

QUENCHING OF THE FIRST EXCITED SINGLET STATE OF CF₃-SUBSTITUTED BENZENES BY DIMETHYLAMINE[†]

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Summary

The quenching of the first excited singlet states of CF₃-substituted benzenes by dimethylamine was studied as a function of the exciting wavelength. It was found that increasing the excitation wavelength causes the quenching efficiency of dimethylamine to increase. As the electron affinity and ionization potential increase, the quenching efficiency increases, as would be expected if an encounter complex stabilized by charge transfer from dimethylamine to the excited aromatic molecule were formed.

1. Introduction

The quenching of the first excited singlet states of CF₃-substituted benzenes in the gas phase has been the subject of several studies [1 - 8]. Extensive previous work on F- and CF₃-substituted benzenes has been reviewed [9].

Brown and Phillips [2] have investigated the correlation between the quenching rate constant and the estimated electron affinity of the aromatic compound produced as a result of the formation of an encounter complex stabilized by charge transfer from a diolefin to an excited aromatic. They found that the efficiency of quenching by nitric oxide was similar to the efficiency of quenching by molecular oxygen [6].

Breuer and Lee [10] have investigated the relative contribution of the dipole-dipole and exchange mechanisms of electron energy transfer to the quenching of the fluorescence of various substituted benzenes by cyclopentanone and 1-pyrazoline, but these mechanisms are believed to be inoperative for quenching moieties such as olefins, diolefins and molecular oxygen.

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An attempt to select a good electron donor such as dimethylamine is reported in this work. The substituted benzenes have a high electron affinity because of the presence of the CF_3 group and should therefore increase the stability of energy transfer complex formation, leading to an extremely efficient quenching process.

2. Experimental details

The apparatus used in these studies was similar to that described in earlier reports [11].

The vacuum system was evacuated to a pressure of better than 10^{-4} Torr by a rotary pump and a two-stage mercury diffusion pump. The use of the optical system and its associated electronics have been described in an earlier report [12].

The purity of the substituted benzenes has been described elsewhere [6]. Dimethylamine with a purity of about 99% containing traces of trimethylamine and methylamine was obtained from the Merck Company. It was transferred directly from a lecture bottle to the vacuum line where it was purified further by bulb-to-bulb distillation.

3. Results

The quenching of the substituted benzenes used in this study by dimethylamine was analysed in terms of the Stern–Volmer relationship

$$\frac{\Phi_{f0}}{\Phi_f} = 1 + k_q \tau Q \quad (1)$$

where Φ_{f0} and Φ_f are the quantum yields of the aromatic molecule in the absence and the presence respectively of a concentration Q of dimethylamine, k_q is the quenching rate constant and τ is the fluorescence decay time of the aromatic molecule in the absence of the additive.

Plots of Φ_{f0}/Φ_f against the partial pressure of dimethylamine at wavelengths of 242, 248, 254, 258, 260, 265 and 270 nm are shown in Figs. 1, 2 and 3 for trifluoromethylbenzene, 1,3-bis(trifluoromethyl)benzene and 1,4-bis(trifluoromethyl)benzene respectively.

The slopes of these plots together with the values of τ [1] were used to calculate the k_q values reported in Table 1. The quenching rate constants were then used to calculate the quenching cross sections $\sigma^2 Q$ from the relationship

$$\sigma^2 Q = k_q (8\pi k T)^{(1/2)\mu^{-1/2}} \quad (2)$$

where μ is the reduced mass of the substituted benzene molecule and the dimethylamine molecule.

