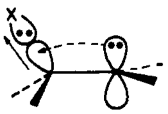
conclusions of Traylor and coworkers on σ–π conjugation in cations.[15,16] Several ancillary points follow.

1. An argument equivalent to that given above is that a polar C–X bond is at its C end a better π acceptor than C–H, provided that X is more electronegative than H; that bond, however, is a better π donor if X is less electronegative than H. Increased π-bonding opportunities follow.



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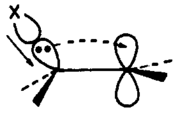

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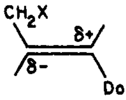
2. The anions XCH_2–CH_2^- certainly pyramidalize at the carbanion end. Sizable V_1 and V_3 torsional terms then enter, but our argument accounts for the magnitude and sign of the twofold barrier component, V_2.[18] While the reliability of the numerical results for the anions remains to be established, it is the trend, opposite to that in the cations, which we stress.[19]

3. In the geometries we have studied, the conformationally dominating factor appears to be the hyperconjugative aptitude discussed above, rather than a direct 1,3 interaction of substituent lone pairs or vacant orbitals with $-CH_2^+$ or $-CH_2^-$. The 1,3 through-space interaction, significant in that it may lead to bridging as a consequence, appears to be important only in the unstable A conformations of FCH_2–CH_2^+ and BH_2CH_2–CH_2^-.

4. The arguments constructed here obviously can be extended to YCX_2–CZ_2^+ species, where the X–Y electronegativity difference is determinative. It also plays an important role in setting the equilibrium conformations of YCX_2–NZZ', YCX_2–OZ, NXY–OZ,[18,20,21] and other unsymmetrical neutral molecules, as well as ligands such as PX_2Y. Attenuated traces of this effect should influence the conformations of propylenes **5** and **6** substituted by π donors or acceptors.[22]



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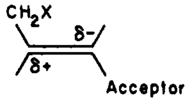

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Acknowledgment. This work was supported by the National Science Foundation (GP 29078X Princeton, GP 25617 Carnegie-Mellon, GP 28137 Cornell), the Petroleum Research Fund administered by the American Chemical Society (Princeton, Cornell), and Hoffmann-La Roche, Inc., Nutley, N. J. (Princeton). R. H. and L. S. are grateful for the hospitality of the Laboratorium für Organische Chemie der ETH, Zürich, in the course of this work.

Roald Hoffmann*
Department of Chemistry, Cornell University
Ithaca, New York 14850

Leo Radom, John A. Pople
Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Paul von R. Schleyer
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Warren J. Hehre
Laboratoire de Chimie Théorique, Université de Paris Sud
Orsay, France

Lionel Salem
Laboratorium für Organische Chemie
Eidgenoessische Technische Hochschule
Zürich, Switzerland

Received May 13, 1972

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(17) (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971); T. Kawamura and J. K. Kochi, *ibid.*, **94**, 648 (1972); *J. Organometal. Chem.*, **30**, C8 (1971); T. Kawamura, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 1752 (1972); (b) A. R. Lyons and M. C. R. Symons, *Chem. Commun.*, 1068 (1971); *J. Amer. Chem. Soc.*, **93**, 7330 (1971).

(18) For a detailed analysis of torsional barriers, see L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **94**, 2371 (1972).

(19) There is some disagreement on the role of fluorine hyperconjugation between our work and that of ref 4 and 14c.

(20) X, Y, Z, and Z′ are substituents of different electronegativity.

(21) See also S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971).

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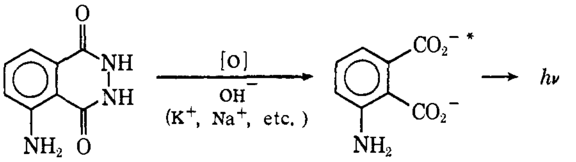
Differences between Excited States Produced Chemically and Photochemically. Ion Pairs of Excited States

Sir:

Electronically excited states produced chemically, as in chemi- and bioluminescence, usually are identical with the corresponding states arrived at through light absorption.[1–3] Thus, in the chemiluminescence of luminol (I), 3-aminophthalate ion (II) is formed in an excited singlet state (eq 1), and the chemiluminescence



(1)

I II

spectrum under most conditions is identical with the fluorescence spectrum of the aminophthalate ion.[2,4] In aqueous dimethyl sulfoxide, however, the chemiluminescence and fluorescence spectra differ.[4] We have verified and extended this observation and now show that the presence of the counterion (sodium in the earlier work[4]) is the causative factor.

The Water Effect. The chemiluminescence of luminol and the fluorescence of aminophthalate peak at 425 nm in water are independent of the base concentration

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(1) (a) K. D. Gundermann, "Chemilumineszenz Organischer Verbindungen," Springer-Verlag, Berlin, 1968; (b) K. D. Gundermann, *Angew. Chem., Int. Ed. Engl.*, **4**, 566 (1965); (c) F. McCapra, *Pure Appl. Chem.*, **24**, 611 (1970).

