

## Short Communication

## Quenching of 9-cyanophenanthrene fluorescence by bifunctional compounds

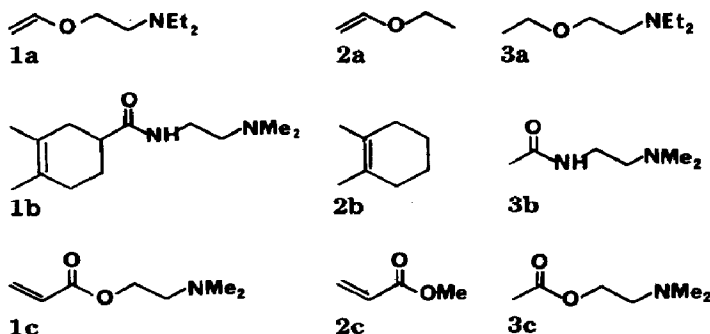
FREDERICK D. LEWIS and PAUL E. CORREA

*Department of Chemistry, Northwestern University, Evanston, IL 60201 (U.S.A.)*

(Received July 8, 1982)

## 1. Introduction

The quenching of excimers  $MM^*$  and exciplexes  $MQ_1^*$  by a third molecule  $Q_2$  has been the subject of numerous investigations [1]. Such quenching leads to the formation of an excited termolecular complex or triplex ( $MMQ_2^*$  or  $MQ_1Q_2^*$ ). In most cases the triplex decays to the component ground states by non-radiative pathways; however, in some cases emission from the triplex or an exciplex substitution product is observed. In a very few cases chemical reactions have been attributed to excimer or exciplex quenching [1, 2]. Davidson and coworkers [3, 4] have recently reported the efficient quenching of singlet naphthalene and rose bengal by  $\alpha,\omega$ -diaminoalkanes. The use of bifunctional quenchers ( $Q_1 \sim Q_2$ ) favors triplex formation by providing a high local concentration of the second quencher molecule  $Q_2$  near the initially formed exciplex  $MQ_1^*$ . We report here on the quenching of singlet 9-cyanophenanthrene ( $M^*$ ) by the bifunctional molecules 1a - 1c which contain trialkylamino and olefin functional groups  $Q_1 \sim Q_2$  and the monofunctional model compounds 2a - 2c and 3a - 3c.



The choice of this system was prompted by reports that  $M^*$  reacts with tertiary amines to yield fluorescent non-reactive exciplexes [1], whereas it reacts with electron-rich olefins to yield non-fluorescent chemically reactive

exciplexes [5]. Thus the occurrence or absence of exciplex or triplex fluorescence and chemical reactions can be used as probes of termolecular interactions.

## 2. Experimental details

9-cyanophenanthrene (Aldrich) was recrystallized four times from absolute ethanol. Ethyl vinyl ether (2a) obtained from Aldrich, 1,2-dimethylcyclohexene (2b) obtained from Chemical Samples and methyl acrylate (2c) obtained from Aldrich were used as received. 2-*N,N*-diethylaminoethyl ethyl ether (3a) was prepared via the reaction of ethyl bromide with the sodium salt of 2-*N,N*-diethylaminoethanol and was characterized by a boiling point of 88 - 89 °C at 760 Torr and the following nuclear magnetic resonance (NMR) (solvent, CDCl<sub>3</sub>) data (chemical shifts,  $\delta$  (parts per million)): 1.00, triplet (6 H); 1.11, triplet (3 H); 2.1 - 2.6, multiplet (4 H); 3.0 - 3.5, multiplet (4 H). *N*-(2-*N',N'*-dimethylaminoethyl)acetamide (3b) was prepared via the reaction of acetyl chloride with *N,N*-dimethylethylenediamine and was characterized by a boiling point of 116 - 118 °C at 3 Torr and the following NMR (solvent, CDCl<sub>3</sub>) data ( $\delta$  (parts per million)): 1.95, singlet (3 H); 2.18, singlet (6 H); 2.35, triplet (2 H); 3.27, quartet (2 H); 7.9, triplet (1 H). 2-*N,N*-dimethylaminoethyl acetate (3c) was prepared via the reaction of acetyl chloride with 2-*N,N*-dimethylaminoethanol and was characterized by a boiling point of 84 - 85 °C at 65 Torr and the following NMR (solvent, CDCl<sub>3</sub>) data ( $\delta$  (parts per million)): 1.69, singlet (6 H); 1.92, singlet (6 H); 2.20, triplet (2 H); 3.78, triplet (2 H). 2-*N,N*-diethylaminoethyl vinyl ether (1a) was prepared by the method of Atarin *et al.* [6]. 2-*N,N*-dimethylaminoethyl acrylate (1c) was prepared via the reaction of acryloyl chloride with 2-*N,N*-dimethylaminoethanol and was characterized by a boiling point of 25 - 26 °C at 3 Torr and the following NMR (solvent, CDCl<sub>3</sub>) data ( $\delta$  (parts per million)): 1.90, singlet (6 H); 2.2, triplet (2 H); 3.8, triplet (2 H); 5.2 - 5.8, multiplet (3 H).

