

and thin layer chromatographic mobility.¹⁴ Further, coupled gas chromatographic-mass spectral measurements of the trimethylsilyl ether-methyl ester derivative of synthetic and naturally derived HETE gave identical results, both with regard to GC retention time and mass spectrum.^{1,14} Since ¹H NMR data for **1** and **17** have not previously been reported, some of the characteristic peaks for **17** are presented here (CDCl₃ as solvent): H-10, 6.55 (d of d, $J_{10,11} = 15$ Hz and $J_{9,10} = 10$ Hz); H-9, 5.95 (t, $J_{8,9} = J_{9,10} = 10.5$ Hz); H-11, 5.70 (d of d, $J_{10,11} = 15$ Hz and $J_{11,12} = 6$ Hz); H-(5,6,8,14,15), 5.3-5.5 (m); H-12, 4.2 (q, $J_{11,12} = J_{12,13} = 6$ Hz); COOCH₃, 3.65 (s); H-7, 2.90 (br t); H-2, 2.30 (t, $J_{2,3} = 6$ Hz); and H-20, 0.87 ppm (br t).

The methyl ester **17** was observed to be weakly dextrorotatory, $[\alpha]^{25}_D +1.50^\circ$ (c 0.2, CHCl₃). Hydrolysis of the ester **17** with aqueous alcoholic base readily afforded the corresponding free acid **1** (HETE).

The synthesis of HETE described above not only allows the preparation of larger amounts of this substance, but it also confirms completely the original¹ structural and stereochemical assignment.¹⁵

References and Notes

- M. Hamberg and B. Samuelsson, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 3400 (1974).
- M. Hamberg, J. Svensson, and B. Samuelsson, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 3824 (1974).
- S. Hammerström, M. Hamberg, B. Samuelsson, E. A. Duell, M. Stawiski, and J. J. Voorhees, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 5130 (1975).
- M. S. Newman and M. C. Vander Zwan, *J. Org. Chem.*, **38**, 2910 (1973).
- A. F. Klug, K. G. Untch, and J. H. Fried, *J. Am. Chem. Soc.*, **94**, 7827 (1972).
- Satisfactory infrared, ¹H NMR, and mass spectral data were obtained for all synthetic intermediates.
- E. J. Corey, H. Shirahama, H. Yamamoto, S. Terashima, A. Venkateswarlu, and T. K. Schaaf, *J. Am. Chem. Soc.*, **93**, 1490 (1971).
- Prepared from the lithio derivative of propargyl alcohol and excess ethylene oxide in THF at -78 °C for 2 h and 12 h at 25 °C in 80% yield. See R. F. Borch, A. J. Evans, and J. J. Wade, *J. Am. Chem. Soc.*, **99**, 1612 (1977).
- Prepared by Rosenmund reduction of the acid chloride of monomethyl glutarate using palladium/charcoal and 1 equiv of 2,6-lutidine in THF (1 atm H₂, 1 h at 25 °C); see A. W. Burgstahler and L. O. Weigel, and C. G. Schaefer, *Synthesis*, 967 (1976).
- See, A. J. Fatiadi, *Synthesis*, 65 (1976). The manganese dioxide used was prepared from manganous chloride and permanganate (see p. 67).
- The α - β -cis aldehyde **15** showed $J = 8$ Hz for CH-CHO and $J = 10$ Hz for protons α and β to formyl; upon standing at 25 °C the ¹H NMR spectrum indicated gradual formation of the more stable α,β -trans aldehyde.
- See E. J. Corey, P. Ulrich, and A. Venkateswarlu, *Tetrahedron Lett.*, 3231 (1977), and references cited therein.
- The ¹H NMR and mass spectra of the methyl ester of naturally derived HETE (from blood platelets) were provided by Drs. T. K. Schaaf and J. Egger of the Charles Pfizer Co.
- We are indebted to Drs. Bengt Samuelsson and Sven Hammerstrom of the Karolinska Institutet, Stockholm, for making TLC and GC-mass spectral comparisons.
- We are grateful to the National Science Foundation for financial assistance.

E. J. Corey,* Haruki Niwa, Jochen Knolle

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received November 11, 1977

Crown Ether Model Systems for the Study of Photoexcited-State Response to Oriented Perturbers. How Does a Naphthalene Derivative Respond to an Alkali Metal Cation in Its π Face?

