  Bull. Chem. Soc. Jpn., 64, 3137—3141 (1991)

Fluorescence Quenching of Few Aromatic Amines by Chlorinated Methanes

Debabrata GOSWAMI, Ranjit S. SARPAL, and Sneh K. DOGRA*
Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India
(Received February 1, 1991)

Fluorescence quenching of few aromatic amines; aniline (AB), 1-naphthylamine (1-AN), 2-naphthylamine (2-AN), 2,3-naphthalenediamine (2,3-DAN), 9-phenanthrenamine (9-AP), 1-pyrenamine (1-APy), 2-chrysenamine (2-AC), 6-chrysenamine (6-AC), and 3-fluoranthenamine (3-AF) by dichloromethane, chloroform, and carbon tetrachloride has been studied in cyclohexane and acetonitrile. The quenching rate constants (k_q) have been determined in both the solvents and these values are nearly independent of the solvent polarity. The values of k_q are nearly equal to diffusion-controlled limits (k_{diff}) for $CHCl_3$ and CCl_4 in both the solvents, whereas for CH_2Cl_2 it is three to four order of magnitude less than k_{diff}. For a given amine, k_q increases with the increase in electron affinity of the quencher, whereas for a given quencher (dichloromethane) k_q increases with the increase in singlet state energy of fluorophore. The results obtained are explained in terms of a quenching mechanism involving an intermediate donor–acceptor (DA)* complex formed between the excited aromatic amine and quencher.

In our recent study, regarding the effect of solvents on the absorption and fluorescence spectra of some aromatic amines,[1] it has been observed that the Stokes shifts [$\bar{\nu}_{abs}(max)-\bar{\nu}_{flu}(max)$], observed in the chlorinated methanes, do not follow the Lippert's equation and in some cases the fluorescence intensity was completely quenched in these solvents, especially the carbon tetrachloride. This indicates that there is some kind of specific interaction between these solvents and the aromatic amines. This kind of behavior has also been observed where the fluorescence of aromatic hydrocarbons,[2–5] ketones,[6,7] and heterocyclic[8,9] molecules has been quenched by halogenated alkanes.

In recent years, the quenching of fluorescence by these systems has been the focus of many investigations, as in the above-mentioned systems, energy transfer from aromatic hydrocarbons to halogenated alkanes are energetically not possible. In the above cases the fluorescence quenching of the fluorophores by the halogenated alkanes is observed without the appearance of any new fluorescence band. Thus in these cases, the formation of a transient excited-state complex as an intermediate in the fluorescene-quenching process is inferred on the basis of more indirect evidence. In any event, it seems clear that in those cases where the quencher possesses no low lying excited singlet state, which can be populated by dipole–dipole resonance transfer of energy from the excited fluorophore, the two molecules must approach one another at least to distances where the mutual interaction of the species is effective i.e. initial step in the fluorescence quenching process will be limited by the diffusion-limited approach of the excited fluorophore and quencher to form an encounter complex. Klein et al.[3] have postulated that halogenated alkanes form contact complexes as an intermediate which lie energetically above the S_1 state of the fluorophores and formation of this exciplex is considered as the rate-determination step in the excitation quenching process. The following equation was derived by Klein et al.[3] to express the quenching rate constant (k_q).

$$k_q \propto \exp[-(I.P.-E.A.-C-P-S_1)/k_bT], \quad (1)$$

where $I.P.$ are S_1 are the ionization potential and singlet state energy of the fluorophore, $E.A.$ is the electron affinity of the quencher, C is the coulomb energy, and P is the polarization energy of the separated charges, k_b is the Boltzman's constant.

The aim of the present study is to test the above model from two points i.e. to correlate (i) $\log k_q$ vs. $(IP-S_1)$ for a single quencher and (ii) $\log k_q$ vs. $E.A.$ for a single fluorophore. For this purpose we have chosen nine aromatic amines; aniline (AB), 1-naphthylamine (1-AN), 2-naphthylamine (2-AN), 2,3-naphthalenediamine (2,3-DAN), 1-pyrenamine (1-APy), 9-phenanthrenamine (9-AP), 2-chrysenamine (2-AC), 6-chrysenamine (6-AC), and 3-fluoranthenamine (3-AF), and three different quenchers, dichloromethane, chloroform, and carbon tetrachloride.

