STRUCTURE–REACTIVITY RELATIONSHIP FOR FLUORESCENCE QUENCHING OF *trans*-STILBENE BY TERTIARY AMINES

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Summary

The quenching of *trans*-stilbene fluorescence by ten amines of formula $(CH_3)_2NCH_2R$ in *n*-hexane has been examined. There is an excellent linear free energy relationship between the Stern–Volmer quenching constants and the inductive substituent constants σ_I, giving a slope ρ of -1.24 and a correlation coefficient of -0.997 for amines with $R \cong H$, $CH=CH_2$, Ph, $C\equiv CH$, $C\equiv CCH_3$, CO_2Et or CN. The negative and small absolute value of ρ is indicative of a mechanism involving exciplexes with a moderate degree of charge transfer character (contact ion pairs) with partial positive charge on the amine molecules.
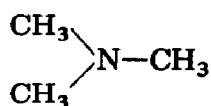
1. Introduction

Substituent effects may be regarded as perturbations on unsubstituted systems. If the perturbation is not large, there should be a linear relationship between the change in electron density at the reaction site and the change in the reaction energies resulting from the substituent. The Hammett correlation [1] is the appropriate parameter for the structure–reactivity relationship and is usually suitable for molecules in their ground state. For the excited state, there are a great variety of possible combinations.

A number of Hammett correlations for excited state reactions have been reported [2 - 6]. Eaton [4] studied the quenching of a singlet excited state of 9,10-dicyanoanthracene by para-substituted benzylstannanes in benzene and reported a Hammett correlation between the substituent constants σ_p and the quenching constants, with a slope ρ of -1.4. This value of the Hammett ρ parameter may be rationalized in terms of a rate-determining electron transfer during the exciplex formation from the ground state quencher stannane to the excited singlet state of the 9,10-dicyano-anthracene. Tamaki [3] reported ρ values of 2.8 in benzene and 1.3 in acetonitrile for the quenching of anthracene fluorescence by para- or meta-substituted benzoyl chlorides. The observed large and positive ρ values
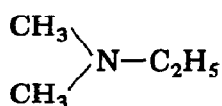
supported a charge transfer interaction in which electron transfer occurs from singlet anthracene to the ground state of the benzoyl chloride. Marcondes *et al.* [2] studied the fluorescence quenching of various substituted anthracenes by triphenylphosphine and speculated that two distinct mechanisms were involved. McCullough and Yeroushalmi [6] reported a linear free energy relationship between the rate of fluorescence quenching for a series of naphthalenes and the sum of the substituent σ constants and found $\rho = -1.613$, indicating the formation of moderately polar complexes with partial positive charge on the naphthalene ring.

The choice of a suitable substituent constant σ is of primary concern in the studies of linear free energy relationships. Up to the present time, much of the work has involved substituents attached directly to the aromatic ring, since σ_p, σ_m and σ^- are well documented and can be easily applied to studies of excited state reactions. The nature of the substituent constant σ_x appears to depend upon the hybridization state of the carbon atom to which the substituent is bonded.
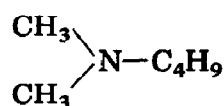
We have studied the fluorescence quenching of *trans*-stilbene by a series of tertiary amines (1 - 10) of structure $(CH_3)_2NCH_2R$ for which the substituent R is bonded to an sp^3-hybridized carbon atom.

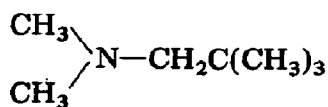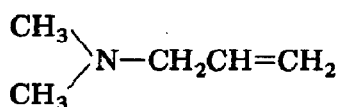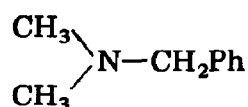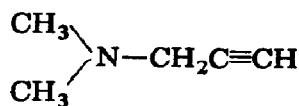$$CH_3\!\!\diagdown\!\!N\!\!-\!\!CH_3 \qquad CH_3\!\!\diagdown\!\!N\!\!-\!\!C_2H_5 \qquad CH_3\!\!\diagdown\!\!N\!\!-\!\!C_4H_9$$
$$CH_3\!\!\diagup \qquad\qquad CH_3\!\!\diagup \qquad\qquad CH_3\!\!\diagup$$