Sir:

Crown ether naphthalene derivatives **1**,¹ **2**, and **3** have been designed as model systems for the study of the geometric requirements of perturber-chromophore interactions. In this report² the changes in the emission properties of **1** caused by

Table I. Emission Quantum Yields^a and Lifetimes of 1,5-Naphtho-22-crown-6 (**1**) in Alcohol Glass^a at 77 K with Alkali Metal Chloride Salts Added in 5:1 Molar Excess (Crown at $1.00 \times 10^{-4} F$)

Salt added	ϕ_f^b	τ_f , ns	ϕ_p^b	τ_p , s
None	0.11	35	0.17	2.2
NaCl	0.075	29	0.13	2.1
KCl	0.061	27	0.12	2.2
RbCl	0.018	<i>c</i>	0.19	1.6
CsCl	0.0015	<i>c</i>	0.34	0.42

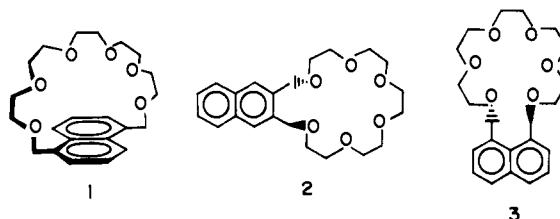
^a See note 4. ^b ϕ_f and ϕ_p are relative to naphthalene in ref 7a. ^c ϕ_f was too low to allow reliable measurement of τ_f .

Table II. Estimates^{a,b} of Rate Constants for Excited-State Processes of 1,5-Naphtho-22-crown-6 (**1**) in Alcohol Glass^c at 77 K with Alkali Metal Chloride Salts Added in 5:1 Molar Excess (Crown at $1.00 \times 10^{-4} F$)

Salt added	$10^{-6}k_f$	$10^{-6}k_{nr}$	$10^2k_p^d$	k_{dt}^d
None	3.1	25	8.7	0.37
NaCl	2.6	32	6.7	0.41
KCl	2.3	35	5.8	0.39
RbCl	1 ^e	52	12.	0.50
CsCl	1 ^e	670	81.	1.57

^a All rate constants in s⁻¹. ^b $k_f = \phi_f\tau_f^{-1}$; $k_{nr} = (1 - \phi_f)\tau_f^{-1}$; $k_p = \phi_p(1 - \phi_f)^{-1}\tau_p^{-1}$; $k_{dt} = \tau_p^{-1} - k_p$. ^c See note 4. ^d With $\phi_f + \phi_{isc} = 1.0$ assumed. ^e Estimated from 77 K UV absorption spectra.

alkali metal cations held near the face of the naphthalene π system are described and compared to earlier results with **2** and **3**.³ This study illustrates the extent to which external heavy-atom perturbation is dependent on the orientation of the perturber.



The fluorescence and phosphorescence quantum yields (ϕ_f and ϕ_p , respectively) and lifetimes (τ_f and τ_p , respectively) of pure **1** were measured in alcohol glass⁴ at 77 K and the effects of added Na⁺, K⁺, Rb⁺, and Cs⁺ chloride⁵ salts determined (see Table I). In the cases of Rb⁺ and Cs⁺ perturbation, ϕ_f is decreased to the extent that reliable measurement of τ_f is not feasible with the equipment available to us. Plots of ϕ_f and also ϕ_p vs. the mole fraction of added salt showed that the emission observed when a 5-fold excess of salt is present is that of completely complexed, and therefore specifically perturbed, crown **1**, and not that due to a small fraction of free **1**. Table II lists estimates of the rate constants for fluorescence (k_f), nonradiative decay of the singlet excited state (k_{nr}), phosphorescence (k_p), and nonradiative decay of the triplet state (k_{dt}).^{6,7}

Perturbation by a light cation (K⁺) of **1**,⁸ **2**, and **3** (pictured in the upper portion of Figure 1) causes real but not overpowering changes in all rate constants. Holding a light cation in the face of the π system does not increase the overall perturbing capability of the cation as compared with its effect when held at the side or end of the naphthalene chromophore.