Materials and Method

1-AN, 2-AN, 2,3-DAN, 2-AC, 6-AC, 9-AP, 3-AF, and 1-APy were procured from Aldrich Chemical Company. 1-AN, 2-AN, and 2,3-DAN were first crystallized from ethanol and were further purified by vacuum sublimation. 1-APy and 9-AP were purified by repeated crystallization from 50% ethanol (v/v) and ethanol respectively. Aniline (SD Fine Chem.) was purified by distilling under vacuum repeatedly. 2-AC, 6-AC, and 3-AF were purified by repeated crystallization from ethanol. The purity of the compounds was checked by noting the mp and comparing the spectral data with the literature data. Analytical grade cyclohexane (SD Fine Chemicals) and acetonitrile (E. Merck) were further purified according to literature procedures.[10] Spectroscopic grade dichloromethane, chloroform, and carbon tetrachloride (all BDH) were used as such. Chloranil and *p*-benzoquinone were procured from K and K Fine Chemicals. These compounds were further purified by repeated crystallization from acetone.

The absorption spectra were recorded on Shimadzu UV 190, equipped with U-135 chart recorder. Fluorescence measurements were carried out on scanning spectrofluorimeter, details are available elsewhere.[11] The concentration of the fluorophores used was of the order of 0.6—2.5×10^{-5} M (1 M=1

mol dm^{-3}), whereas those of chloroform and carbon tetrachloride varied from 0.001 to 0.7 M, except for 3-AF. Dichloromethane is a very poor quencher and thus very high concentration had to be used to get any meaningful fluorescence quenching.

Fluorescence lifetimes at 300 K were measured with the help of Applied Photophysics limited nanosecond fluorescence spectrofluorimeter (model SP-70/80) using time correlated single photon counting device. The electronic processing equipment was from Ortec. The pulse width of the flash lamp is ca. 4 ns and the convolution method was applied to determine the fluorescence lifetimes less than 10 ns.

Results and Discussion

Absorption Spectra. The absorption spectra of all the aromatic amines in cyclohexane and acetonitrile at various concentrations of chlorinated methanes do not change i.e. the band shape and full band width at half the absorbance remain same. This indicates that no complex formation between the amines and chlorinated quenchers are occuring in the ground state.

Fluorescence Spectra. The fluorescence spectra of all the aromatic amines in cyclohexane and acetonitrile at various concentration of chlorinated methanes were recorded. It has been observed that the fluorescence intensity of the fluorophore decreases with the increase of quencher concentration without the appearance of any other new fluorescence band. The fluorescence band shape and full width at half the maximum intensity did not change. Further, the fluorescence intensity as well as the absorbance of any solution containing highest concentration of quencher did not change when the spectrum was recorded after the experiment was carried out once. This indicates that no detectable photoproduct is formed under our experimental conditions. This could be due to the very small amount of quencher (less than 0.6 M) used and time used to excite the sample is also very small. Dichloromethane was the exception. In this case, the concentration of quencher used was upto 10 M. Even at such a high concentration of dichloromethane, no detectable amount of decomposition of aromatic amines is observed. Further, the Stern–Volmer plot for dichloromethane as a quencher, is linear and thus indicates that no ground state or contact complex between the fluorophore and dichloromethane is formed even at such a high concentration of the quencher.

The Stern–Volmer plot of the fluorescence quenching of 2-AN by CCl_4 is shown in Fig. 1. The plot is linear throughout the concentration of CCl_4 used.

$$\frac{I_o}{I} = 1+K_{sv}[Q] = 1+k_q\tau_o[Q] \quad (2)$$

where I and I_o are the fluorescence intensities of the fluorophore with and without the quencher Q, $K_{sv}=k_q\tau_o$ is the Stern–Volmer constant, k_q is the second order fluorescence quenching rate constant and τ_o is the lifetime of the fluorophore in the absence of quencher. Similar plots were observed for other fluorophores using different quenchers. The quenching rate constants k_q for the chlorinated methanes can be easily determined from K_{sv}/τ_o. The values of k_q in cyclohexane and acetonitrile as solvents are compiled in Table 1.

