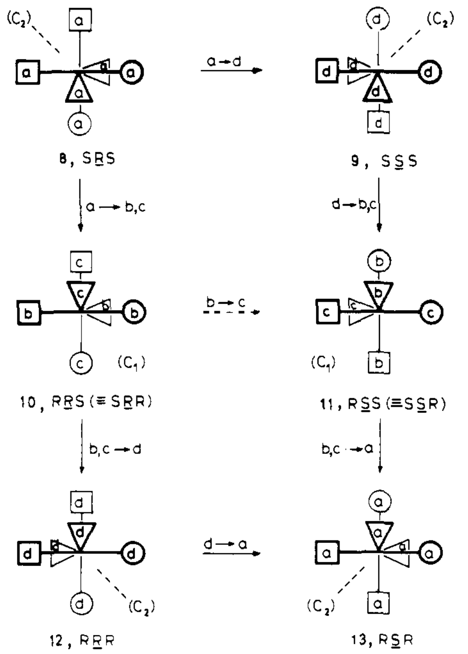


Figure 2. Symbolic representation of nickel inversion (horizontal transitions) and of substituent inversions (vertical) in **5**: diastereomerizations (→) and enantiomerizations (⇢).

metry reasons, only one signal (a) is expected for each of the three homotopic pairs □, ○, and ◁ (*o*-methyl groups). The central chirality at nickel will be labeled ***R*** and ***S***; in **8**, its configuration is ***R***.[7] Both bidentate ligands of **5/8** possess axial chirality and *S* configuration.[4,5] Hence **8** may be denoted at *S**RS***. Its mirror image is **13** with *R**SR*** configuration.

If only the front tolyl group rotates by 180°, the ligand chirality changes to *R*, producing a totally asymmetric[11] (C_1) isomer **10** (*R**RS***). Therefore, structurally equivalent substituents are diastereotopic and may have different NMR signals b and c. Further rotation of the rear tolyl group leads to the third diastereomer **12** (*R**RR*** with shifts d). When the rear ligand of **8** is rotated as a whole, only the nickel configuration will be inverted to the diastereomer **9** (*S**S**S*). The same rotation in **10** to yield **11** constitutes an enantiomerization.

Consequently, up to *four* NMR signals a–d (b and c must be equally intense) are expected. As shown in the lower part of Figure 1, we detected all four methyl absorptions (◁) at −20, −60, −105, and −135 Hz upfield from Me_4Si (60 MHz). Intensities were close to a molar ratio 1:2:1 for (**8** + **13**):(**10** + **11**):(**9** + **12**). Signal coalescences yielded $\Delta G^{\ddagger} = 17.7$ kcal/mol (380 K in tetralin), corresponding to easier tolyl rotation in **5** than in **4**.

Whereas chiral tetrahedral complexes are known of transition metals with four different ligands[12] and with bidentate ligands,[13,14] compounds **1a** and **2–5** appear to be the first clear-cut examples of the paramagnetic, open-shell type.[8,10,14,15] Chirality is normally not preserved even with similar ligands.[8-10,14] The nickel in an O_2N_2-tetrahedron could only be forced into stable chirality by a nonracemizing ligand cage[8] or by the bulky adamantyl substituent.[17] It is, however, quite possible that more examples of chirality went unrecognized.[18-22]

The old explanation of signal splitting by some conformational preference of the *N*-aryl substituents (but rapid nickel inversion) is vitiated by the NCH_3 groups of **3** and also incompatible with **1a**, **2**, **4**, and **5**. Such conformations should relax after one nickel inversion to produce the enantiomer and hence coalescence. Furthermore, *N*-phenyl rotation in **5** is quite fast with $\Delta G^{\ddagger} = 13.1$ kcal/mol (253 K).

We intend to report on additional chiral complexes, on the reasons for their rigidity, and on the mechanism of inversion in due course.

Acknowledgment. Support by the Deutsche Forschungsgemeinschaft and the Stiftung Volkswagenwerk is gratefully acknowledged.