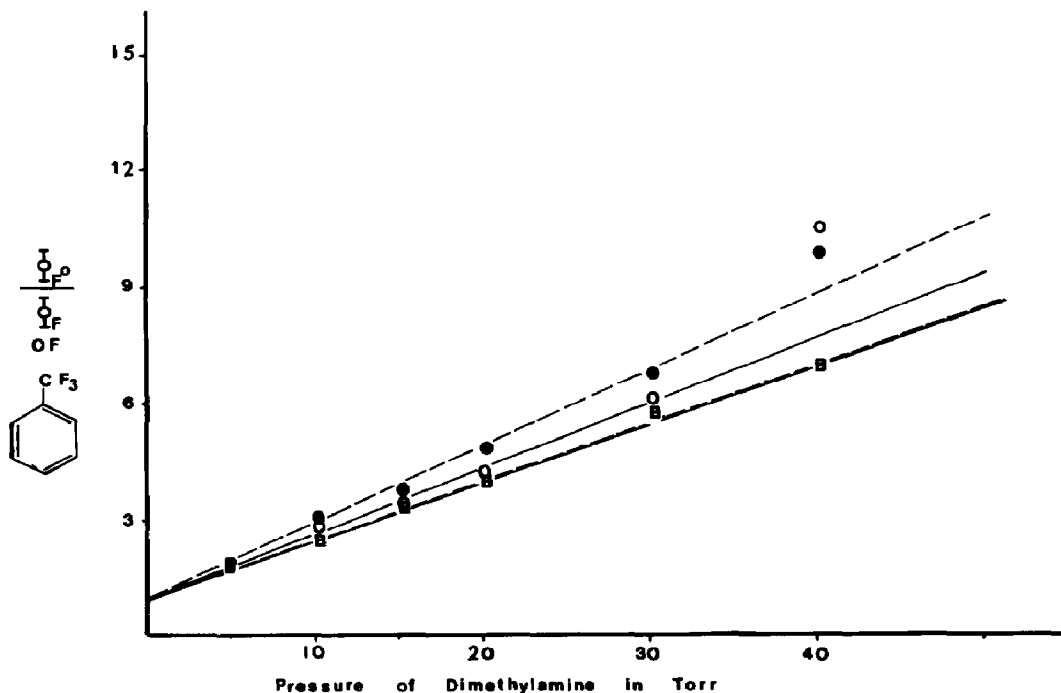


Fig. 1. Stern-Volmer plots for the fluorescence quenching of trifluoromethylbenzene by dimethylamine at various wavelengths: ●, 265 and 254 nm; ○, 254 nm; □, 248 and 242 nm.

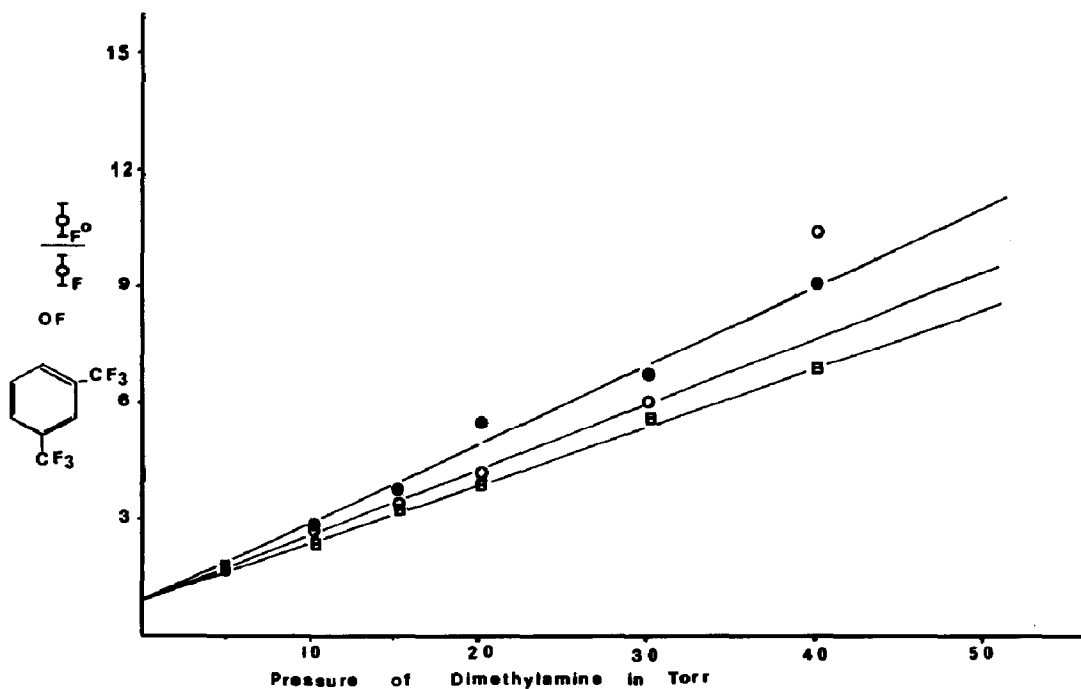


Fig. 2. Stern-Volmer plots for the fluorescence quenching of 1,3-bis(trifluoromethyl)benzene by dimethylamine at various wavelengths: ●, 270, 265 and 260 nm; ○, 254 and 258 nm; □, 242 nm.