Heavy-cation perturbation (by Cs⁺) gives an interesting pattern shown in the lower part of Figure 1. The rate constants for processes involving singlet-triplet interchanges (k_{dt} , k_p ,

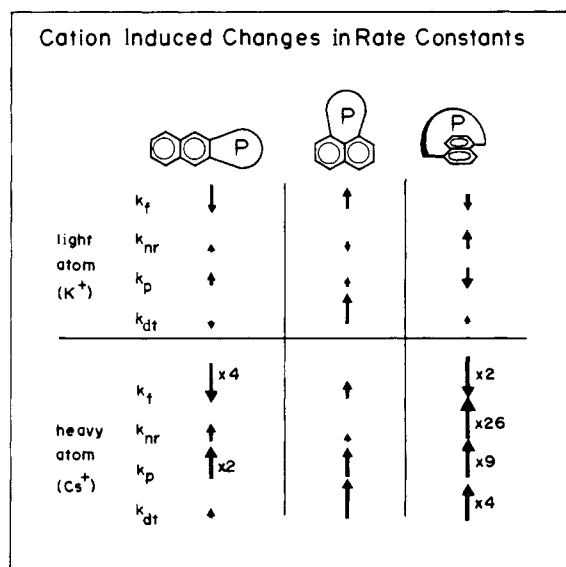


Figure 1. Changes in rate constants of excited-state processes of crowns **1**, **2**, and **3** caused by K⁺ (a light cation) and Cs⁺ (a heavy cation). The arrows are to scale and represent the difference from unity of the ratio of the perturbed and unperturbed rate constants (larger rate constant taken as the numerator). An arrow pointing up indicates that the cation perturber increases the rate constant relative to that of free crown, and vice versa.

and k_{nr}) are increased by complexed Cs⁺ for all three crowns, and are increased relative to the values seen with K⁺ perturbation. The postulation of Cs⁺ enhanced spin-orbit coupling^{9,10} in **1**, **2**, and **3** seems reasonable.

A major feature of the results is the very much larger effect of Cs⁺ on k_{nr} , k_p , and k_{dt} of **1** compared with **2** and **3**. Apparently, the enhancement of spin-orbit coupling is very much greater when the Cs⁺ heavy atom is held near the face as opposed to the end or side¹¹ of the π system. For comparison, changes in the rate constants of **1**, **2**, and **3** caused by 20% (v/v) ethyl bromide in ethanol-methanol (4:1 v/v)¹² at 77 K are similar to each other, and similar to those caused by the complexed Rb⁺ (except that ethyl bromide increases k_p of **1** three times more than Rb⁺ does).

A second feature is that the order of susceptibility of the rate constants of **1** to Cs⁺ ($k_{nr} > k_p > k_{dt}$) is different from that found in studies of the effects of external heavy-atom perturbation of unsubstituted naphthalene. Greater susceptibility of k_p compared with k_{dt} was seen in work by Kearns,¹³ Siegel,¹⁴ and El-Sayed,¹⁵ but not that of McGlynn.¹⁶ However, the observation that k_{nr} of **1** is the most perturbed rate constant is consistent with the work on naphthalene by McGlynn,^{16,17} but not that of Siegel.¹⁴ The order is also different from that observed when crowns **1**, **2**, or **3** are perturbed by ethyl bromide.¹² In those cases k_p is increased about twice as much as k_{dt} which is only slightly more affected than k_{nr} . It is not yet clear whether the difference between Cs⁺ perturbation of **1** and that of unoriented alkyl halides¹²⁻¹⁶ is due to the added presence of a positive charge, the precise orientation¹⁸ required by **1**, different thresholds of k_{nr} , k_p , and k_{dt} to the spin-orbit perturbation, or some property of cesium.

Acknowledgments. We thank David Carr for technical assistance, Houston S. Brown for computer programming, Professor Peter J. Wagner for heavy use of his Hitachi Perkin-Elmer spectrophotofluorometer, Professor Harry A. Eick for the use of his PDP-8 computer, and Professor M. Ashraf El-Bayoumi for the use of his single photo counting apparatus. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society,

and to the National Science Foundation (Grant No. CHE76-05175) for partial support of this work.

