100 ml of EtOH. Recrystallization from EtOH gave 9.4 g (69%) of VIIIe, mp 100°.

N,N′-Diethoxycarbonyl-6-aminofulvene-2-aldimine (VIIIf). To a solution of 1.2 g of VIIIa and 10 ml of triethylamine in 100 ml of absolute ether, a solution of 2.2 g of ethyl chloroformate in 10 ml of ether was added at 0°. After stirring for 30 min, the brown ether solution was washed with water and, after drying, evaporated under vacuum. The residue was recrystallized from cyclohexane, giving 1.4 g (53%) of fine yellow needles, mp 133°.

6-*t*-Butylaminofulvene-2-(N-methyl)aldimine (VIIIg). In a separatory funnel, a solution of 5.1 g of VII, R_1 = *t*-Bu, in 100 ml of ether was shaken with 75 ml of 40% aqueous methylamine. The ether layer was washed twice with water and dried. Evaporation of the solvent afforded a yellow oil, which solidified upon cooling. Recrystallization from hexane (−60°) gave 4.3 g (91%) of yellow crystals, mp 52°.

6-*t*-Butylaminofulvene-2-(N-cyclohexyl)aldimine (VIIIh). A mixture of 2.0 g of VII, R_1 = *t*-Bu, and 1.0 g of cyclohexylamine in 50 ml of MeOH was refluxed for 1 hr. Upon cooling, 2.4 g (93%) of yellow needles precipitated, which, after recrystallization from MeOH, had mp 98°. In some instances, a mixture of two crystalline forms (mp 84 and 98°) was obtained. Differential scanning calorimetry confirmed that above 84° an exothermic crystallization occurred.

6-*t*-Butylaminofulvene-2-(N-phenyl)aldimine (VIIIi). A solution of 2.0 g of VII, R_1 = *t*-Bu, and 0.95 g of aniline in 100 ml of hexane was refluxed for 1 hr. On cooling, yellow crystals precipitated which were recrystallized from hexane. The yield is 2.4 g (96%), mp 99°.

6-Methylaminofulvene-2-aldehyde (i). A solution of 1.0 g of VIIIb in 50 ml of EtOH and 30 ml of water was heated on a steam bath for 2 hr. On cooling, 0.90 g (96%) of crystals precipitated. Recrystallization from hexane gave yellow neddles, mp 71.5°.

Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36; mol wt, 135.17. Found: C, 71.26; H, 6.71; N, 10.15; mol wt, 134.

Acknowledgments. The synthesis and the physical investigations of the symmetrically substituted aminoimines were carried out in K. Hafner's laboratory at the Institut für Organische Chemie der Technischen Hochschule, Darmstadt, as part of the author's dissertation. I wish to thank Professor Hafner for his valuable advice and many discussions. I am also indebted to Mrs. L. W. Mansperger, Miss M. Woscheé, and Mr. T. T. Horikawa for their technical assistance.

Energy Transfer in Chemiluminescence.[1,2] II

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Abstract: Both 2,3-dihydro-6-[(9,10-diphenyl-2-anthryl)methyl]benzo[*g*]phthalazine-1,4-dione (**4**) and 2,3-dihydro-6-[(9-oxo-10-acridanyl)methyl]phthalazine-1,4-dione (**6**) have been synthesized. These compounds are chemiluminescent under oxidative conditions. The chemiluminescence emission spectra of **4** and **6** show that intramolecular energy transfer is occurring in these compounds. The relative chemiluminescence quantum yields, with respect to luminol (about 1.0), have been measured and are, for **4** and **6**, 0.26 and 0.08, respectively. The rate of energy transfer in compound **4** was calculated to be 2.4×10^7 sec^{-1}.

The concept that an electronically excited state can transfer its energy to a ground state of another atom or molecule, raising it in turn to an excited state, was first predicted by Franck in 1922.[3] Since that time intermolecular energy transfer has been studied extensively and it forms the basis for sensitized photochemistry.[4]

Intramolecular energy transfer also has been studied using molecules containing two nonconjugated chromophores, *i.e.* D–A. When the donor (D) is raised to an excited state by light absorption, emission is observed from the acceptor (A) portion of the molecule. Examples of this type of transfer have been reported by several groups of workers.[5-7]

In chemiluminescence, in which chemically produced electronically excited states are involved,[8,9] intermolecular energy transfer has been shown to be an important process. Examples of this process include the reaction of oxalyl chloride or oxalate esters with hydrogen peroxide in the presence of fluorescent acceptors,[10] the decomposition of dicyclohexyl peroxycarbonate in the presence of acceptors,[11] the autoxidation of tetralin in the presence of 9,10-diphenylanthracene,[12] and the decomposition of tetralin hydroperoxide in the presence of porphyrins.[13]

To observe intramolecular energy transfer in chemiluminescene, we have prepared hydrazides in which the energy-generating and light-emitting functions are separated.

The chemiluminescene of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione, **1**, 5 = NH_2) and related hydrazides (**1**) has been studied extensively.[8,9,14-18]

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(1) For paper I see E. H. White and D. F. Roswell, *J. Amer. Chem. Soc.*, 89, 3944 (1967).

(2) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 15, 1967.