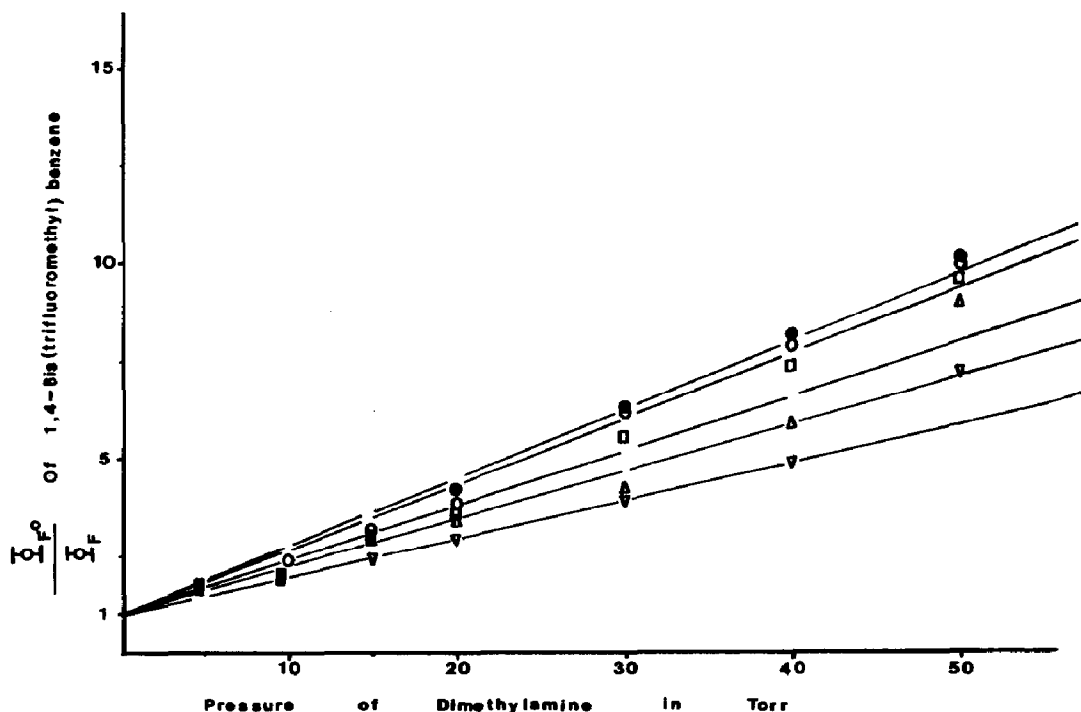


Fig. 3. Stern-Volmer plots for the fluorescence quenching of 1,4-bis(trifluoromethyl)benzene by dimethylamine at various wavelengths: ●, 270 and 265 nm; ○, 258 and 260 nm; □, 254 nm; △, 248 nm; ▽, 242 nm.

4. Discussion

The results of the experiments reported here indicate that the first excited singlet states of the substituted benzenes are quenched efficiently by dimethylamine in the gas phase.

Before proceeding to a discussion of the nature of the quenching mechanism, it is necessary to consider what effect collisional redistribution and relaxation might have on these excited substituted benzene molecules. Table 1 clearly shows that vibrational relaxation can have an important effect since a change in the quenching efficiency of dimethylamine is observed: the quenching efficiency for the 1,4 isomer at 265 nm is almost a factor of 1.5 greater than those for the 1,3 isomer and for trifluoromethylbenzene at the same exciting wavelength. The results obtained are in full agreement with the results reported previously for quenching by olefins [14] and by heterocyclic molecules [16].

The ionization potential for dimethylamine is 8.14 eV [15] which is close to those for furan, pyrrole and thiophene. These compounds also have similar quenching efficiencies to those observed for dimethylamine, and therefore we can assume that the results for the quenching of fluorescence in substituted benzenes by dimethylamine are explicable in terms of the

TABLE 1
Dimethylamine quenching parameters for CF₃-substituted benzenes

Substituent	Wavelength (nm)	Lifetime τ_F [13] (ns)	k_q ($\times 10^{10} \text{ mol}^{-1} \text{ s}^{-1}$)	$\log k_q$	$\sigma^2 Q$ ($\times 10^{-6} \text{ cm}^3$)	Ionization potential [6] (eV)	Electron affinity [14] (eV)	Slope (Torr^{-1})
None	254	77	0.25	9.40	0.30	9.25	-1.4	0.060
CF ₃	248	17.6	1.60	10.20	1.71			0.075
	255	19.0	1.59	10.20	1.71	9.68	-0.4	0.085
	265	19.0	1.99	10.30	2.12			0.01
1,3-CF ₃ CF ₃	248	17.5	1.62	10.21	2.44			0.065
	254	17.0	1.80	10.26	2.68	10.1	0.6	0.070
	265	18.1	2.10	10.32	3.16			0.90
1,4-CF ₃ CF ₃	248	12.0	1.70	10.23	2.55			0.075
	254	10.7	2.25	10.35	3.40	10.1	0.6	0.080
	265	10.7	3.05	10.48	4.60			0.100

Aromatic pressure, 5 Torr; dimethylamine pressure, 50 Torr; ionization potential for dimethylamine, 8.14 eV [15].

formation of an energy transfer complex in which the amine molecule acts as an electron donor. Singlet-singlet energy transfer is not possible because of the higher energy levels of the dimethylamine molecule with respect to those of the substituted benzenes and the complete absence of overlap between the absorption spectrum of dimethylamine and the fluorescence of these aromatics.

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