_{2u}-type porphyrin radical.[6]

Registry No. **2**, 83435-86-3; **3**, 83435-87-4; [Fe(TPP)]$_2$O, 12582-61-5; ferric perchlorate, 13537-24-1.

Supplementary Material Available: Listing of positional and thermal parameters (11 pages). Ordering information is given on any current masthead page.

Conformations and Competitive [2 + 2] Cycloadditions of Intramolecular Exciplexes of Some Anisylalkenyl 9-Phenanthrenecarboxylates

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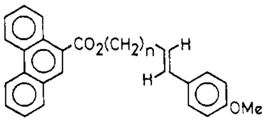
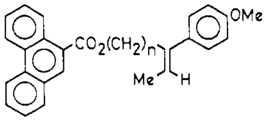
Exciplexes are intermediates in the [2 + 2] photocycloadditions of 9-cyanophenanthrenes with styrene derivatives, and the products formed are those of maximum "sandwich" overlap of the chromophores at the transition state for the reaction.[1] With 9-cyanophenanthrene and *trans*-anethole, only a "head-to-head" product was obtained, but substituents in some cases caused the formation of "head-to-tail" products.[2] Others[3] have amply demonstrated the value of interchromophoric links in studying geometric and conformational relationships between reacting chromophores. In the course of studying the effect of conformational constraints on the phenathrene–styrene reaction, we have found that interchromophoric links with an ester group bring about a novel aspect of the reaction, a competitive cycloaddition of intramolecular exciplexes involving carbonyl addition. We have prepared esters **1–3** from 9-phenanthrenecarbonyl chloride and the corresponding alcohols.[4] We have compared photochemical[5] and photophysical results for **1–3** with those for 9-(methoxycarbonyl)phenanthrene (**4**) and *trans*-anethole (**5**) as an unlinked model. In the B series, head-to-head cycloaddition can and does result, while in the A series cyclobutane photoproducts are not detected. The major photochemical process are in both series those of carbonyl addition.



A-n
1 : A-2, 2 : A-3



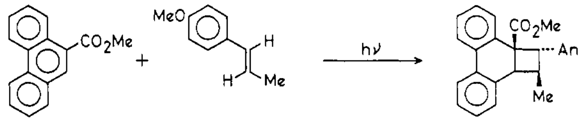
B-n
3 : B-2

Table I. Disappearance Quantum Yields and Photophysical Parameters for **1–4**

compd	ϕ(disapp)[a]	ϕ_f[b]	τ_f, ns[c]	λ_m(exciplex), nm[e]
1	0.36	0.07	3.9	NO[f]
2	0.61	0.04	3.2	450
3	0.70	0.06	5.2	450
4	0.11[d]	0.25	15.3	450

[a] In benzene at 366 nm vs. potassium ferrioxalate. Substrate concentration 5×10^{-4} M. [b] Recorded on a Hitachi MPF4 spectrofluorimeter and calculated relative to $\phi_f = 0.13$ for phenanthrene; see: Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1971; p 376. [c] By single-photon counting with an Applied Photophysics SP-3X system. [d] Extrapolated to infinite anethole concentration. [e] Obtained by subtraction of the fluorescence spectrum of **4** after normalization. Results are identical for normalization at 367 (0, 0) or 383 nm (λ_{max}). [f] Not observed.

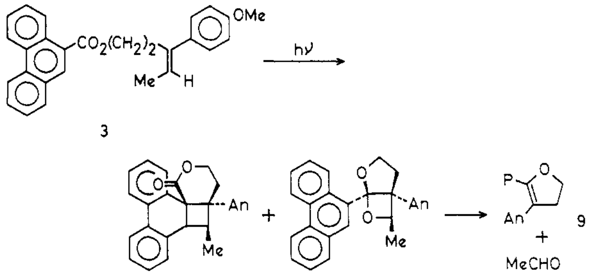
The photochemical cycloaddition of **5** to **4**[6] clearly affords a head-to-head adduct **6** of the expected[2] stereochemistry. The reaction is a singlet process. We observe $k_Q\tau$ = 46 M^{-1} for quenching of **4** fluorescence by **5**. Weak exciplex emission (λ_{max} 450 nm) was observed.



4 5 6

An : p-anisyl

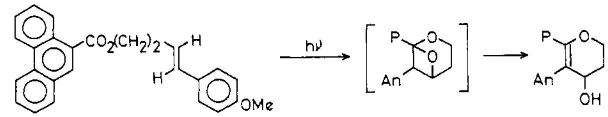
Irradiation of **3** in benzene[5] afforded a cyclobutane (**7**, 15% yield) and a bicyclic acetal (**8**, 65%). The structure of **7** is analogous to **6** as demonstrated by comparison of their NMR spectra. Compound **8** is a [2 + 2] cycloadduct between the ester carbonyl group and the olefinic double bond.[7] During the measurement of an NMR spectrum in CDCl$_3$, **8** slowly decomposed to give a dihydrofuran **9** (loss of acetaldehyde). Repeated chromatography of **8** on silica gel with CHCl$_3$ gave **9** (51% yield based on **3** consumed).[8]



3 7 8 9

P : 9-phenanthryl

Irradiation of esters **1** and **2** in benzene gave a dihydropyranol (**10**, 54%) and a dihydrooxepine (**11**, 57%) respectively.[5] There



1 12 10

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(2) Caldwell, R. A.; Ghali, N. I.; Chien, C.-K.; DeMarco, D.; Smith, L. *J. Am. Chem. Soc.* **1978**, *100*, 2857.

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(4) Synthetic procedures will be reported elsewhere. Spectral data and elemental analyses were satisfactory.

(5) Preparative irradiations were carried out at 5×10^{-4} M with a high-pressure mercury lamp. Product structures were assigned from spectral data and are consistent with elemental analyses.

(6) At 0.02 M **4** and 0.03 M **5** in 9:1 benzene–isoprene with a low-pressure mercury lamp. Analysis was satisfactory and the NMR spectrum was nearly identical (except for the ester methyl) with that for the 9-cyanophenanthrene–**5** photoadduct.[2]

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