(3) J. Franck, *Z. Phys.*, 9, 259 (1922).

(4) For example, see N. J. Turro, "Molecular Photochemistry," 1st ed, W. A. Benjamin, New York, N. Y., 1967.

(5) O. Schnepp and M. Levy, *J. Amer. Chem. Soc.*, 84, 172 (1962).

(6) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, 87, 995 (1965).

(7) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, 87, 2322 (1965).

(8) E. H. White in "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961, p 183.

(9) (a) K. D. Gundermann, "Chemilumineszenz Organisher Verbindungen," Springer-Verlag, Berlin, 1968; (b) R. F. Vassil'ev in "Progress in Reaction Kinetics," G. Porter, Ed., Pergamon Press, New York, N. Y., 1967, p 305.

(10) M. M. Rauhut, *Accounts Chem. Res.*, 2, 80 (1969), and references contained therein.

(11) D. Philips, V. Anissimov, O. Karpukhin, and V. Shiliapintokh, *Nature*, 215, 1163 (1967).

(12) G. Lunden and R. Livingston, *Photochem. Photobiol.*, 4, 1085 (1965).

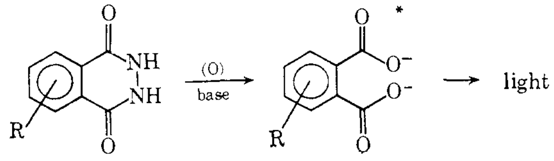
(13) H. Linschitz in "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961, p 173.

Table I. Chemiluminescence and Fluorescence Results[a] with **4**

	Wavelength maxima (nm)	
	Aqueous system[b]	Aprotic system[c]
Chemiluminescence of **4**	355, 425, 440 (sh)	425, 440 (sh)
Fluorescence of total reaction products	355, 425, 440 (sh)	425, 440 (sh)
Fluorescence of 9,10-diphenylanthracene	425, 440 (sh)[d]	425, 440 (sh)
Fluorescence of sodium 2,3-naphthalenedicarboxylate	358	355[e]

[a] Slit widths and scanning speeds constant in all runs; concentration $<10^{-4}$ *M*; error ±3 nm. [b] 0.1 *N* sodium hydroxide, hydrogen peroxide, and hemin. [c] 90% dimethyl sulfoxide–10% *t*-butyl alcohol and potassium *t*-butoxide. [d] Dissolved initially in a small amount of ethanol to effect solution. [e] Extremely weak.

The reaction involves an oxidation of the hydrazide and the formation of an excited singlet state of the resulting product, the dicarboxylate ion **2**; emission of a photon then completes the process.[14,15] Two general



1 **2**

systems have been used for the oxidation reaction: (1) the "aqueous system" (hydrazide plus aqueous alkaline hydrogen peroxide and a peroxide-decomposing catalyst or oxidizing agent) or (2) the "aprotic system" (hydrazide in an aprotic solvent plus oxygen and a strong base).[14]

A general correlation between the fluorescence quantum yield of the phthalate ions and the quantum yield of chemiluminescence of the hydrazides has been noted.[8] Thus highly chemiluminescent hydrazides require structures leading to highly fluorescent phthalate ions. This approach is not always successful, however, because the conjugated systems needed to achieve high fluorescence efficiency are readily destroyed by the oxidizing agents used; furthermore, the larger systems have absorption bands in the visible region and self-quenching reduces light yields at higher concentrations. By using difunctional molecules B–A, highly fluorescent groups A can be attached, yet insulated from a basic energy generating structure, B. Not only should intramolecular energy transfer be observed but also high chemiluminescent quantum yields should be obtainable. The following reaction path should be available where D represents the dicarboxylate ion obtained from the oxidation, and B is the starting hydrazide.

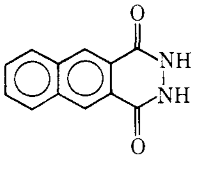
$$\text{B–A} \xrightarrow{[\text{O}]} \text{D}^*\text{–A} \longrightarrow \text{D–A}^* \longrightarrow \text{D–A} + h\nu$$

Results and Discussion

For the preparation of the first difunctional compound, **4**, 2,3-dihydrobenzo[*g*]phthalazine-1,4-dione (**3**) was selected as the hydrazide portion and 9,10-diphenylanthracene as the acceptor. The actual donor in this case is the excited state of 2,3-naphthalate ion formed by oxidation of the hydrazide. The fluorescence of 2,3-naphthalate ion occurs at 358 nm and this emission overlaps the absorption of 9,10-diphenylanthracene; this overlap is a necessary condition for certain types of energy transfer to occur.[19]

To provide a means of attaching the donor to the acceptor, N-methyl-2,3-naphthalenedicarboimide was chloromethylated to give compound **5**. Chloromethylation occurred at the 5 position of the naphthalene ring as shown by a 100-Mcps nmr spectrum. The splitting pattern (see Experimental Section) was consistent with the three remaining protons being on adjacent carbons.