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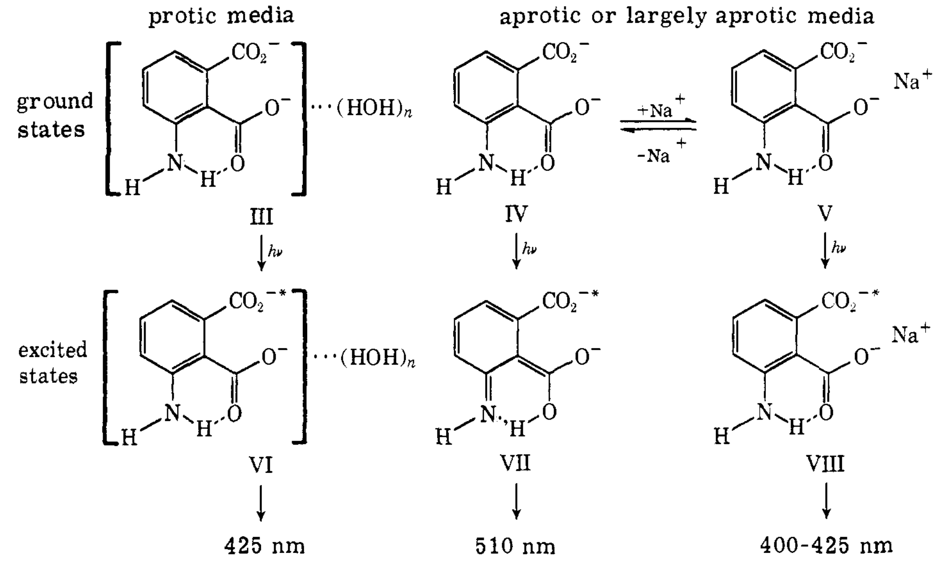
(3) (a) E. H. White, E. Rapaport, H. H. Seliger, and T. Hopkins, *Bioorg. Chem.*, **1**, 92 (1971); (b) E. H. White and M. J. C. Harding, *Photochem. Photobiol.*, **4**, 1129 (1965); (c) C. C. Wei and E. H. White, *Tetrahedron Lett.*, 3559 (1971).

(4) (a) E. H. White, O. Zafiriou, H. H. Kägi, and J. H. M. Hill, *J. Amer. Chem. Soc.*, **86**, 940 (1964); (b) E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964).



(2)

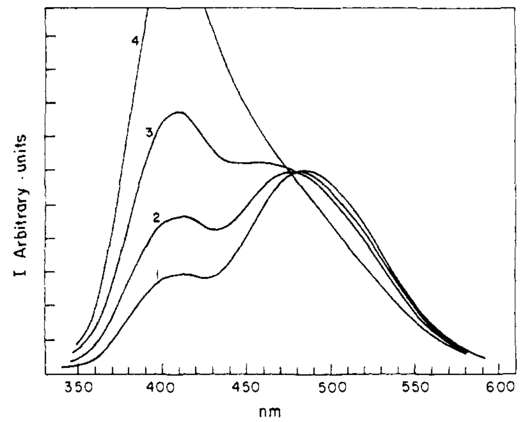


Figure 1. Effect of added sodium chloride on the fluorescence of 3-aminophthalate (5 × 10^{-5} M) in 30 mol % water, 70 mol % DMSO; 0.004 M TBH; $\lambda_{\text{excitation}}$ = 300 nm. Curves 1-4: sodium chloride concentration 0.0, 0.002, 0.005, and 0.007 M, respectively. (Spectra uncorrected for instrument response.)

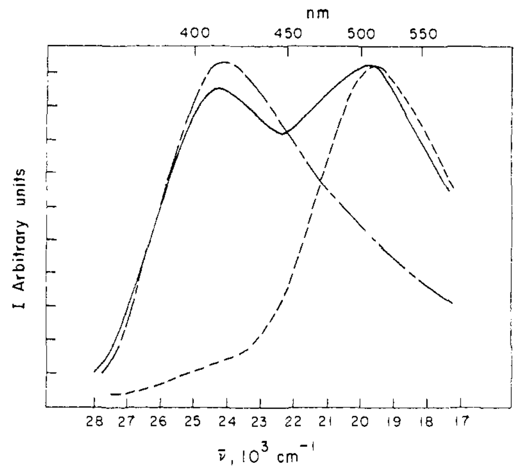


Figure 2. Luminol chemiluminescence (- - -) and 3-aminophthalate fluorescence, $\lambda_{\text{excitation}}$ = 300 nm (—) and $\lambda_{\text{excitation}}$ = 350 nm (— — —) in 17 mol % water, 83 mol % DMSO (0.017 M in TBH and 0.017 M in sodium chloride). (Spectra corrected for variations in spectral response of the spectrophotofluorometer.[5])