References and Notes

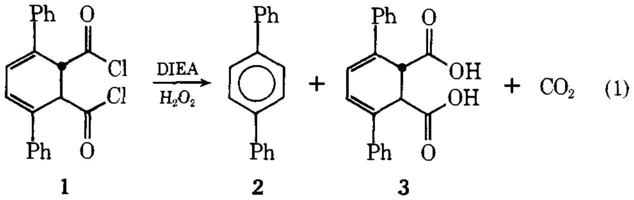
(1) R. Knorr, H. Polzer, and E. Bischler, *J. Am. Chem. Soc.*, **97**, 643–644 (1975).
(2) T. Schaefer, L. Kruczynski, and W. Niemczura, *Chem. Phys. Lett.*, **38**, 498 (1976), and references cited therein.
(3) S. G. McGeachin, *Can. J. Chem.*, **46**, 1903–1912 (1968).
(4) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem.*, **78**, 413–447 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 385, 511 (1966).
(5) IUPAC Tentative Rules, Section E, *J. Org. Chem.*, **35**, 2849–2867 (1970).
(6) The orthogonality of the π-systems follows from shifts of **4** and **5**: R. Knorr, A. Weiss, H. Polzer, and E. Bischler, *J. Am. Chem. Soc.*, **97**, 644–646 (1975).
(7) We prefer the IUPAC recommendations.[4,5] In Holm's nomenclature,[8,9,10a] **8** would have Λ configuration.
(8) M. J. O'Connor, R. E. Ernst, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 4561–4568 (1968), and references cited therein.
(9) R. H. Holm, *Acc. Chem. Res.*, **2**, 307–316 (1969).
(10) R. H. Holm and C. J. Hawkins in "NMR of Paramagnetic Molecules", G. N. LaMar, W. DeW. Horrocks, Jr., and R. H. Holm, Ed., Academic Press, New York and London, 1973, pp 243–332, (a) p 301, (b) p 315.
(11) Note that **10** (*RRS*) is not a meso compound like Λ(+,−)[8] when the nickel retains its chirality, as was clearly shown in a chiral solvent:[10b] R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 5305–5306 (1968).
(12) H. Brunner, *Angew. Chem.*, **83**, 274–285 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 249 (1971).
(13) S. S. Eaton and R. H. Holm, *Inorg. Chem.*, **10**, 1446–1452 (1971).
(14) R. H. Holm and M. J. O'Connor, *Prog. Inorg. Chem.*, **14**, 241–401 (1971).
(15) A tetrahedral structure is less certain for some optically active complexes.[14,16]
(16) T.-M. Hseu, D. F. Martin, and T. Moeller, *Inorg. Chem.*, **2**, 587–590 (1963).
(17) G. W. Everett and C. R. Powers, *Inorg. Chem.*, **9**, 521–527 (1970).
(18) C. R. Powers and G. W. Everett, *J. Am. Chem. Soc.*, **91**, 3468–3476 (1969); see p 3474.
(19) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397–406 (1963); see p 405.
(20) J. E. Parks and R. H. Holm, *Inorg. Chem.*, **7**, 1408–1416 (1968); see p 1415.
(21) C. L. Honeybourne and G. A. Webb, *Chem. Phys. Lett.*, **2**, 426–428 (1968); compare C. L. Honeybourne, *ibid.*, **8**, 493–496 (1971).
(22) R. Bonnett, D. C. Bradley, K. J. Fisher, and I. F. Rendall, *J. Chem. Soc. A*, 1622–1627 (1971).