The synthesis of 2,3-dihydro-6-[(9,10-diphenyl-2-anthryl)methyl]benzo[*g*]phthalazine-1,4-dione (**4**) involved condensing the N-methyl-5-chloromethyl-2,3-naphthalenedicarboimide (**5**) with 9,10-diphenylanthracene under Friedel–Crafts conditions. The structure of the resulting N-methylimide was established from its spectral properties (the ultraviolet spectrum was shown to be a summation of the spectra of the parts rather than that of a new conjugated system), and by analogy to other reactions (it has been shown that acylation of 9,10-diphenylanthracene occurs at the 2 position of the anthracene ring[20]). The N-methylimide was converted into the hydrazide (**4**) with hydrazine hydrate.



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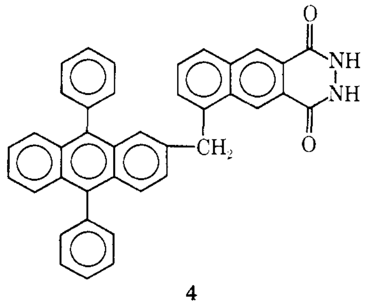

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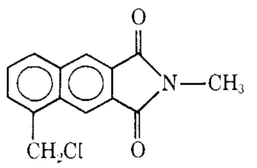

5

The chemiluminescence results (Table I) indicate that energy transfer between excited 2,3-naphthalate

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(14) E. H. White, O. C. Zafiriou, H. M. Kagi, and J. H. M. Hill, *J. Amer. Chem. Soc.*, **86**, 940 (1964).

(15) E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964).

(16) K. D. Gundermann, W. Horstmann, and G. Bergmann, *Ann. Chem.*, **684**, 127 (1965).

(17) K. D. Gundermann, *Angew. Chem., Int. Ed. Engl.*, 4, 566 (1965).

(18) E. H. White and D. F. Roswell, *Accounts Chem. Res.*, **2**, 54 (1969).

(19) T. Förster, *Discuss. Faraday Soc.*, 27, 7 (1959).

(20) R. G. Douris, *Compt. Rend.*, **229**, 224 (1949).

ion and 9,10-diphenylanthracene is occurring. In the aqueous reaction system (aqueous base, hydrogen peroxide, hemin), the observed chemiluminescence emission occurs from both portions of the molecule. From the data (Table I) it is apparent that the excited 2,3-naphthalate ions formed in the chemical reaction undergo partitioning. Some of the excited states decay by emitting a photon and this leads to light emission from the naphthalate portion of the molecule (emission at *ca.* 358 mμ). Some of the excited naphthalate ions transfer their energy to the 9,10-diphenylanthracyl moiety, which in turn emits a photon (emission at 425 and 440 mμ). The fine structure from the emission of the 9,10-diphenylanthracyl portion is not as pronounced as in the normal fluorescence of 9,10-diphenylanthracene. This difference is presumably due to the relatively large slit widths used as well as to the fact that scanning was fairly rapid to ensure constant intensity during the time the chemiluminescence spectrum was recorded.

Table I also shows the results from **4** in 90% dimethyl sulfoxide–10% *t*-butyl alcohol with potassium *t*-butoxide and air (the aprotic system). Only the diphenylanthracene portion emits under these reaction conditions. This fact is not surprising because in dimethyl sulfoxide the chemiluminescence of **3** is very weak and the fluorescence yield of disodium 2,3-naphthalenedicarboxylate is vanishingly low.[21]

The total light from the chemiluminescent reaction in the dimethyl sulfoxide system was found to be linear with concentration in the range 1.1×10^{-6} to 5.5×10^{-6} *M* (the dimethyl sulfoxide system was used for total light measurements since the rate of the chemiluminescent reaction was moderate in this system whereas in the aqueous system it was quite slow). A mixture of **3** and 9,10-diphenylanthracene (10^{-4} *M*) gave, visually, no more light than a 10^{-4} *M* solution of **3** itself and the emission spectrum of this mixture was identical with one obtained from the chemiluminescence of **3**. From these observations it may be concluded that the energy transfer occurring in compound **4** is intramolecular.

The fact that in the aqueous reaction system excited 2,3-naphthalate ions emitted light in addition to transferring energy to the diphenylanthracene moiety allowed the calculation of the rate of energy transfer. This calculation was performed as follows. (1) The following definitions were used: * = excited state; k_f = rate of fluorescence; k_{et} = rate of energy transfer; k_d = rate of all other unimolecular excited state decay processes; A = diphenylanthracene portion of the molecule (the acceptor); B = 2,3-naphthalic acid ion portion (the donor); Φ_A = fluorescence quantum yield of diphenylanthracene in the product molecule. (2) Total emission = emission from A* + emission from B*. (3) Number of B* that emit = $k_f/(k_f + k_d + k_{et})$(total B* formed). (4) Number of B* that transfer = $k_{et}/(k_{et} + k_d + k_f)$(total B* formed). (5) Number of A* that form = number of B* that transfer. (6) Number of A* that emit = (number of A* formed)·(Φ_A). Solving the equation gives us

$$\frac{\%\ \text{B emission}}{\%\ \text{A emission}} = \frac{k_f}{k_{et}\Phi_A}$$

The rate of fluorescence of B (k_f) can be obtained from the absorption spectrum of B from the following approximate relationships[22] where τ° is

$$\tau^\circ = \frac{1}{k_f} = \frac{3.5 \times 10^8}{\bar{\nu}_m{}^2 \epsilon_m \Delta\bar{\nu}_{1/2}}$$