*N*-(2-*N',N'*-dimethylaminoethyl)-3,4-dimethyl-3-cyclohexene-1-carboxamide (1b) was prepared as follows. The reaction of 7.8 ml of 2,3-dimethyl-1,3-butadiene and 15 ml of methyl acrylate at 120 °C in a sealed tube produced 10.9 g (94%) of methyl 3,4-dimethyl-1,2-cyclohexene-1-carboxylate with a boiling point of 47 - 49 °C at 0.5 Torr. Alkaline hydrolysis yielded the free acid which was converted to the acid chloride via reaction with thionyl chloride. Reaction of the crude acid chloride with *N,N*-dimethylethylenediamine followed by chromatography on alumina (ethyl acetate) produced 3.5 g (34%) of 1b as a white solid with a low melting point. The NMR (solvent, CDCl<sub>3</sub>) data were as follows ( $\delta$  (parts per million)): 1.59, singlet (6 H); 1.2 - 2.2, multiplet (5 H); 2.18, singlet (6 H); 2.36, triplet (2 H); 3.3, triplet (2 H); 6.15, singlet (1 H).

Benzene (Aldrich spectrophotometric grade) was refluxed overnight over phosphorus pentoxide and distilled. The middle 70% was retained and distilled from sodium as required. Hexane (Aldrich spectrophotometric grade) was used without further purification.

The fluorescence spectra were obtained using a Perkin-Elmer MPF-44A fluorescence spectrometer ( $\lambda_{\text{ex}} = 350 \text{ nm}$ ) and were wavelength corrected. Samples were contained in Pyrex test tubes of outside diameter 13 mm fitted with serum caps and were deoxygenated by purging with prepurified nitrogen. All the solutions contained  $5 \times 10^{-5} \text{ M}$  9-cyanophenanthrene and variable amounts of quencher (0.5 M or less). None of the quenchers absorbed appreciably at the excitation wavelength.

### 3. Results and discussion

The rate constants for the quenching of the fluorescence of 9-cyanophenanthrene (M) by the bifunctional quenchers 1a - 1c and the model compounds 2a - 2c and 3a - 3c are given in Table 1. The values for olefins 2a - 2c are substantially lower than the rate constants for diffusion in hexane ( $3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) or benzene ( $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) solutions [7], in agreement with an earlier report by Mizuno *et al.* [5]. In contrast, the values for the amines 3a - 3c and the bifunctional quenchers 1a - 1c are near the diffusion-controlled limit. Rate enhancements of about 50% are observed for 1a compared with 3a and 1b compared with 3b but little rate enhancement is observed for 1c compared with 3c. Fluorescence quenching is accompanied by the appearance of a weak long wavelength exciplex emission for the amines 3a - 3c and 1c, but not for 1a, 1b and 2a - 2c.

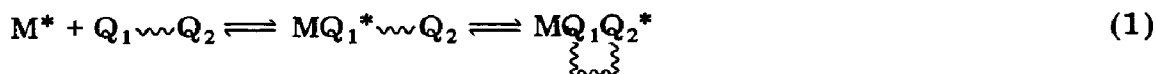
On the basis of the fluorescence quenching data, the bifunctional quenchers 1a and 1b (but not 1c) are more reactive than would be expected if the amine and olefin functional groups reacted independently with singlet M. Furthermore the exciplex emission observed with the amine quenchers is not observed with the bidentate quenchers 1a and 1b. These observations can readily be accounted for if the long-lived exciplex formed between  $\text{M}^*$

TABLE 1  
Fluorescence quenching of 9-cyanophenanthrene

Quencher	$k_{\text{q}} \times 10^{-9}$ <sup>a</sup> ( $\text{M}^{-1} \text{s}^{-1}$ )	$\lambda_{\text{max}}$ (exciplex) (nm)	Adduct formation
1a	14		
2a	0.005		+
3a	10	560	
1b	7.7		
2b	0.3		+
3b	5.0	530	
1c	5.6	530	
2c	< 0.005		
3c	5.4	530	