1   **2**   **3**

$$CH_3\!\!\diagdown\!\!N\!\!-\!\!CH_2C(CH_3)_3 \qquad CH_3\!\!\diagdown\!\!N\!\!-\!\!CH_2CH\!\!=\!\!CH_2 \qquad CH_3\!\!\diagdown\!\!N\!\!-\!\!CH_2Ph$$
$$CH_3\!\!\diagup \qquad\qquad\qquad CH_3\!\!\diagup \qquad\qquad\qquad CH_3\!\!\diagup$$

4   **5**   **6**

$$CH_3\!\!\diagdown\!\!N\!\!-\!\!CH_2C\!\!\equiv\!\!CH \qquad CH_3\!\!\diagdown\!\!N\!\!-\!\!CH_2C\!\!\equiv\!\!CCH_3 \qquad CH_3\!\!\diagdown\!\!N\!\!-\!\!CH_2CO_2Et$$
$$CH_3\!\!\diagup \qquad\qquad\qquad CH_3\!\!\diagup \qquad\qquad\qquad CH_3\!\!\diagup$$

7   **8**   **9**

$$\phi \diagup\!\!=\!\!\diagup \qquad\qquad CH_3\!\!\diagdown\!\!N\!\!-\!\!CH_2C\!\!\equiv\!\!N$$
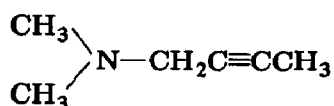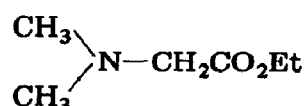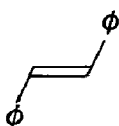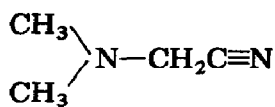$$\phi \qquad\qquad\qquad\qquad CH_3\!\!\diagup$$

trans-Stilbene   **10**

In this paper we wish to report a unique example of a linear free energy relationship using inductive substituent constants σ_I.

2. Experimental details

Fluorescence spectra were recorded on an Aminco—Bowman spectrofluorometer or a Perkin—Elmer LS-5 luminescence spectrometer. The concentration of *trans*-stilbene was 1×10^{-4} M. In order to construct Stern—Volmer plots, measurements were made for at least five quencher concentrations. No curvature was noted for any of the systems, and the intercepts were 1.00 ± 0.02 in each case. The slopes were determined by least-squares analysis and the correlation coefficients γ were always greater than 0.997.

Nuclear magnetic resonance (NMR) spectra were recorded at 90 MHz on a Varian EM-390 spectrometer. The *trans*-stilbene used was of commercial guaranteed grade; it was recrystallized from benzene and then from 90 vol.% ethanol. All the solvents were spectrograde and were used as received. The procedure for the preparation of the tertiary amines has been described elsewhere [7]. *N,N*-Dimethylneopentylamine was prepared by Clarke's method [8] by methylation from the neopentylamine (Merck) which gives a quantitative yield (boiling point, 72 °C (760 mm); 'H NMR (CDCl$_3$) 0.85 (s, 9H, *t*-butyl), 2.02 (s, 2H, C$\underline{H}_2$N), 2.25 (s, 6H, 2XC$\underline{H}_3$)).

3. Results

The reaction of the lowest excited singlet state of *trans*-stilbene with tertiary amines was studied by recording the intensity of the fluorescence of *trans*-stilbene in deaerated *n*-hexane solutions of the tertiary amines (0 - 1 M) under conditions where the *trans*-stilbene absorbs the same amount of light in each solution. Quenching of *trans*-stilbene fluorescence, as reported previously [9], is accompanied by an increase in the exciplex fluorescence band maximum at about $23\,000$ cm^{-1} in *n*-hexane or non-polar solvents. Quenching of *trans*-stilbene fluorescence by tertiary amines follows a Stern—Volmer equation at least up to an 80% reduction in initial fluorescence intensity:

$$\frac{I_f^{\circ}}{I_f} = k_q \tau [\text{amine}] + 1$$

I_f° is the intensity of fluorescence in the absence of any quencher, I_f is the fluorescence intensity after the addition of quencher of known concentration, $k_q \tau$ is the bimolecular Stern—Volmer quenching constant, [amine] is the concentration of the quencher, k_q is the quenching rate constant and τ is the observed lifetime of excited singlet *trans*-stilbene without the quencher. The observed lifetime for excited singlet *trans*-stilbene has been shown to be 105 ps [10]. The quenching constants were derived from least-squares analysis of the linear portion of the plot of I_f°/I_f *vs.* [amine].

