Chemiluminescent Schiff Bases

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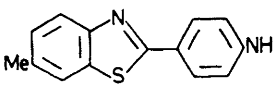
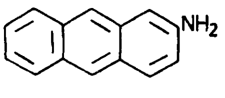
Summary Although very few examples of chemiluminescent Schiff bases have been described, and attempts to extend this class of reaction have hitherto been unsuccessful, it is now shown that these compounds are generally chemiluminescent on oxidation, with reasonable efficiency.

Several years ago[1] we reported that the aminal (4) was chemiluminescent on oxidation in basic Me_2SO, and that the corresponding Schiff base was a likely intermediate. Subsequently White *et al.*[2] prepared a Schiff base from diphenylacetaldehyde and *p*-anisidine and made its hydroperoxide. They failed to observe significant light emission or formation of excited-state products. We have now established some of the criteria for chemiluminescence in such compounds.

Although we have examined a large number of Schiff bases using a variety of aliphatic aldehydes and aromatic amines, only a few are presented in the Table. Compounds of this sort are notoriously difficult to analyse but acceptable micro-analyses have been obtained for (**1**,**A**) and (**2**,**B**). The expected n.m.r. and u.v. spectra have been obtained for some more soluble examples.[3] The structures also follow from the method of preparation[4] and the products formed on decomposition. The fluorescence spectrum of the formamido-anion formed as product is identical to the chemiluminescence spectrum, in each case. Since the fluorescence quantum yield (ϕ_F) and chemical yield (ϕ_C) are both measurable, the excited state yield (ϕ_E) is readily obtained. In all cases the Schiff bases derived from isobutyraldehyde are more chemiluminescent than those obtained using 2-phenylpropionaldehyde. It is possible that the presumed dioxetan decomposes to form exclusively triplet n,π^* excited states, and that the singlet emission observed is the result of energy transfer from the ketonic product. Acetophenone, with a lower triplet excited state than acetone, could then be expected to transfer energy less efficiently. However the singlet energy level (as indicated by the λ_{max} of fluorescence) bears no relationship to the chemiluminescence efficiency, and is in any case very much lower than the triplet level of either ketone. The recent demonstration[5] that n,π^* triplet excited states are populated, even at the expense of lower lying π,π^* states during dioxetan decomposition, prompted us to examine the point further. The formamido-anions clearly have a π,π^* lowest excited singlet state, and we would expect the lowest triplet state to have the same character. It is therefore important to confirm that the observed singlet state is not derived by transfer from triplet ketone. 9,10-Diphenyl- and 9,10-dibromo-anthracene have been used to detect energy transfer from triplet donors in dioxetan and other peroxide decompositions.[6] It is believed that the heavy atoms enhance the triplet to singlet energy transfer, with the result that quantum yields using the dibromoanthracene are about 100 times greater, in spite of its lower fluorescence yield. In the case of the compounds (**5**; R = H) and (**5**; R = Br) we find that the chemiluminescence from the bromo-anthracene is *less* than that from the unsubstituted compound (see Scheme). That the bromo-substitution has the desired effect in promoting intersystem crossing seems reasonable in view of the lower fluorescence quantum yield. The decrease in fluorescence is similar to that observed on brominating anthracene itself.



(1)



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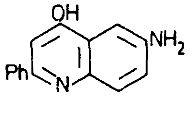
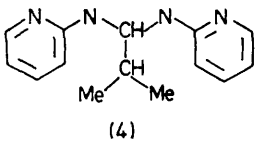




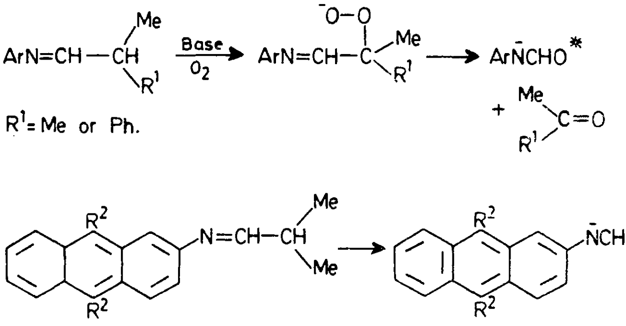
(4)

Table

Amine[a]		ϕ_E (%)	ϕ_C (%)	Fluorescence[b] ϕ_F	Fluorescence[b] λ_{max}/nm
(**1**)	(A)	0·36	53	0·46	455
	(B)	$5{\cdot}5 \times 10^{-4}$	78		
(**2**)	(A)	0·16	48	0·38	540
	(B)	$3{\cdot}1 \times 10^{-2}$	67		
(**3**)	(A)	$7{\cdot}2 \times 10^{-2}$	30	0·62	492
	(B)	$5{\cdot}9 \times 10^{-6}$	53		

[a] (A), Schiff base with isobutyraldehyde; (B), Schiff base with 2-phenylpropionaldehyde. [b] Of the formamido-anion.

We conclude that the singlet state of the emitter is populated directly in these examples. This is an important observation for bioluminescence where a similar direct excitation seems essential. From a variety of quenching experiments it appears that the enolate anion of acetophenone is about 40 times more efficient as a quencher of excited states of the kind described than is the acetone enolate. This accounts in part for the lower chemiluminescence yield using 2-phenylpropionaldehyde. A further observation which may affect the interpretation of chemiluminescence in this series is that the benzamides derived from the amines used in this study are not significantly fluorescent in basic media, in striking contrast to the strongly fluorescent formamide anions. Obviously substituents must be chosen carefully in order to obtain strong light emission.



(5)

	ϕ_E%	ϕ_F	λ_{max}/nm
$R^2 = H$	0·16	0·38	540
$R^2 = Br$	0·03	0·07	575

Scheme

(*Received*, 12*th April* 1976; *Com.* 406.)

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[1] F. McCapra and R. Wrigglesworth, *Chem. Comm.*, 1969, 91.

[2] E. Rapoport, M. W. Cass, and E. H. White, *J. Amer. Chem. Soc.*, 1972, **94**, 3160.

[3] R. Wrigglesworth, D. Phil. thesis, University of Sussex, 1970.

[4] C. S. Irving and P. A. Leermakers, *Photochem. Photobiol.*, 1965, **1**, 665.

[5] H. E. Zimmerman and G. E. Keck, *J. Amer. Chem. Soc.*, 1975, **97**, 3527.

[6] T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, 1971, **93**, 4126; V. A. Belyakov and R. F. Vassil'ev, *Photochem. Photobiol.*, 1970, **11**, 179.