The singlet absorption band for 2,3-naphthalate ion is at 331 mμ; thus $\bar{\nu} = 3.02 \times 10^{-4}$ cm^{-1}. The band width at half-height ($\nu_{1/2}$) is 5×10^2 cm^{-1} and the extinction coefficient is 545. Therefore the inherent radiative lifetime is 1.4×10^{-6} sec and the reciprocal of this, 7.1×10^5 sec^{-1}, is equal to k_f. The per cent emission from A and B was obtained from the respective areas of the total emission spectrum and the ratio of % B:% A was found to be 0.099. The quantum yield of fluorescence of the diphenylanthracene portion of the product molecule under the conditions of the chemiluminescence reactions was found to be 0.3.[23] Therefore, the rate of energy transfer in this system was calculated to be

$$k_{et} = \frac{k_f}{0.099\Phi_A} = \frac{7.1 \times 10^5\ \text{sec}^{-1}}{(0.099)(0.3)} = 2.4 \times 10^7\ \text{sec}^{-1}$$

The energy transfer rate constant thus calculated is similar in magnitude to the ones observed for the naphthalene–benzophenone singlet–singlet energy transfer in bridged molecules; in their case, *i.e.*, $k_{et} \sim 10^7$–10^8 sec^{-1}.[7]

This rate constant is in the range one would expect since k_f was found to be 7.1×10^5 sec^{-1}. From the observed emission, k_{et} and k_f are competitive since emission from both portions of the molecule occurred.

Table II gives the relative chemiluminescent efficiencies of compounds **3** and **4** with respect to luminol. From this table it can be seen that hydrazide **4** demonstrated that not only can energy transfer occur in aromatic hydrazide chemiluminescence but also that it can play an important role in increasing the efficiency of chemiluminescence (that is, compound **4** is 4.33 times as efficient as **3**).

Table II. Chemiluminescence Efficiencies

Compd	Relative efficiency
Luminol	1.00[a]
3	0.06
4	0.26
6	0.08

[a] Absolute Φ_{Ch} = 0.01.

2,3-Dihydrophthalazine-1,4-dione (**1**, R = H) is essentially nonchemiluminescent under aqueous conditions,[9,24] presumably because the reaction product, phthalate ion, is nonfluorescent.[25] Nevertheless, it seems reasonable, by analogy to the reaction pathway of related hydrazides,[14,15] that excited phthalate ions are formed in this reaction (and in the chemiluminescence of **1** (R = H) in aprotic solvents[25]).

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[21] O. C. Zafiriou, Ph.D. Thesis, The Johns Hopkins University, Baltimore, Md., 1966.

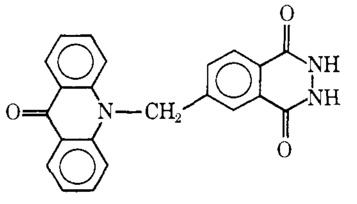
[22] N. J. Turro, "Molecular Photochemistry," 1st ed, W. A. Benjamin, New York, N. Y., 1967, p 49.

[23] We thank Dr. Thomas A. Hopkins for measuring this quantum yield.

[24] M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Amer. Chem. Soc.*, **88**, 3604 (1966).

[25] E. H. White, D. F. Roswell, and O. C. Zafiriou, *J. Org. Chem.*, **34**, 2462 (1969).

To help settle this point, phthalic hydrazide was linked to a fluorescent acceptor molecule to determine if emission from the acceptor could be observed in the aqueous system. The compound selected for this study was 2,3-dihydro-6-[(9-oxo-10-acridanyl)methyl]-phthalazine-1,4-dione (**6**). Its synthesis proved straightforward. Acridonyl anion was prepared with sodium hydride in dimethoxyethane and allowed to react with N-methyl-4-bromomethylphthalimide. The resulting imide was then converted to the hydrazide (**6**) with hydrazine in ethanol.



6

Compound **6** yields a fairly strong blue emission in either hemin–hydrogen peroxide–aqueous base or in dimethyl sulfoxide–*t*-butyl alcohol–potassium *t*-butoxide (in air). Table III shows the emission and fluorescence maxima associated with this hydrazide.

Table III. Chemiluminescence and Fluorescence Results[a]

	—Wavelength maxima (nm)—	
	Aqueous system[b]	Aprotic system[c]
Chemiluminescence of **6**	430,450 (sh)	440
Fluorescence of total reaction products	430,450 (sh)	440
Fluorescence of N-methyl-acridone	430,450 (sh)[d]	440

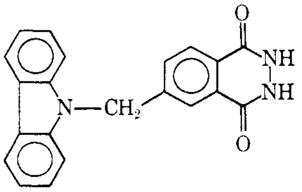
[a] Slit widths and scanning speeds constant in all runs; concentration $<10^{-4}$ *M*; error ±3 nm. [b] 0.1 *N* sodium hydroxide, hydrogen peroxide, and hemin. [c] 90% dimethyl sulfoxide–10% *t*-butyl alcohol, and potassium *t*-butoxide. [d] Dissolved initially in a small amount of ethanol to effect solution.