TABLE 1

Fluorescence quenching constants $k_q\tau$ and inductive substitution constants of R for the interactions between singlet *trans*-stilbene and $(CH_3)_2NCH_2R$

Amine	R	σ_I	IP	$k_q\tau$ (M^{-1})	$\log(k_q{}^X/k_q{}^H)$
1	H	0		1.6	0.000
2	CH_3	−0.04	7.74	1.9	0.0746
3	$n\text{-}C_4H_9$	−0.02		1.7^a	0.0263
4	$t\text{-}C_4H_9$	−0.07		3.06	0.2816
5	$CH{=}CH_2$	0.09	7.84	1.3	−0.0902
6	Ph	0.01	7.69	1.6	0.000
7	$C{\equiv}CH$	0.35	8.29	0.60	−0.4260
8	$C{\equiv}CCH_3$	0.34		0.68	−0.3716
9	CO_2Et	0.21	7.96	0.87	−0.2646
10	CN	0.58	8.72	0.30	−0.7269

^{a}In cyclohexane.

The results of the quenching experiments are presented in Table 1. The values of $\log(k_q{}^X\tau/k_q{}^H\tau)$ are directly used to represent $\log(k_q{}^X/k_q{}^H)$. A Hammett plot is obtained (Fig. 1) between $k_q\tau$ and the inductive substituent constants σ_I. One can divide the amines into two different groups, for amines 1 and 5 - 10, a fairly good linear correlation is obtained with a slope ρ of −1.24 and a correlation coefficient of −0.997. The linear correlation obtained for amines 1 - 4 has a slope of −4.0 and a correlation coefficient of −0.94.
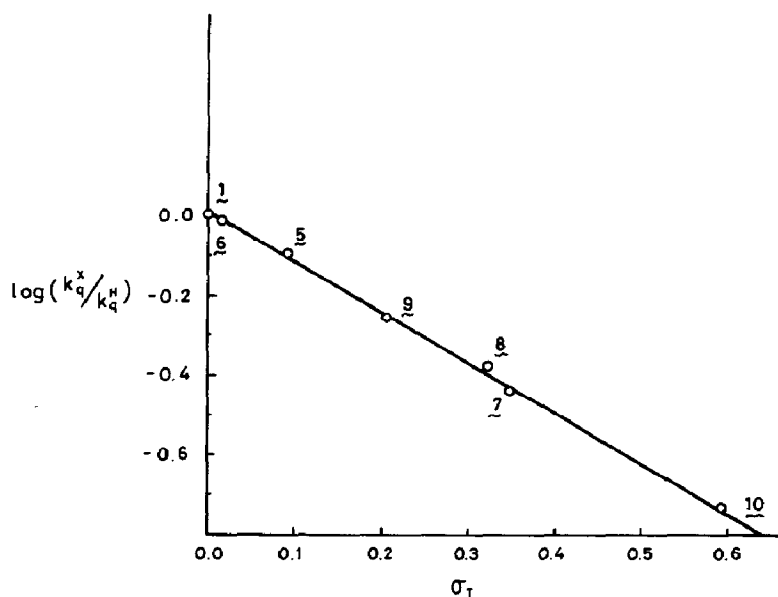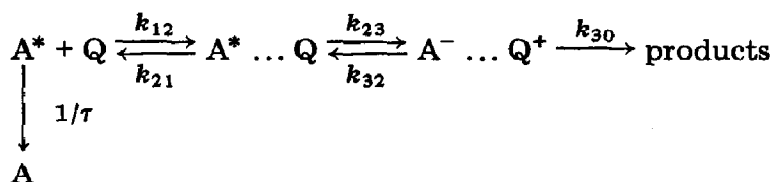

Fig. 1. Hammett plot for fluorescence quenching and σ_1 constants for amines.

4. Discussion

We have studied the quenching of *trans*-stilbene fluorescence by tertiary amines of structure $(CH_3)_2NCH_2R$, where R represents different substituents with varying inductive effects.