<sup>a</sup>Values obtained from linear Stern-Volmer plots assuming  $\tau = 20 \text{ ns}$  [1] for  $5 \times 10^{-5} \text{ M}$  9-cyanophenanthrene in deoxygenated hexane (1a - 1c) or benzene (2a - 2c and 3a - 3c) solution.

and the tertiary amine  $Q_1$  is quenched by the olefin end  $Q_2$  of the bifunctional quencher to yield a non-fluorescent triplex:



The initial formation of an  $MQ_2^* \sim Q_1$  exciplex appears distinctly less likely owing to the much lower rate constants for quenching by model olefins **2a** - **2c** compared with those for amines **3a** - **3c**.

The observation of exciplex quenching by the bifunctional quenchers **1a** and **1b**, but not **1c**, plausibly results from the fact that **2a** and **2b** are electron-rich olefins whereas **2c** is an electron-poor olefin. As initially proposed by Beens and Weller [8] and confirmed by Caldwell *et al.* [1], exciplex quenching by electron donors should occur from the donor (amine) side while quenching by electron acceptors should occur from the acceptor (M) side of the exciplex. Thus **1a** and **1b** would be expected to form  $MQ_1Q_2^*$  triplexes, while **1c** is prevented from forming a  $Q_1MQ_2^*$  triplex by the short linkage between  $Q_1$  and  $Q_2$ .

Photochemical [2 + 2] cycloaddition of  $M^*$  with vinyl ethers and tetraalkyl olefins in non-polar solvents occurs with a high chemical yield, the former reaction occurring via the triplet state and the latter via the singlet state of  $M$  [5]. No reaction is observed upon prolonged irradiation of either the amines **3a** - **3c** or the bifunctional quenchers **1a** - **1c** with 9-cyano-phenanthrene in hexane or benzene solution (the irradiation of 9-cyano-phenanthrene and tertiary amines in polar solvents leads to the formation of photoredox products). The failure of the bifunctional quenchers to yield [2 + 2] cycloadducts provides some insights into the exciplex quenching process. Since cycloaddition requires an arene-olefin sandwich-type complex [9 - 11], quenching of the initially formed  $M^*$ -amine exciplex probably does not result in exciplex substitution to yield an  $M^*$ -olefin exciplex. This conclusion is in accord with the observations of Caldwell *et al.* [1], *i.e.* exciplex substitution is observed only when the product exciplex  $MQ_2^*$  is more stable than the initial exciplex  $MQ_1^*$ . It is unlikely that this situation could be realized using a bifunctional quencher since the more stable exciplex should be formed initially when the concentrations of  $Q_1$  and  $Q_2$  are the same. The failure of 3-( $N',N'$ -dimethylamino)propyltrimethyl tin to quench singlet 9-cyanoanthracene more efficiently than trialkyl amines do can be explained in an analogous manner [12].

Support for this work and matching funds for the purchase of the fluorescence spectrophotometer were provided by the National Science Foundation (Grant CHE 78-01120).

- 1 R. A. Caldwell, D. Creed, D. C. DeMarco, L. A. Melton, H. Ohta and P. H. Wine, *J. Am. Chem. Soc.*, **102** (1980) 2369.
- 2 F. D. Lewis and D. E. Johnson, *J. Am. Chem. Soc.*, **100** (1978) 996.
- 3 R. A. Beecroft, R. S. Davidson and T. D. Whelan, *J. Chem. Soc., Chem. Commun.*, (1978) 911.

- 4 R. S. Davidson, K. R. Trethewey and T. D. Whelan, *J. Chem. Soc., Chem. Commun.*, (1978) 913.
- 5 K. Mizuno, C. Pac and H. Sakurai, *J. Am. Chem. Soc.*, 96 (1974) 2993.
- 6 A. S. Atarin, A. V. Gusarov and B. A. Trofimov, *Zh. Org. Khim.*, 3 (1967) 1407.
- 7 S. L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973.
- 8 H. Beens and A. Weller, *Chem. Phys. Lett.*, 2 (1968) 140.
- 9 F. D. Lewis, *Acc. Chem. Res.*, 12 (1979) 152.
- 10 R. A. Caldwell and D. A. Creed, *Acc. Chem. Res.*, 13 (1980) 45.
- 11 S. L. Mattes and S. Farid, *Acc. Chem. Res.*, 15 (1982) 80.
- 12 E. Vander Donckt, M. R. Barthels, N. Antheunis and M. Swinnen, *Mol. Photochem.*, 8 (1977) 121.