

production is apparently unaffected.^{8b,10} Aromatic anions in general are poor solvated electron sources in alcohols,^{8b} but several are acceptable in the present case.

All the evidence is in accord with a direct charge-transfer excitation of associated ions (path C). Conductivity studies^{4b,11} and vapor pressure measurements show that these salts are appreciably associated at the concentrations employed. Further evidence was obtained by observation of a charge-transfer band at 290 m μ (log ϵ 2.94) for I (R = CN, Y = I) in 10% CH₃OH-CHCl₃. This band is absent in the fluoroborate and in more polar solvents, as expected.¹² Addition of solid KI to a solution of the fluoroborate results in gradual formation of the 290-m μ band.

The pronounced effect of ring substituents is readily understood within this framework. Only when the energy of the charge-transfer state is sufficiently high to allow crossover into the dissociative state will reaction occur. Electron-attracting groups have little effect on the energies of the ground and dissociative states, but can greatly stabilize the charge-transfer state through conjugation.

The interionic charge transfer demonstrated here is not necessarily demanded by other charged benzene derivatives. In fact, benzenediazonium fluoroborate photolyzes smoothly under our conditions to yield 51% benzene after 2 hr, possibly through intervention of N₂⁺.

(10) L. I. Grossweiner, E. F. Zwicker, and G. W. Swenson, *Science*, **141**, 1042 (1963).

(11) P. G. Sears, E. D. Wilhoit, and L. R. Dawson, *J. Chem. Phys.*, **23**, 1274 (1955).

(12) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965).

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Intramolecular Energy Transfer in Chemiluminescence

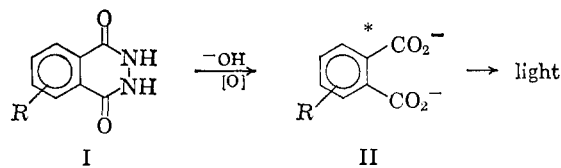
Sir:

We wish to report a type of chemiluminescence that involves intramolecular energy transfer. In the chemiluminescence of luminol and related hydrazides (I), the product, the dicarboxylate ion II, is formed in an excited singlet state; emission of a photon then completes the process.¹⁻³ The direct relationship of the fluorescence quantum yield of II and the quantum yield of I in chemiluminescence has been noted.¹ Thus, for efficient light production, highly fluorescent compounds are required. This simple approach is usually not completely successful, however, because the conju-

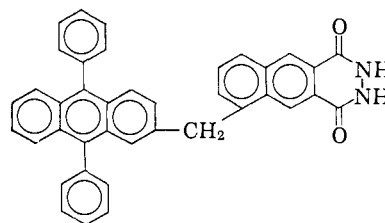
(1) E. H. White, O. C. Zafriou, H. H. Kagi, and J. H. M. Hill, *J. Am. Chem. Soc.*, **86**, 940 (1964); E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964).

(2) K. D. Gundermann, *Angew. Chem.*, **77**, 572 (1965); Symposium on Chemiluminescence, Durham, N. C., 1965 (Army Research Office, Durham).

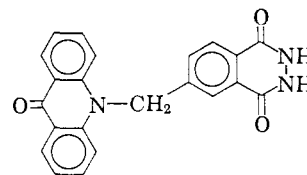
(3) The general mechanism proposed by A. U. Khan and M. Kasha (*J. Am. Chem. Soc.*, **88**, 1574 (1966)) cannot be operating in the chemiluminescence of the hydrazides (and the lophines: E. H. White and M. J. C. Harding, *Photochem. Photobiol.*, **4**, 1129 (1965)) since the critical energy-producing reactions consume, but do not produce, oxygen. See also F. McCapra, *Quart. Rev. (London)*, **20**, 485 (1966), and M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Am. Chem. Soc.*, **88**, 3604 (1966).



gated systems needed to achieve a 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 becomes an important problem. To circumvent these difficulties, we have separated the energy-generating and light-emitting functions (compounds III and IV). The expectation was that intramolecular energy transfer



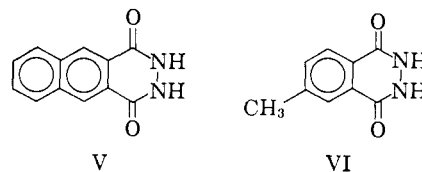
III



IV

would occur from the hydrazide portion to the fluorescent portion. Energy transfer has been shown to occur in difunctional molecules A-B where the donor A was raised to an excited state by light absorption and emission occurred from moiety B;⁴ in the present case, chemical energy is used to reach the excited state of the donor. The use of chemical energy is advantageous since it ensures that all the energy is originally located in the donor.

The energy levels for transfer are satisfactory for compounds III and IV, since naphthalenic hydrazide (V) emits at 355 m μ in the aqueous system (the fluorescence



of the naphthalenedicarboxylate ion is at the same wavelength), whereas diphenylanthracene shows absorption bands out to 405 m μ . Similarly, acridone shows absorption out to 400 m μ and, although the exact value is unknown, it is certain that the excited singlet energy of phthalate ion is higher than that of the naphthalenedicarboxylate ion.