Rudolf Knorr,* Alfons Weiss
Heinz Polzer, Edith Räpple
Institute of Organic Chemistry, University of Munich
8000 Munich 2, West Germany
Received July 7, 1976

New Chemiluminescent Reaction Systems. Light Formation from the Reaction of a Vicinal Diacid Chloride

Sir:

We wish to report the observation of a new, remarkably efficient, chemiluminescent processes.[1] It was found that 3,6-diphenyl-3,5-cyclohexadiene-1,2-*trans*-dicarboxylic acid chloride (**1**) reacts with diisopropylethylamine (DIEA) and hydrogen peroxide in THF to produce an easily detected emission of light from the singlet state (^1L_A) of *p*-terphenyl (**2**).[2-4] This reaction represents one of the most energetic organic chemiluminescent systems and one of the first examples



1 **2** **3**

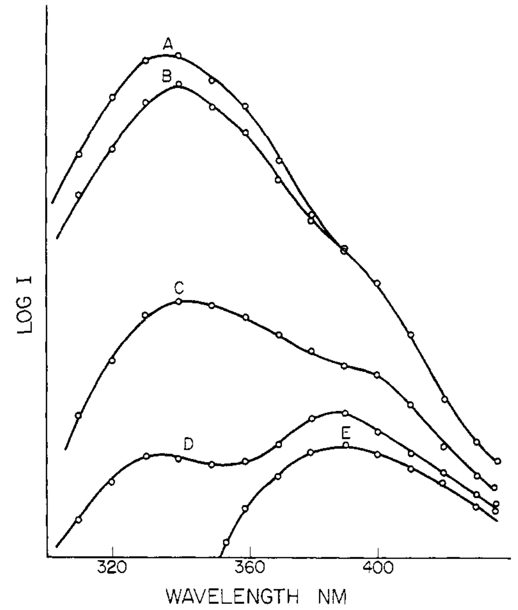


Figure 1. Fluorescence and chemiluminescence emission spectra of *p*-terphenyl in THF: A, *p*-terphenyl; B, *p*-terphenyl and 5×10^{-6} M **1**; C, *p*-terphenyl and 5×10^{-5} M **1**; D, *p*-terphenyl and 1×10^{-4} M **1**; E, chemiluminescence of **1**, 4×10^{-3} M.

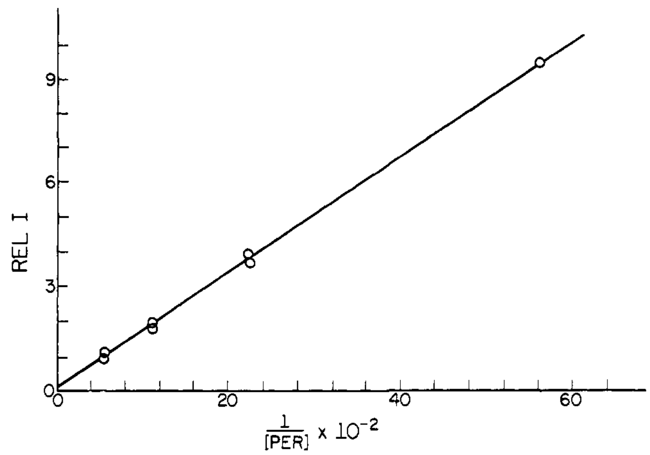


Figure 2. Reciprocal plot to determine lifetime of chemically formed excited singlet state with perylene as acceptor.

of the direct chemical formation of a hydrocarbon π-π^* excited singlet state.[1]

The reaction of **1** with DIEA and H_2O_2 was conveniently followed by UV spectroscopy or by the chemiluminescent emission. In the former, both the depletion of the starting material (**1**) and appearance of product (**2**) was observed and found to be related by an isosbestic point at 300 nm. The rate of the chemiluminescent emission intensity decay was consistent with the observed rate of formation of **2** under similar reaction conditions. Analysis of the product mixture revealed **2**, *trans*-diacid **3**, and CO_2 (eq 1). The relative yields of **2**, **3**, and CO_2 were dependent upon the reaction conditions. Typically, with stoichiometric concentrations, the yields of **2** and CO_2 were ca. 65%.

The chemiluminescent emission spectrum observed during the reaction of **1** was broad and structureless with an apparent maximum at ca. 390 nm. Analysis of the spectrum was complicated because the absorption spectrum of the starting material (**1**) overlapped the emission spectrum. However, the spectrum could be synthesized by the superposition of the *p*-terphenyl emission spectrum on the absorption spectrum of **1** (Figure 1). Inclusion of an energy accepting fluorophore such as perylene, 9,10-diphenylanthracene, or rubrene in the reaction solution resulted in a large increase in chemiluminescent intensity and a shift of the emission spectrum to that of the added fluorophore. The rate of the chemiluminescent reaction was independent of both the particular fluorophore and its concentration over a 100-fold range.[5] Thus, the energy transfer to the fluorophore must occur subsequent to the chemical formation of the electronically excited state.