and the cation used. In dimethyl sulfoxide (DMSO), the maxima in the two cases are at 510 nm[5] provided that a quaternary base such as tetrabutylammonium hydroxide (TBH) is used. In mixtures of DMSO and water,[6] both peaks are seen,[7-9] the short-wavelength band slightly shifted depending on the amount of water in the medium. As the water content of the medium is increased, a gradual increase in the intensity of the short-wavelength peak occurs with a concomitant decrease in the long-wavelength peak. At any mixed solvent composition with a quaternary base, the chemiluminescence and fluorescence spectra are identical and the latter spectra are constant for exciting wavelengths ranging from 260 to 360 nm. Thus, two emitting states exist in the mixed solvents and the photo- and chemically produced sets appear to be identical.

Similar double emissions have been seen in aqueous DMSO for the chemiluminescence and fluorescence of related compounds; the long-wavelength emission, however, is seen only in compounds containing amino and carboxylate groups in an ortho arrangement.[7a,8] This fact suggests that a phototautomerism occurs in the aprotic solvent to give a quininoid species VII (eq 2).[7-11] The emitter in the protic media is presumably a hydrated aminophthalate ion VI.

The Metal Ion Effect. A more complex behavior is seen for the emissions in the presence of sodium ion. In DMSO containing 30 mol % water, the addition of

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(5) See D. R. Roberts and E. H. White, *J. Amer. Chem. Soc.*, **92**, 426 (1970), for experimental details. The position 510 nm is uncertain because of the relatively large correction required for wavelengths above *ca.* 500 nm.

(6) 2-Methyl-2-propanol and other alcohols behave similarly to water.

(7) (a) M. M. Bursey, Ph.D. Thesis, The Johns Hopkins University, 1963; (b) O. C. Zafiriou, Ph.D. Thesis, The Johns Hopkins University, 1966.

(8) (a) J. Lee and H. H. Seliger, *Photochem. Photobiol.*, **15**, 227 (1972); (b) J. Lee and H. H. Seliger, *ibid.*, **11**, 247 (1970).

(9) J. D. Gorsuch and D. M. Hercules, *Photochem. Photobiol.*, **15**, 567 (1972). We thank Professor Hercules for making the results of his experiments available to us prior to publication.

(10) For effects of excitation on acidity see: (a) A. H. Weller, *Progr. React. Kinet.*, **1**, 187 (1961); (b) E. Vander Donckt and G. Porter, *Trans. Faraday Soc.*, **64**, 3215 (1968); (c) Th. Förster, *Z. Elektrochem.*, **54**, 531 (1950).

(11) For related examples, see: H. Beens, K. H. Grellmann, M. Gurr, and A. H. Weller, *Discuss. Faraday Soc.*, **39**, 183 (1965); A. Tramer, *J. Phys. Chem.*, **74**, 887 (1970); C. A. Taylor, M. A. El-Bayoumi, and M. Kasha, *Proc. Nat. Acad. Sci. U. S.*, **63**, 253 (1969); G. Jackson and G. Porter, *Proc. Roy. Soc., Ser. A*, **260**, 13 (1961); J. Menter and Th. Förster, *Photochem. Photobiol.*, **15**, 289 (1972); P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

sodium chloride causes the conversion of the double emission (2.8/1 ratio of 510/410) to about a 0.33/1 ratio with an isoemissive point at 480 nm (over the mid-range of salt concentrations) (Figure 1). We believe that the sodium ion leads to emission at ~410 nm by virtue of its ability to form an ion pair V with the aminophthalate ion.[12] Photoisomerization does not occur in the excited state VIII, presumably because of the resulting lower net charge on the carboxylate group. Consistent with this view is the observation that potassium ion in aqueous DMSO is less effective than sodium in enhancing the short-wavelength peak, and that calcium, lithium, and the proton (as in the hydrated species VI) are more effective.[13] Further, in 1 mol % water in acetonitrile (a less polar medium than aqueous DMSO) even potassium is effective in blocking the tautomerism, leading to essentially only the short-wavelength emission.

Chelation by sodium can also be detected in the ground state (eq 2); the absorption maximum at 310 nm for a 10^{-4} *M* solution in aqueous DMSO (17 mol % water), 4×10^{-3} *M* in TBH, is broadened at longer wavelengths and shifted to 320 nm as sodium chloride is added (up to $\sim 6 \times 10^{-3}$ *M*). Further, the shape of the fluorescence emission depends on the excitation wavelength. Irradiation in the short-wavelength region of the absorption spectrum (300 nm or below, where both IV and V absorb strongly) leads to a two-banded emission, whereas irradiation at 350 nm (mainly absorption by V) leads to preponderant emission from VIII (short wavelength) (Figure 2).