Different values of excitation wavelengths were used

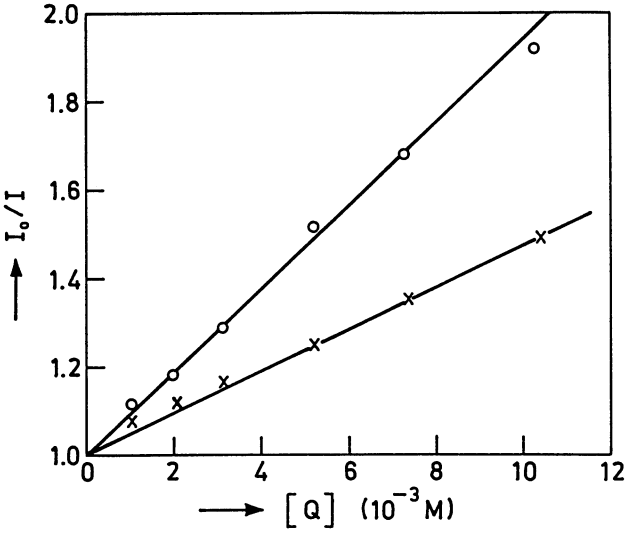

Fig. 1. Stern–Volmer plot of the fluorescence quenching of 2-AN by CCl_4 at 298K. —○—, CH_3CN; —×—, cyclohexane.

Table 1. Singlet State Energy (E_s), Lifetimes (τ_o, ns) and Quenching Rate Constants ($M^{-1}s^{-1}$) for Various Aromatic Amines in Cyclohexane and CH_3CN

S. No.	Compound	E_s	τ_o	k_q(Cyclohexane)			τ_o	k_q(CH_3CN)		
		eV	ns	CH_2Cl_2 ($\times10^6$)	$CHCl_3$ ($\times10^9$)	CCl_4 ($\times10^9$)	ns	CH_2Cl_2 ($\times10^6$)	$CHCl_3$ ($\times10^9$)	CCl_4 ($\times10^9$)
1	AB	4.1	4.3	885	13.1	15.50	5.1	212	11.83	14.20
2	1-AN	3.54	5.98	7.94	3.37	10.08	8.6	—	2.24	10.26
3	2-AN	3.72	6.2	8.82	1.89	7.59	7.3	4.52	1.12	10.11
4	2,3-DAN	3.51	6.8	2.94	2.10	11.76	4.9	2.14	4.45	10.36
5	9-AP	3.28	10.6	0.57	0.69	6.06	7.7	—	0.74	10.14
6	1-APy	3.12	5.6	0.13	0.23	10.02	4.3	3.93	0.60	10.33
7	2-AC	3.06	7.5	—	0.046	8.03	5.4	—	0.049	15.71
8	6-AC	3.06	7.5	—	0.049	6.55	6.0	—	0.0695	17.95
9	3-AF	2.80	8.1	—	0.001	0.046	8.8	—	—	0.147

for 1-AN–$CHCl_3$ system and it was found that the Stern–Volmer plot (thus K_{sv}) did not depend upon the excitation wavelength above 300 nm, (λ_{exc}=300 nm, K_{sv}=20.1 M^{-1}; λ_{exc}=325 nm, K_{sv}=19.6 M^{-1}; λ_{exc}=335 nm, K_{sv}=20.45 M^{-1}). This indicates that no distinct complex formation between $CHCl_3$ and 1-AN in the ground state is observed. Though no similar study has been carried out with other compounds, similarity of the absorption spectra of these compounds with each other does indicate that no ground-state complexes are formed in these systems also. This has also been manifested from the study of absorption characteristics as said earlier. But these results are different from those of anthracene and CCl_4,[2,3] where it has been shown that the photoproducts are formed.