The chemiluminescence of hydrazide **6**, in both solvent systems, must be arising from energy transfer, since only emission from the N-methylacridone portion of the molecule is observed. Therefore excited phthalate ion, or some other excited molecule, must form in the chemical reaction and transfer its energy, instead of emitting or being quenched. The only organic product isolated from the reaction of phthalic hydrazide is phthalate ion (as its salt)[25] and in the reaction of **6** the only product detectable (by paper chromatography) was shown to be identical with the corresponding diacid (4-[(9-oxo-10-acridanyl)methyl]phthalic acid) prepared by heating the N-methyl imide with alcoholic potassium hydroxide. The excited molecule that leads to energy transfer to N-methylacridone may, in principle, be some intermediate in the chemical reaction. This is unlikely, however, since substituted phthalate ions are known to be the excited molecules in the chemiluminescent reactions of all the efficient hydrazides that have been tested;[14,15] phthalate ion is thus probably the species formed in an excited state from **6**.

The total light emitted from solutions of **6** was shown to be linear with concentration. A solution of 4-methylphthalic hydrazide and N-methylacridone (10^{-4} *M* in both) was shown to give no measurable light in the chemiluminescence reaction systems used. These facts, plus the wavelengths of emission, show that the light emission from **6** arises from intramolecular energy transfer.

Compound **6** is 0.08 as efficient as luminol (Table II); this factor was found to be the same in both the aqueous and dimethyl sulfoxide systems. The difference in chemiluminescence yields for other hydrazides in dimethyl sulfoxide *vs.* water is ascribed to a difference in fluorescence efficiency of the emitter. For example, compound **3** is more chemiluminescent in the aqueous system than in the dimethyl sulfoxide one and the emitter, 2,3-naphthalate ion, is more fluorescent in water than in dimethyl sulfoxide.[21] In **6**, the emitter is N-methylacridone and its fluorescence efficiency in dimethyl sulfoxide was found to be at least 90% of that in water. This fact suggests that in compound **6** the yield of excited states is the same in both reaction systems.

Since energy transfer occurred in **6** from presumably excited phthalate ion to N-methylacridone, it was of interest to see whether transfer could occur to other acceptor molecules. The alkylation of acridone had proven facile; therefore the next acceptor chosen was carbazole, since the corresponding hydrazide (**7**) could be prepared in an analogous fashion. Compound **7** proved to be only weakly chemiluminescent. An explanation of its inefficiency is discussed in the following paper.[26]



7

Experimental Section[27]

Materials. 2,3-Naphthalic acid, 2,3-dihydrobenzo[*g*]phthalazine-1,4-dione (3), and 5-amino-2,3-dihydrophthalazine-1,4-dione were obtained as analytically pure samples from Dr. O. C. Zafiriou.[21] 9,10-Diphenylanthracene was obtained from the Aldrich Chemical Co., shown to be pure by tlc, and used as received. Potassium *t*-butoxide (MSA Research Corp.) was used as received. Dimethyl sulfoxide (Matheson Coleman and Bell) was stirred overnight over crushed potassium hydroxide, decanted, and distilled from potassium *t*-butoxide. The distillations were performed with grease-free systems under oil pump vacuum (<1 Torr) and at temperatures from 30 to 60°. A center cut of about 80% of the material was used.

Acridone. Commercial material was purified by vacuum sublimation at 0.1 Torr and crystallization from a 2:5 mixture of aniline:acetic acid to give yellow needles, mp 350–352° (lit.[28] 348–352°).

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(26) D. R. Roberts and E. H. White, *J. Amer. Chem. Soc.*, **92**, 4861 (1970).

(27) Melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed either by Mr. Joseph Walters in this department or by Galbraith Laboratories (Knoxville, Tenn.). Infrared spectra were determined on either Model 137 or 337 Perkin-Elmer instruments. Ultraviolet and visible spectra were determined on a Cary Model 14 instrument and proton magnetic resonance spectra (pmr) were determined on a Varian Associates A-60 instrument. Chemical shifts are reported in τ units relative to internal tetramethylsilane (TMS). Solvents, except where stated, were reagent grade and used as received.

(28) H. Blatt, Ed., "Organic Synthesis," Coll. Vol. II, 1st ed, Wiley, New York, N. Y., 1946, p 15.

Carbazole. Commercial material recrystallized from absolute ethanol had mp 243–244.5° (lit.[29] 245°).

Naphthalene-2,3-dicarboxylic Acid Anhydride. A solution of 10 g (0.0463 mole) of naphthalene-2,3-dicarboxylic acid in 300 ml of acetic anhydride was refluxed for 3 hr, during which time 200 ml of acetic anhydride was slowly distilled off from the reaction mixture. The remaining solution was filtered, concentrated to about 50 ml, and cooled. The anhydride that crystallized out was filtered and dried in a vacuum desiccator to give 6.6 g of product (0.0333 mol, 72%); mp 244–246° (lit.[30] mp 245°).

Naphthalene-2,3-dicarboimide. A well-powdered mixture of 2 g (0.01 mol) of naphthalene-2,3-dicarboxylic acid anhydride and 0.62 g (0.01 mol) of urea was heated in a bath maintained at 240° until the evolution of ammonia ceased. The material was cooled and crystallized from acetic acid to give 1.54 g of crystals (0.0078 mol, 77.2%), mp 275° (lit.[31] mp 275°).