Compounds III and IV were tested in an aqueous system (H₂O-NaOH-H₂O₂, hemin) and also in the dimethyl sulfoxide system (DMSO + H₂O (9:1)-NaOH-O₂). The data indicate (Table I) that intra-

(4) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, **87**, 2322 (1965); S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, **87**, 995 (1965).

molecular energy transfer occurs in these molecules, since (1) light emission occurs from the diphenylanthracene and acridone portions of the molecules, and (2) compounds III and IV are more efficient in light production than the parent compounds V and VI. Naphthalic hydrazide (V) itself chemiluminesces with low efficiency at 355 $m\mu$ in the aqueous system and at the same wavelength, but very weakly in DMSO. Compound III, on the other hand, shows strong emission at 425 and 440 $m\mu$, the fluorescence wavelengths of diphenylanthracene, with only a weak emission at 355 $m\mu$. A similar wavelength match was found in the DMSO system and also in the comparison of compound IV with N-methylacridone (Table I).

Table I. Comparison of Chemiluminescence and Fluorescence Wavelengths

	Wavelength maxima, $m\mu^a$	
	Aqueous system	90% dimethyl sulfoxide
A. Compound III		
Chemiluminescence of III	355, ^b 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) ^c	425, 440 (sh)
Fluorescence of disodium 2,3-naphthalenedicarboxylate	358	355 ^d
B. Compound IV		
Chemiluminescence of IV	430, 450 (sh)	440
Fluorescence of total reaction products	430, 450 (sh)	440
Fluorescence of N-methylacridone	430, 450 (sh) ^c	440

^a Concentrations $<10^{-4} M$; error $\pm 3 m\mu$. ^b About 5% intensity of 425 $m\mu$ emission. ^c Dissolved initially in a small amount of ethanol to effect solution. ^d Extremely weak.

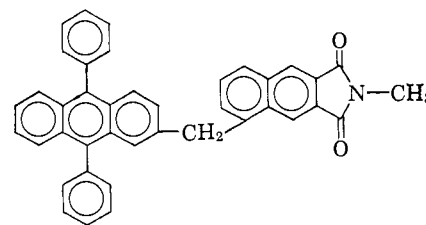
Concerning the quantum efficiencies, 4-methylphthalic hydrazide (VI) does not emit light in the aqueous system and naphthalic hydrazide is inefficient. Furthermore, a mixture of VI and N-methylacridone ($10^{-4} M$) does not yield light in the aqueous system, and a mixture of V and diphenylanthracene ($10^{-4} M$) yields no more light than a $10^{-4} M$ solution of V itself. Thus the intermolecular transfer of energy between the separate components is far less efficient than the intramolecular transfer in compounds III and IV at the concentrations used. In the water system the relative efficiencies of compounds VI, V, IV, and III in light production (relative to luminol at 100) are 0, 5, 8, and 26, respectively. Further improvements in the quantum yield should result from separate modifications at the energy production, transfer, and emission stages.

Syntheses.⁵ N-Methyl-2,3-naphthalenedicarboimide was chloromethylated with bis(chloromethyl) ether and chlorosulfonic acid to give N-methyl-5-chloromethyl-2,3-naphthalenedicarboimide, mp 225–227° (the substitution pattern was determined by nmr spectroscopy). This material was allowed to react with 9,10-diphenylanthracene at 160° (with zinc in nitrobenzene) to give N-methyl-5-(9,10-diphenyl-2-anthracylmethylene)-2,3-naphthalenedicarboimide (VII), mp 259–261°.⁶ Re-

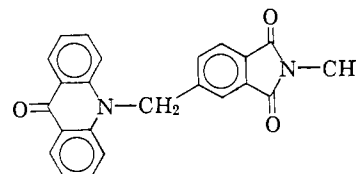
(5) All compounds gave satisfactory analyses and spectral data.

(6) Friedel-Craft reactions of diphenylanthracene occur at the 2 position (R. G. Douris, *Compt. Rend.*, **229**, 224 (1949)).

action of this imide with 95% hydrazine then gave hydrazide III, mp 252–256°. For the synthesis of com-



VII



VIII

pound IV, N,4-dimethylphthalimide was treated with NBS (or Br_2) and light to give the 4-bromomethyl compound, mp 129–131°. A condensation with the anion of acridone, prepared with NaH, gave 4-(9-acridonyl-10-methylene)-N-methylphthalimide (VIII), mp 291–293°. This imide was converted to hydrazide IV (mp 290° dec) with hydrazine.

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The Effect of Nonbridging Ligands on the Rate of Electron-Transfer Reactions

Sir:

The effect of nonbridging ligands on the rate of electron-transfer reactions has been the subject of several recent investigations.^{1–5} The results of these experiments have been interpreted on the basis of a model originally proposed by Orgel⁶ and developed by Haim and co-workers.¹ According to this model, a variation in the nonbridging ligands leads to two effects that change the rate of electron transfer to a Co(III) or Cr(III) complex: the relative stabilization of the d_{z^2} orbital, and the ease with which the ligand *trans* to the bridge can be stretched. Benson and Haim proposed¹ that the ligand field strength of the variable ligand and the ease of aquation of the complex, respectively, could be used as a measure of these two

(1) P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965), and references therein.

(2) R. D. Cannon and J. E. Earley, *ibid.*, **87**, 5264 (1965); **88**, 1872 (1966).

(3) A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

(4) D. E. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966).

(5) There are numerous earlier papers that have found rate laws containing an anion path that is reasonably attributed to a nonbridging ligand effect, but the lability of the systems makes the interpretation of these results ambiguous.

(6) L. E. Orgel, Report of the Tenth Solvay Conference, Brussels, 1956, p 289.