More importantly, however, at no excitation wavelength in the presence of sodium ion is the fluorescence emission spectrum identical with the chemiluminescence spectrum of luminol measured under identical conditions (Figure 2). *Thus, the photo- and chemically produced excited states under these conditions must differ in detail.* In view of the short lifetime of the singlet excited state of aminophthalate in aqueous DMSO (~5 nsec),[14] the excited states produced in fluorescence must emit from a sodium ion pair distribution largely fixed by the ground-state ion before light absorption (eq 2). On the other hand, the excited states produced chemically emit from an environment determined at the transition-state stage of the reaction, and apparently a lower fraction of ion pairs with sodium results compared to the photoproduced case. Differences of excited states of this type can serve as probes into the nature of the transition states leading to chemically produced excited states.

Acknowledgment. We thank the Public Health Service for its financial support (Research Grant No. 5 RO 1 NS-07868 from the National Institute of Neurological Diseases and Stroke), and Professor L. Brand and Mr. M. Loken for helpful discussions.

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(12) For a ground-state analog see: M. Svoboda, J. Hapala, and J. Zavada, *Tetrahedron Lett.*, 265 (1972), and references therein.

(13) See P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry," Wiley, New York, N. Y., 1962, p 408, for the covalent character of these metal bonds.

(14) L. Brand and M. Loken, unpublished results.

Emil H. White,* David F. Roswell, C. C. Wei, Peter D. Wildes
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Received April 28, 1972

Bivalent and Monovalent Rhodium Porphyrin Complexes

Sir:

Although reports of rhodium(III) porphyrin complexes have appeared,[1-3] there are no reports on porphyrin complexes of bivalent rhodium. Yoshida and coworkers[4] have recently reported on rhodium(I) porphyrin complexes, containing one porphyrin bound to two rhodium atoms and formulated as $H^+[(\text{porphyrin})Rh_2(CO)_4Cl]^-$. Lower valent rhodium porphyrin complexes are of particular interest as possible homogeneous catalysts and also for comparison with cobalt(II) porphyrins which are known to reversibly carry oxygen at low temperatures.[5,6] We wish to report on the synthesis and characterization of rhodium(I) and rhodium(II) porphyrins and their chemical reactivity.

During attempts to synthesize the tetraphenylporphyrin (TPP) complex Rh(TPP)Cl by the method of Fleischer and Sadasivan,[2] we found that some preparations contained an esr signal other than that attributable to porphyrin impurities. This signal is due to the presence of a rhodium(II) complex Rh(TPP) which we have now obtained in reasonable yield. The rhodium(III) complex, characterized by analysis and visible, ir, and nmr spectroscopy, is isolated in small yield as $Rh(TPP)Cl \cdot H_2O$ when $[Rh(CO)_2Cl]_2$ is refluxed with TPP in glacial acetic acid under nitrogen; most of the rhodium precipitates as metal. If the carbonyl dimer is added slowly to the TPP in refluxing glacial acetic acid, then the major product is a bivalent rhodium complex. For example, 2 g of $[Rh(CO)_2Cl]_2$ was added to a refluxing solution of 3 g of TPP and 5 g of sodium acetate in 500 ml of acetic acid under nitrogen; about 0.5 g of the Rh(TPP) product was obtained after work-up and chromatography on Fluorosil.

The esr spectrum of the Rh(TPP) complex in chloroform at 77°K is shown in Figure 1 and is typical of previously reported esr spectra for a number of rhodium(II) systems.[7-9] The signals occur at $g = 2.089$, 2.029, 1.990; at room temperature, the average of the three anisotropic signals is observed at $g = 2.036$.

The magnetic moment, as determined in the solid state by the Gouy method and in solution by an nmr method,[10] was *ca.* 1.2 BM, but the value is subject to some uncertainty owing to the large diamagnetic correction. The expected moment for a rhodium(II) compound is *ca.* 2 BM,[11] although metal–metal bonding is typical in rhodium(II) compounds,[12-14] *e.g.*, Rh_2-

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(2) N. Sadasivan and E. B. Fleischer, *Chem. Commun.*, 159 (1967).

(3) E. B. Fleischer, R. Thorp, and D. Venerable, *ibid.*, 475 (1969).

(4) Z. Yoshida, H. Ogoshi, T. Omura, E. Watanabe, and T. Kurosaki, *Tetrahedron Lett.*, 1077 (1972).

(5) F. A. Walker, *J. Amer. Chem. Soc.*, **92**, 4235 (1970).

(6) H. C. Stynes and J. A. Ibers, *ibid.*, **94**, 1559 (1972).

(7) R. P. A. Muniz, N. V. Vugman, and J. Danon, *J. Chem. Phys.*, **54**, 1284 (1971).

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(10) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

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