N-Methylnaphthalene-2,3-dicarboimide.[32] Naphthalene-2,3-dicarboimide (1.0 g, 5.0 mmol) was dissolved in 15 ml of dimethylformamide and 3 ml of methyl iodide and 2.0 g (14.5 mmol) of potassium carbonate were added. This mixture was refluxed for 3 hr and then poured onto ice. The white precipitate was collected (1.07 g, 5.0 mmol, 100%), mp 242–244°. An analytical sample was prepared by crystallization from ethanol [mp 244–245°; infrared (KBr) 1760 and 1710 cm^{-1}; ultraviolet (95% ethanol) 360 (log ϵ 4.55), 290 (log ϵ 4.87), 260 (log ϵ 5.69), and 235 nm (log ϵ 5.36)].

Anal. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.29. Found: C, 74.07; H, 4.46.

N-Methyl-5-chloromethyl-2,3-naphthalenedicarboimide (5). A well-stirred suspension of N-methylnaphthalene-2,3-dicarboxylic acid imide (1 g, 0.0048 mol) in 5 ml of bischloromethyl ether was cooled to 10° and treated with 0.7 ml (0.0074 mol) of chlorosulfonic acid during 0.5 hr. The reaction mixture was left stirring at room temperature for 24 hr. The reaction mixture was diluted with ice–water and extracted repeatedly with chloroform. The combined chloroform extracts were washed with water, dried over anhydrous Na_2SO_4, and concentrated to give 1.14 g of crude material, mp 188–200°. Analysis by nmr indicated approximately 35% of the required chloromethylated product in the total crude material. Repeated fractional crystallization from chloroform–ether afforded 0.25 g of the pure product, (0.96 mmol, 20%): mp 227–229°; infrared ($CHCl_3$) 1700 and 1760 cm^{-1}; nmr ($CDCl_3$) τ 1.0–2.5 (4.96 H, m), 4.92 (2.00 H, s), 6.73 (3.08 H, s); an expanded-scale 100-Mcps nmr spectrum of the aromatic region showed the 1 and 4 protons as singlets at τ 1.39 and 1.69, the 6 proton as a pair of doublets centered at τ 2.00 with $J_{6,8}$ = 4.5 cps, and the 7 and 8 protons as a six-line multiplet between τ 2.2 and 2.5 with $J_{7,8}$ = 13.0 cps.[33]

Anal. Calcd for $C_{14}H_{10}O_2NCl$: C, 64.73; H, 3.85; N, 5.39. Found: C, 64.72; H, 4.07; N, 5.33.

Attempts to prepare this compound using bischloromethyl ether in carbon disulfide or paraformaldehyde were unsuccessful and only starting material was recovered.

N-Methyl-5-(9,10-diphenyl-2-anthrylmethyl)-2,3-naphthalenedicarboimide. A mixture of 9,10-diphenylanthracene (0.13 g, 0.39 mmol), N-methyl-5-chloromethyl-2,3-naphthalenedicarboimide (0.10 g, 0.38 mmol), and zinc dust (0.02 g, 0.3 mg-atom) in 5 ml of dry nitrobenzene was heated in a bath maintained at 160° while a stream of dry nitrogen was passed over the reaction mixture. At the end of 2 hr, tlc indicated the complete disappearance of the starting chloromethyl compound. The reaction mixture was then diluted with chloroform and filtered into a separatory funnel where it was washed with dilute hydrochloric acid and water. Chloroform and nitrobenzene were removed from the organic extract *in vacuo* (0.1 Torr) leaving 0.24 g of a resinous material. This was chromatographed over 10 g of neutral alumina (activity III). After removal of unreacted 9,10-diphenylanthracene, elution with 1:1 benzene–petroleum ether (bp 30–60°) gave 90 mg of the crude product. Crystallization of this material from a chloroform–ether mixture afforded 62 mg (0.11 mmol, 28%) of the product: mp 259–262°; infrared ($CHCl_3$) 1710 and 1765 cm^{-1}; ultraviolet ($CHCl_3$) 398 (log ϵ 3.86), 378 (3.98), 364 (3.94), and 269 nm (4.94) (this spectrum is as expected for the two nonconjugated chromophores); nmr ($CDCl_3$) τ 1.5–3.0 (22.01 H, multiplet), 5.48 (1.89 H, singlet), and 6.78 (3.00 H, singlet).

Anal. Calcd for $C_{40}H_{27}NO_2$: C, 86.78; H, 4.92; N, 2.53. Found: C, 86.59; H, 5.02; N, 2.49.

2,3-Dihydro-6-[(9,10-diphenyl-2-anthryl)methyl]benzo[*g*]phthalazine-1,4-dione (4). A suspension of the preceding N-methylimide (0.2 g, 0.36 mmol) in 20 ml of 95% hydrazine hydrate was heated under nitrogen in a bath maintained at 100°. At the end of 1 hr, tlc indicated the total disappearance of starting material and the formation of a new product. The reaction mixture was diluted with water and filtered, and the insoluble product washed well with water. After drying *in vacuo*, 174 mg (0.31 mmol, 87%) of the product was obtained. Crystallization of this material proved difficult, and it was finally purified by chromatography over neutral alumina (activity III) with 25% acetic acid in ether to give crystals: mp 252–256°; infrared (KBr) 1620 and 1650 cm^{-1}; ultraviolet (C_2H_5OH) 398 (log ϵ, 3.89), 377 (4.01), 358 (4.00), 340 (4.02), and 266 nm (4.84).