The lifetime (τ) of the excited state responsible for the chemiluminescence was determined by measuring the total chemiluminescent intensity as a function of added acceptor molecule concentration.[6] A reciprocal plot of light intensity against concentration of acceptor is shown in Figure 2 for perylene. The ratio of the intercept to the slope of this plot is related to the lifetime of the initially formed excited state by

$$\text{intercept/slope} = k_{\mathrm{et}}\tau \qquad (2)$$

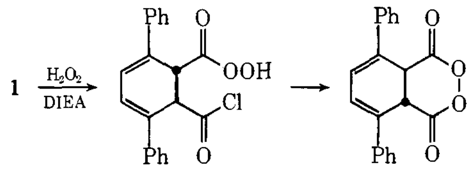
where k_{et} is the rate of energy transfer to the perylene. With the assumption of diffusion-limited energy transfer, a lifetime of 3 ± 2 ns was calculated for the chemically formed excited state.[7] The singlet lifetime of *p*-terphenyl is reported to be ca. 1-2 ns.[8] Thus, the combination of spectral and lifetime data permits the tentative conclusion that *p*-terphenyl excited singlet is formed during the reaction of **1**.

Attempts were made to detect the presence of singlet oxygen in the reaction mixture as a precursor to the excited state *p*-terphenyl. Inclusion of 0.1 M tetramethylethylene (TME) in the reaction solution did not change the rate of the chemiluminescent reaction nor did it change the quantity of light formed. Furthermore, it was not possible to detect any 2,3-dimethyl-3-hydroperoxy-1-butene, the "ene" reaction product of TME and singlet oxygen, among the products of the reaction to an extent greater than 0.1%.[9] 1,3-Diphenylisobenzofuran (DPIBF) is one of the most efficient singlet oxygen acceptors known.[10] Addition of DPIBF to the reaction mixture resulted in the observation of DPIBF fluorescence. The rate of the chemiluminescent reaction with this fluorophore was the same, within experimental error, as when the other fluorophores were used. If singlet oxygen were a precursor to excited *p*-terphenyl, then DPIBF would have quenched the chemiluminescence.

Estimates of the yield of chemically formed singlet excited states from the reaction of **1** were made by several techniques. Qualitatively, the light formed from 2 mg of **1** in 5 ml of THF is bright enough to be easily seen in a darkened room for 10 min. The total light emission of **1** with perylene as acceptor was compared to the light emission from bis(2,4-dinitrophenyl) oxalate under similar conditions.[11] Extrapolation of the intensity data to infinite perylene concentration ($\phi_{\mathrm{et}} = 1.0$) gave a total yield of excited *p*-terphenyl singlet of ca. 1.5 ± 1%. A second method for estimating the yield of chemically formed excited singlet states measures the emission intensity from the reaction of **1** in the presence of DPIBF with a standardized photomultiplier tube through a rhodamine B quantum counter.[12] After correction for inefficiency in the energy transfer step, a yield of excited *p*-terphenyl singlet of 3 ± 1% was calculated. Thus excited singlet state production during the reaction of **1** appears to occur with moderate efficiency.