In this study the excited acceptor A^* is *trans*-stilbene and the donors are amines $Q(-X)$. It is well known that a variety of physical and chemical processes can lead to the quenching of an excited singlet state, including energy transfer, electron transfer, exciplex formation, enhanced intersystem crossing and hydrogen-atom transfer. For electron transfer systems

$$A^* + Q \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} A^* \ldots Q \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} A^- \ldots Q^+ \overset{k_{30}}{\longrightarrow} \text{products}$$

$$\Big\downarrow \; 1/\tau$$

$$A$$

Rehm and Weller [11] showed that the observed rate constant for the quenching of the excited acceptor A^* by the quencher Q is expressed as

$$k_q = \frac{k_{12}}{1 + k_{21}/k_{30}\{\exp(\Delta G_{23}^{\neq}/RT) + \exp(\Delta G_{23}^{\circ}/RT)\}} \tag{1}$$

where $\Delta G_{23}^{\neq}$ is the free energy of activation and ΔG_{23}° is the free energy difference. $A^* \ldots Q$ and $A^- \ldots Q^+$ denote the encounter complex and the geminate ion pair respectively. When ΔG_{23}° is negative and large the rate constant k_{23} for the charge transfer process of the encounter complex is much larger than the rate constant k_{21} for its dissociation process, and the quenching rate constant k_q becomes equal to the diffusion-controlled rate constant $(k_q \approx k_{12})$. When ΔG_{23}° is positive and large, $\Delta G_{23}^{\neq}$ is approximately equal to ΔG_{23}° and eqn. (1) can be rewritten as

$$k_q \approx \frac{k_{12}k_{30}}{2k_{21}} \exp\left(-\frac{\Delta G_{23}^{\circ}}{RT}\right) \tag{2}$$

Hence a linear free energy relationship of fluorescence quenching should be obtained if the system involves electron transfer or exciplex formation with a degree of charge transfer.

Charton [12] defined σ_I in terms of the pK_a values for the corresponding substituted acetic acid in water, as in the equation
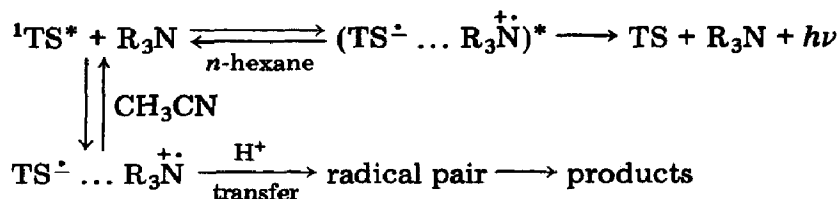
$$\sigma_{I, X} = b(pK_{a, X}) + d \tag{3}$$

where b is the slope of the regression line which minimizes the deviation of the pK_a values and d is the intercept of this line.
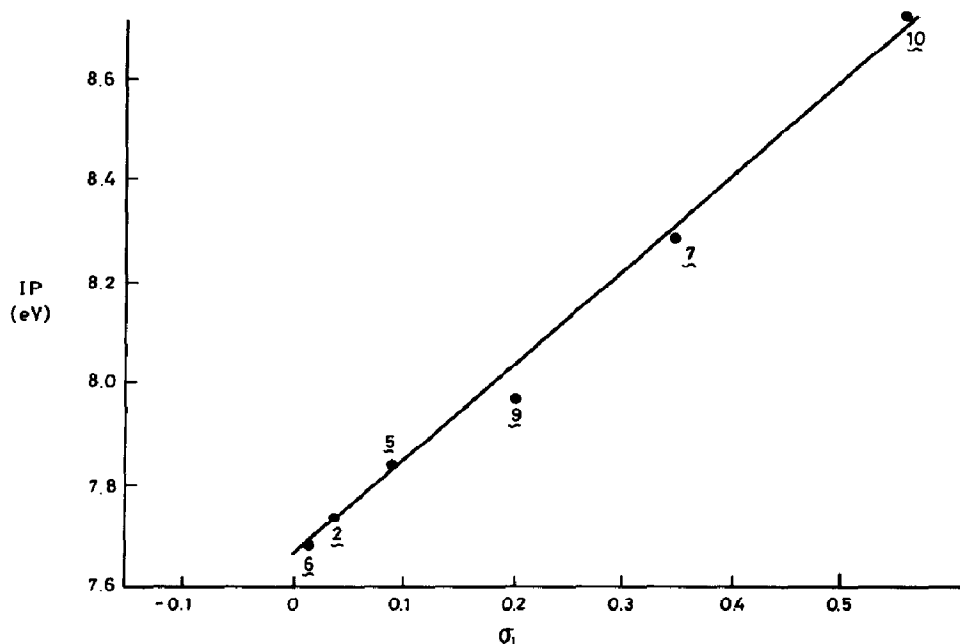
Since proton transfer in water is not sensitive to steric effects [13], no steric effects were observed for Charton's σ_I values. A plot of Charton's original σ_I values *vs.* the ionization potentials (IP) for the tertiary amines