Anal. Calcd for $C_{39}H_{27}N_2O_2$: C, 84.46; H, 4.72; N, 5.05. Found: C, 84.18; H, 4.69; N, 4.87.

4-Methyl-1,2,3,6-tetrahydrophthalic Anhydride. This compound was prepared according to the method of Farmer and Warren.[34] Once crystallized, material (53.6 g, 0.32 mol, 84.5%) gave mp 63–64.5° (lit.[34] 64–65°); infrared (CCl_4) 1780 and 1850 cm^{-1}.

4-Methylphthalic Anhydride. This compound was prepared by bromination of 4-methyl-1,2,3,6-tetrahydrophthalic anhydride following by dehydrobromination according to the method of Rabjohn.[35] The crude material was crystallized from benzene–isooctane to give material (32.2 g, 0.2 mol, 63%) melting at 88–90° (lit.[35] 89–90°); infrared ($CHCl_3$) 1780 and 1840 cm^{-1}; nmr ($CDCl_3$) τ 7.38 (3.00 H, s), 1.9–2.2 (3.05 H, m).

N,4-Dimethylphthalimide. 4-Methylphthalic anhydride (15.0 g, 0.043 mol) and 1,3-dimethylurea (30.0 g, 0.39 mol) were heated together at *ca.* 200° for 20 min. After that period, the hot reaction mixture was poured into water (300 ml) and the precipitate was filtered, washed with water, and dried. This crude material was crystallized from toluene–isooctane to give pure material (13.1 g, 0.074 mol, 80%): mp 126–128°; infrared (KBr) 1770 and 1700 cm^{-1}; nmr ($CDCl_3$) τ 7.00 (3.01 H, s), 6.85 (3.00 H, s), 2.2–2.6 (3.01 H, m).

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.60; H, 5.39; N, 7.93.

N-Methyl-4-bromomethylphthalimide. To a well-stirred solution of N,4-dimethylphthalimide (1.25 g, 7.15 mmol) in carbon tetrachloride (100 ml) was added, dropwise, a solution of bromine (1.15 g, 7.2 mmol) in carbon tetrachloride (50 ml). As the bromine solution was added, the reaction mixture was irradiated with a sunlamp (G.E., 275 W). The temperature of the reaction mixture was kept just below the reflux point by careful positioning of the lamp. When all the bromine had been added (45 min), irradiation was stopped and the carbon tetrachloride was removed *in vacuo*. Cyrstallization of the crude material from anhydrous ether gave pure material (1.05 g, 4.1 mmol, 58%): mp 129–130.5°; infrared ($CHCl_3$) 1775, 1725, and 1380 cm^{-1}; nmr ($CDCl_3$) τ 2.0–2.2 (3.00 H, m), 5.40 (1.91 H, s), 6.80 (3.09 H, s).

Anal. Calcd for $C_{10}H_8BrNO_2$: C, 47.28; H, 3.08; Br, 31.45. Found: C, 47.53; H, 2.78; Br, 31.82.

This compound was also prepared by bromination with N-bromosuccinimide. N,4-Dimethylphthalimide (3.0 g, 17 mmol) was dissolved in carbon tetrachloride (200 ml) and N-bromosuccinimide (Eastman, 3.2 g, 18 mmol) was added. Irradiation with a sunlamp (G.E., 275 W) for *ca.* 0.5 hr at the reflux point of the reaction mixture gave the crude product. After filtration, to remove the succinimide formed, the above work-up procedure was followed. A total of 1.31 g (5.2 mmol, 30%) of pure material was isolated after crystallization.

N-Methyl-4-[(9-oxo-10-acridanyl)methyl]phthalimide. Acridone (0.5 g, 2.57 mmol) in dimethoxyethane (50 ml, distilled from sodium hydride) was treated with 0.125 g (2.65 mmol) of a 54% dispersion of sodium hydride in mineral oil. The reaction mixture was stirred and refluxed gently for 2 hr under an atmosphere of nitrogen. Then a solution of N-methyl-4-bromomethylphthalimide (0.70 g, 2.65 mmol) in dry dimethoxyethane (20 ml) was added dropwise. After addition was complete, reflux was continued for 6 hr and the

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(29) S. H. Tucker, *J. Chem. Soc.*, 546 (1926).

(30) M. Freund and K. Fleischer, *Ann.*, **339**, 182 (1913).

(31) M. Freund and K. Fleischer, *ibid.*, 402, 51 (1914).

(32) We thank Dr. K. Matsuo for the preparation of this compound.

(33) We wish to thank Mr. W. Jankowski of Varian Associates for obtaining this spectrum and for his interpretation that this splitting was consistent with the structure of compound **5** rather than the isomer chloromethylated in the 6 position.

(34) E. H. Farmer and F. L. Warren, *J. Chem. Soc.*, 3221 (1931).