Detection and quantification of chemically formed triplet *p*-terphenyl was also carried out. Fluorescein and its derivatives have been shown to be efficient acceptors for long range triplet to singlet energy transfer from both aromatic and carbonyl donors.[13] The fluorescence of added tetrabromofluorescein (TBF) was observed during the reaction of **1**. A plot of the reciprocal of the TBF fluorescence intensity against the reciprocal of the TBF concentration was linear. The ratio of the slope to the intercept of this plot indicated interception of an excited state with a lifetime of 0.2 ± 0.12 μs.[14] We surmise that this long lived transient is the triplet excited state of *p*-terphenyl. The yield of triplet *p*-terphenyl was estimated by comparing the sensitized TBF fluorescence intensity at extrapolated infinite TBF concentration from **1** and from tetramethyldioxetane (TMD) under similar reaction conditions. This analysis indicated that 35 ± 10% of the **1** that is consumed becomes a *p*-terphenyl triplet.[15] Correction of the total yield of excited states for the chemical yield of *p*-terphenyl leads to the conclusion that ca. 60% of the *p*-terphenyl formed in the reaction of **1** is produced in an electronically exicted state. This system, therefore, represents one of the most efficient chemielectronic reactions yet discovered.

The reasonable mechanisms for this chemiluminescent reaction involve at least one intermediate. A reasonable candidate for the intermediate immediately preceding formation of the excited state is the cyclic diacyl peroxide **4**. Rearrangement of **4** to *p*-terphenyl and carbon dioxide is exothermic by ca. 85 kcal/mol.[17] The lowest excited singlet state of *p*-terphenyl is 90 kcal/mol above the ground state.[18] Thus, fragmentation of **4** almost certainly produces sufficient energy to form the observed excited states.[19] This fragmentation may occur by either a stepwise mechanism through a biradical or by a concerted bond cleavage. If concerted, the symmetry "allowed" $2_s + 2_s + 2_s$ path would generate an unlikely trans bond in the central benzene ring of **2**. Alternatively, the "forbidden" $2_s + 2_a + 2_s$ path would be sterically permitted. This path is predicted to lead directly to an electronically excited state of **2**.[21] In any event, the large exothermicity of this rearrangement may be the key factor in promoting the efficient formation of electronically excited states. Further experimental work is aimed at the conclusive identification of the reactive intermediate and elucidation of the mechanism for this interesting chemiluminescent reaction.



4

Acknowledgment. The author wishes to thank Professor S. G. Smith for his assistance throughout this work. This work was supported in part by the Office of Naval Research and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

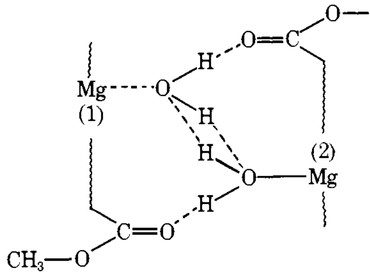
(1) E. H. White and D. F. Roswell, *Acc. Chem. Res.*, **3**, 54 (1970); K. D. Gundermann, *Fortschr. Chem. Forsch.*, **46**, 61 (1974); N. J. Turro, P. Lechtken, G. B. Schuster, H. C. Steinmetzer, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974).
(2) Prepared from the diacid[3] with thionyl chloride. Anal. ($C_{20}H_{14}O_2Cl_2$) C, H, Cl.
(3) L. E. Fieser and M. J. Haddidian, *J. Am. Chem. Soc.*, **86**, 2392 (1964).
(4) Light was detected with an EMI 9813B photomultiplier by the photon counting technique.
(5) Typical conditions: acid chloride = 2×10^{-4}, DIEA = 5×10^{-3}, H_2O_2 = 4×10^{-3}, perylene = 4×10^{-3} M, resulting in an observed pseudo-first-order rate constant at room temperature in air saturated THF of $(9.2 \pm 0.3) \times 10^{-3}\ s^{-1}$.
(6) N. J. Turro, G. B. Schuster, R. G. Bergman, K. J. Shea, and J. H. Davis, *J. Am. Chem. Soc.*, **97**, 4758 (1975).
(7) Any long range component to the energy transfer would result in a shorter calculated lifetime.
(8) C. D. Amata, M. Burton, W. P. Helman, P. K. Ludwig, and S. A. Rodemeyer, *J. Chem. Phys.*, **48**, 2374 (1968); M. Burton, P. Ludwig, and J. T. D'Allessio, *Acta. Phys. Pol.*, **26**, 517 (1964).
(9) Control experiments showed that amine quenching of singlet oxygen did not compete with trapping by TME at the concentrations used: E. A. Ogryzlo and C. W. Tang, *J. Am. Chem. Soc.*, **92**, 5034 (1970); K. Gollnick, *Adv. Photochem.*, **6**, 1 (1968); C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
(10) T. Wilson, *J. Am. Chem. Soc.*, **88**, 2898 (1966).
(11) M. M. Rauhut, *Acc. Chem. Res.*, **2**, 80 (1969).
(12) P. R. Michael and L. R. Faulkner, *Anal. Chem.*, **48**, 1188 (1976).
(13) R. G. Bennet, R. P. Schwenker, and R. E. Kellog, *J. Chem. Phys.*, **41**, 3040 (1964); R. E. Kellog and R. G. Bennet, *ibid.*, 41, 3042 (1964); V. L. Ermolaev and E. B. Sveshnikova, *Opt. Spectrosc. (USSR)*, 17, 321 (1964).
(14) Estimation of the donor lifetime requires an assumed value for the rate constant of energy transfer. Based upon the observed R_0 values for transfer to fluorescein from phenanthrene and 2-acetonaphthone,[13] the rate constant for energy transfer was set equal to 1×10^{11} l. mol/s. If energy transfer is slower, the calculated lifetime is longer.
(15) The yield of *p*-terphenyl triplet from this analysis of course depends upon the yield of excited acetone from thermal decomposition of TMD. The literature[16] value of 50% for this quantity was employed.
(16) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **94**, 2886 (1972).
(17) S. W. Benson, F. R. Cruichshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
(18) I. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, London, 1965.
(19) Another possible energy sufficient intermediate is the diperoxycarboxylic acid. However, bimolecular decomposition of peroxycarboxylic acids has been shown to lead to the acid.[20]
(20) J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).
(21) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970.