is linear except for two points ($R \equiv CO_2Et$ and $R \equiv Ph$). Recently, Charton [14] and Bowden *et al.* [15] noted that the σ_I value for the phenyl group in non-protic media should be 0.0118. Marriott and Topson [16] showed that molecular orbital calculations at the *ab initio* level can provide an estimate of field effects which is in good agreement with experimental values for the gas phase or for non-polar solvents. For amine 9 ($R \equiv CO_2Et$), the Taft [17] ^{19}F shielding parameter ($\sigma_F = 0.21$) was chosen. The inductive substituent constants σ_I and the quenching data are listed in Table 1. A plot of the σ_I values against the IP for the tertiary amines is linear (Fig. 2).

The difference in ρ values implies that there is a change in the mechanism of fluorescence quenching. Usually, reactions in which a full positive charge is developed have ρ values between -3.0 and -5.0 [18]. For amines 1 - 4 with $\rho = -4.0$, the exciplexes (contact ion pairs) were formed with a full charge transfer. This is consistent with our former report [9] that reversible exciplex formation (Scheme I) occurs with moderate charge transfer.
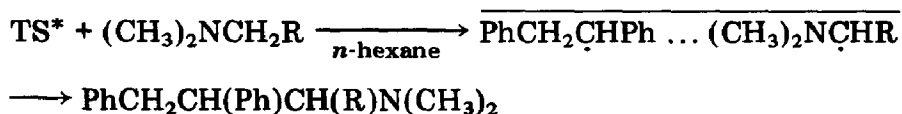
$$^1TS^* + R_3N \underset{n\text{-hexane}}{\overset{}{\rightleftharpoons}} (TS^{\cdot -} \ldots R_3\overset{+\cdot}{N})^* \longrightarrow TS + R_3N + h\nu$$

$$\Big\updownarrow CH_3CN$$

$$TS^{\cdot -} \ldots R_3\overset{+\cdot}{N} \xrightarrow[\text{transfer}]{H^+} \text{radical pair} \longrightarrow \text{products}$$

Scheme I.

Fig. 2. Plot of IP and σ_I for amines $(CH_3)_2NCH_2R$.

The dipole moment for the amine–stilbene exciplexes is about 15 debyes. The polar exciplex is chemically inactive in non-polar solvents, in which radiative decay and back electron transfer [19] are the major deactivation pathways. In polar solvents the polar exciplex can lead to fast proton transfer resulting in radical pair formation. Hub et $al.$ [10] provided evidence of the presence of $trans$-stilbene radical anions by a combination of steady state measurements and time-resolved resonance Raman spectroscopy.

For the amines with $\rho = -1.24$, in non-polar solvents the extent of charge transfer is only about 30%, but the structure of the exciplex (contact ion pair) is so different that the proton with the rest of the charge is transferred from the amine to the $trans$-stilbene molecule, leading to the formation of a radical pair and an addition product (Scheme II).

$$TS^* + (CH_3)_2NCH_2R \xrightarrow[\text{n-hexane}]{} \overline{PhCH_2\dot{C}HPh \ldots (CH_3)_2N\dot{C}HR}$$

$$\longrightarrow PhCH_2CH(Ph)CH(R)N(CH_3)_2$$

Scheme II.

The fate of this moderately polar exciplex is not so simple in polar solvents, and competitive hydrogen-atom and electron transfer processes occur [20]. The timing of the electron and proton transfer processes is important in determining whether electron transfer and proton transfers occur as opposed to hydrogen-atom transfer. If the electron transfer and proton transfer processes are synchronous, the hydrogen-atom transfer mechanism operates, otherwise it is proton transfer which takes place.

We have provided the first experimental data for a linear correlation of fluorescence quenching with inductive substituent constants. The reaction site (in the quenching process, the nitrogen lone pair electrons of the amine) is one carbon away from the substituents. From the reaction constants, one can easily obtain information concerning the intermediates formed through fluorescence quenching. This information is not usually obtainable from a time-resolved experiment. The Hammett correlation is equally as suitable for excited state systems as for ground state reactions.

Acknowledgments

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