(35) N. Rabjohn, M. F. Drumin, and R. L. Elliot, *J. Amer. Chem. Soc.*, **78**, 1631 (1956).

reaction mixture was then poured into water. The product was filtered off, dried, and chromatographed on neutral alumina with chloroform. Crystallization from toluene gave pure material (0.36 g, 0.98 mmol, 38%): mp 292–293°; infrared (KBr) 1780 and 1730 cm^{-1}; nmr (DMSO-d_6) τ 1.6–2.9 (11.00 H, m), 4.13 (1.97 H, s), 7.08 (2.82 H, s); ultraviolet (95% C_2H_5OH) 396 (log ϵ 4.06) and 378 nm (log ϵ 3.96). This spectrum is as expected for the two nonconjugated chromophores.

Anal. Calcd for $C_{23}H_{16}N_2O_3$: C, 74.99; H, 4.38; N, 7.60. Found: C, 74.73; H, 4.44; N, 7.66.

N-Methyl-4-[(9-carbazolyl)methyl]phthalimide. This compound was prepared from carbazole (0.425 g, 2.5 mmol) in essentially the same manner as described for the preceding compound to give material, crystallized from toluene–isooctane (0.31 g, 0.8 mmol, 34%), melting at 180–181.5°; infrared ($CHCl_3$) 1775 and 1720 cm^{-1}; nmr ($CDCl_3$) τ 1.8–2.9 (11.40 H, m), 4.53 (2.07 H, s), 6.95 (3.00 H, s); ultraviolet (95% C_2H_5OH) 339 (log ϵ 3.67) and 325 nm (log ϵ 3.63). This spectrum is as expected for the two nonconjugated chromophores.

Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.48; H, 4.69; N, 8.09.

2,3-Dihydro-6-[(9-oxo-10-acridanyl)methyl]phthalazine-1,4-dione (6). N-Methyl-4-[(9-oxo-10-acridanyl)methyl]phthalimide (100 mg, 0.28 mmol) was added to glacial acetic acid (3 ml) containing 95% hydrazine (*ca.* 0.1 ml, 3 mmol). This reaction mixture, after degassing (three freeze–thaw cycles), was sealed off in a glass tube. The tube was heated at 120° for 8 hr, and then cooled and opened, and the contents poured into water. The resulting precipitate was collected and crystallized from aqueous acetic acid to give material (80 mg, 0.21 mmol, 75%) pure by paper chromatography (Whatman no. 3, alcohol:water:ammonium hydroxide, 8:1:1). This product was recrystallized from glacial acetic acid to give material, decomposing above 290°; infrared (KBr) 1640, 1610, and 1505 cm^{-1}; ultraviolet (95% C_2H_5OH) 398 (log ϵ 4.08) and 387 nm (4.02).

Anal. Calcd for $C_{22}H_{15}N_3O_3 \cdot C_2H_4O_2$: C, 67.13; H, 4.46; N, 9.78. Found: C, 67.15; H, 4.53; N, 9.87.

2,3-Dihydro-6-[(9-carbazoyl)methyl]phthalazine-1,4-dione (7). This substance was prepared by the method used for compound **5**. N-Methyl-4-[9-carbazoylmethyl]phthalimide (25 mg, 0.073 mmol) and hydrazine gave a white precipitate which was recrystallized twice from aqueous ethanol to give small needles (15 mg, 0.044 mmol, 60%): mp 258–260° dec; infrared (KBr) 1660 and 1610 cm^{-1}; ultraviolet (95% C_2H_5OH) 347 (log ϵ 3.69) and 333 nm (log ϵ 3.77).

Anal. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43. Found: C, 73.94; H, 4.51.

Emission Spectra. Fluorescence and chemiluminescence emission spectra were determined on an Aminco-Bowman spectrophotofluorimeter and recorded on a Houston Instrument Co. HR-96T X-Y recorder. Many of these spectra were rerun on a Hitachi Model MPF-2A recording spectrophotofluorimeter. Spectra are not corrected for phototube sensitivity, instrumental distortion, or source intensity fluctuation. Wavelengths were determined by superposition of a low-pressure mercury arc spectrum (Pen-Ray lamp) on the recorded spectrum. Reported maxima are estimated to be accurate to within ±3 nm.

Chemiluminescence spectra were obtained by reacting solutions of the hydrazides ($<10^{-4}$ *M* in the 0.1 *N* sodium hydroxide) with aqueous solutions of hemin and hydrogen peroxide ($\sim$3%) and running the spectrophotofluorimeter with the source off. For emission spectra in the aprotic system the hydrazides were dissolved in air-saturated dimethyl sulfoxide and allowed to react with a solution of potassium *t*-butoxide in *t*-butyl alcohol.

Total Light-Emission Studies. Chemical-screening experiments were performed in a dark room after dark adaptation of the eye, and were witnessed by a second observer. Chemiluminescence relative efficiencies were determined using either RCA IP21 or IP28 phototubes, biased by a Fluke Model 4128 dc power supply. The output of the phototube was amplified with a unit designed and built by Mr. John Veise (Department of Biochemistry, The Johns Hopkins University). The amplifier signal was collected on a capacitor and recorded for total light yields, reported as coulombs per micromole at 700-V phototube bias.

The determinations were performed as described for luminol.[36]

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