Gary B. Schuster
Department of Chemistry, Roger Adams Laboratory
University of Illinois
Urbana, Illinois 61801
Received July 12, 1976

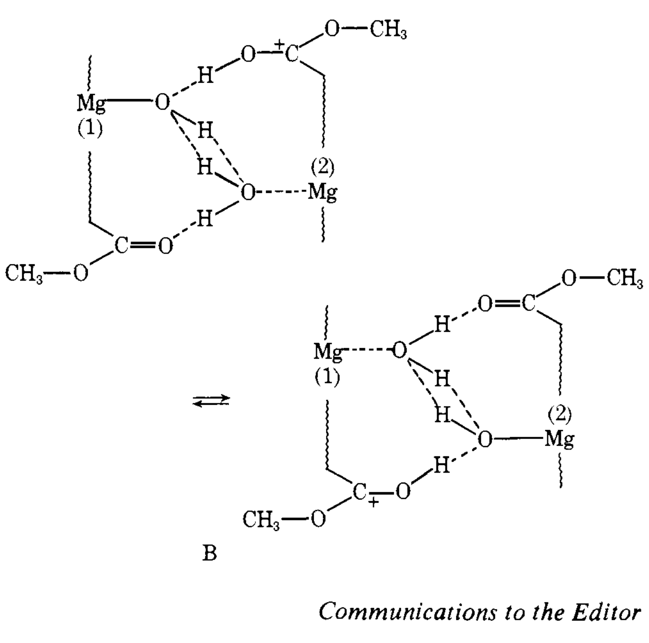
The Role of Water on the Photoactivity of Chlorophyll a. In Vitro Experimental Characterization of the PSI Light Reaction in Photosynthesis[1]

Sir:

Recent experimental studies in this laboratory have been concerned with the preparation[2] and characterization[3] of the P700 chlorophyll a monohydrate dimer $(\text{Chl a}\cdot\text{H}_2\text{O})_2$ after the proposed model for the photosystem I reaction center in plant photosynthesis.[4] It is believed[4] that a singlet-triplet upconversion interaction[5-7] in $(\text{Chl a}\cdot\text{H}_2\text{O})_2$ brings about a tautomeric proton shift that results in the creation of a symmetrical charge transfer state[4] (B). The observation[8,9] of positive



A



B