References and Notes

- 1,5-Naphtho-22-crown-6 (**1**) (mp 55–56 °C) was synthesized by reaction of 1,5-bis(bromomethyl)naphthalene with pentaethylene glycol in tetrahydrofuran with potassium *tert*-butoxide.
- L. R. Sousa and J. M. Larson, presented in part at the 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1977.
- (a) L. R. Sousa and J. M. Larson, *J. Am. Chem. Soc.*, **99**, 307 (1977). (b) A detailed description of results with **2** and **3** has been submitted for publication.
- Quantum yields and phosphorescence lifetimes were measured in uncracked 95% ethanol glasses at 77 K with crown generally at 1.0×10^{-4} *F*. Fluorescence lifetimes and 77 K UV absorption spectra were measured in absolute ethanol-methanol (4:1) glasses.
- Results with NaCl, NaBr, NaI, CsCl, and CsBr show anion independence.
- The values of k_p and k_{dt} are calculated assuming that $\phi_f + \phi_{isc} = 1.0$: (a) V. L. Ermolaev and E. B. Sueshnikova, *Opt. Spectrosc.*, **16**, 320 (1964); (b) A. R. Horrocks and F. Wilkinson, *Proc. R. Soc. London, Ser. A.*, **306**, 257 (1968); (c) R. H. Fleming, F. H. Fleming, F. H. Quina, and G. S. Hammond, *J. Chem. Phys.*, **59**, 3433 (1973).
- With Rb⁺ and Cs⁺ perturbation, the k_f values (which also affect k_{nr}) are low estimates based on a comparison of the integrated intensities of the 77 K UV absorption spectra. The approximate integrated intensities of the L_a absorptions of **1** fully complexed with Na⁺, K⁺, Rb⁺, and Cs⁺ relative to that of uncomplexed **1** are, respectively, 1.9:2.0:1.7:2.0:1.0.
- Attachment of the crown ring to naphthalene in the case of **1** causes relatively large changes in most rate constants compared with naphthalene which has $k_f = 1.4 \times 10^6$, $k_{nr} = 3.3 \times 10^6$, $k_p = 0.017$, and $k_{dt} = 0.38 \text{ s}^{-1}$ under the conditions of Table I. However, complexation of Cs⁺ by **1** causes changes in the rate constants which are clearly larger than those due to the crown substituent effect.
- (a) M. Kasha, *Discuss. Faraday Soc.*, **No. 9**, 14 (1950); (b) M. R. Wright, R. P. Frosch, and G. W. Robinson, *J. Chem. Phys.*, **33**, 934 (1960); (c) S. P. McGlynn, T. A. Zumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969, p 284.
- For a report of external heavy-atom perturbation by CsCl, see L. K. Patterson and S. J. Rzed, *Chem. Phys. Lett.*, **31**, 254 (1975).
- An x-ray crystal structure of **2** plus KSCN (D. L. Ward, H. S. Brown, and L. R. Sousa, *Acta Crystallogr., Sect. 13*, **33**, 3537 (1977)) and a partial structure of **3** plus the same salt show the cations to be on C_2 axes in the plane of the naphthalene π system.
- Unpublished work by James M. Larson.
- G. G. Giachino and D. R. Kearns, *J. Chem. Phys.*, **52**, 2964 (1970).
- S. Siegel and H. S. Judeikis, *J. Chem. Phys.*, **42**, 3060 (1965).
- K. B. Eisenthal and M. A. El-Sayed, *J. Chem. Phys.*, **42**, 794 (1965).
- (a) S. P. McGlynn, J. J. Reynolds, G. W. Daigre, and N. D. Christodouleas, *J. Phys. Chem.*, **66**, 2499 (1962); (b) S. P. McGlynn, J. Daigre, and F. J. Smith, *J. Chem. Phys.*, **39**, 675 (1963).
- The order of rate constant susceptibilities is the same as that seen when naphthalene is perturbed by charge-transfer complexers (even without heavy atoms); however, there is no indication of a charge-transfer component in the emission spectra in this case. See ref 10c, p 322, and N. Christodouleas and S. P. McGlynn, *J. Chem. Phys.*, **40**, 166 (1964).
- The difference in the perturbing effectiveness of Cs⁺ complexed by **1** as compared with **2** and **3** might in principle be rationalized by a superposition of a distance effect and some type of angular dependence (perhaps with small effects when Cs⁺ is on the nodal plane of the π system). These results do not provide a separation of effects, however, since **1** allows (but does not require) Cs⁺ to contact the π system while models (Corey, Pauling, Koltun) suggest that **2** and **3** hold Cs⁺ so that 1.6 and 2.0 Å, respectively, separate the edge of the π system from the Cs⁺ van der Waals radius.

James M. Larson, Lynn R. Sousa*

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

Received October 25, 1977

Structural Diversity in Iron Porphyrins: Solution Characterization of a High-Spin Six-Coordinate Ferric Complex

Sir:

The detailed characterization of solid-state structures and magnetic susceptibilities of iron porphyrin complexes in various ligation, oxidation, and spin states has produced what is generally accepted as a predictable correlation between stereochemistry and spin state that is directly applicable toward understanding certain structure-function relationships in hemoglobins.¹ The cornerstone of this correlation is that high-spin