A popular mechanism, generally used to explain the fluorescence quenching has the following reaction scheme:

$$A + h\nu \longrightarrow A^* \quad (2)$$

$$A^* + Q \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (AQ)^* \xrightarrow{k_3} A + Q \quad (3)$$

$$A^* \xrightarrow{k_f} A + h\nu_f, \qquad A^* \xrightarrow{k_I} A$$

where A, Q and $h\nu$ represent the fluorophore, quencher and the light quantum, A* and (AQ)* are the excited states of the fluorophore and of the encounter complex between A* and Q respectively, k's reaction rate constants, k_f and k_I are the rate constants for radiative and nonradiative decay processes. The apparent quenching rate constant k_q, for the collisional quenching process can be given by

$$K_q = \gamma k_1, \quad (4)$$

where γ is the efficiency of the quenching reaction, which is given by $k_3/(k_2+k_3)$ approaches unity if $k_2 \ll k_3$ (the quenching process is very fast) or it approaches k_3/k_2 when not every encounter between Q and A* results in quenching. Thus the values of $k_q=k_1$ in the former case and k_1k_3/k_2 in the latter case. As said earlier, fluorescence quenching process in the present case requires that the fluorophore and the quencher should approach each other, the maximum value of k_1 can be equal to the diffusion controlled limits. The values of k_1 thus determined, using the modified Debye equation[12] ($8\,RT/3000\,\eta$, where η is viscosity of the medium in centipoise, R is a gas constant and T the temperature in Kelvin) are found to be 9.8×10^9 $M^{-1}s^{-1}$ and 1.8×10^{10} $M^{-1}s^{-1}$ in cyclohexane and acetonitrile respectively.

The data of Table 1 clearly indicate that fluorescence quenching rate constants for all the aromatic amines by CCl_4 are nearly equal to the diffusion-controlled rate constant (k_{diff}) whereas the quenching efficiency of CH_2Cl_2 is three to four orders of magnitude less than CCl_4 and that of $CHCl_3$ is between CH_2Cl_2 and CCl_4. The quenching rate constants even in case of CH_2Cl_2 is considerably faster than can be accounted for chemical quenching (for example, the rate constant of alkyl radicals with CCl_4 does not exceed 10^4—10^5 $M^{-1}s^{-1}$, see Ref. 3). The data of Table 1 thus clearly indicate that quenching is believed to proceed via an intermediate donor-acceptor (DA)* complex formed between the excited aromatic amine and quencher and not by classical energy transfer. To test the validity of this model, Eq. 1 can be varified from two angles as mentioned below:

i) Equation 1 reduces to

$$k_q \propto \exp[-(\text{const} - E.A.)/k_bT],$$

$$\text{i.e.} \qquad \log k_q = \text{const} + \frac{E.A.}{2.303\,k_bT}, \quad (6)$$

if the fluorophore is kept the same but quencher is varied. Figure 2 depicts the plot of $\log k_q$ vs. $E.A.$ Although the number of quenchers are only three, it is clear from Fig. 2 that plot is a curve for each amine and it levels off to a diffusion controlled rate constant. Though quantitatively we cannot get much information, qualitatively it is clear that k_q increases with increase of $E.A.$ of the quencher. Similar behavior has been observed in case of fluorescence quenching of aromatic molecules by inorganic ions.[14–17]

ii) Equation 1 reduces to Eq. 7 if we choose different fluorophores and one quencher,

$$k_q \propto \exp[-(I.P. - S_1 - \text{const})/k_bT],$$

$$\text{or} \qquad \log k_q = \text{const} + \frac{S_1 - I.P.}{2.303\,k_bT}, \quad (7)$$

The singlet state energy of all the aromatic amines were calculated by taking the average of the long wavelength band maximum of absorption spectrum and short wavelength band maximum of fluorescence spectrum in cyclohexane. This is because in this solvent, the interactions between the solvent and the fluorophore is minimum. These values are compiled in Table 1.

The ionization potential data for all the aromatic amines are not available, except for AB, 1-AN, and 2-AN[18] (i.e. 7.7, 7.3, and 7.25 eV respectively). The experiments were carried out to calculate the ionization potentials of aromatic amines by measuring the energy of the charge-transfer band (E_{CT}) of the molecular complexes formed by these amines with different electron acceptor molecules (e.g. chloranil and benzophenone).

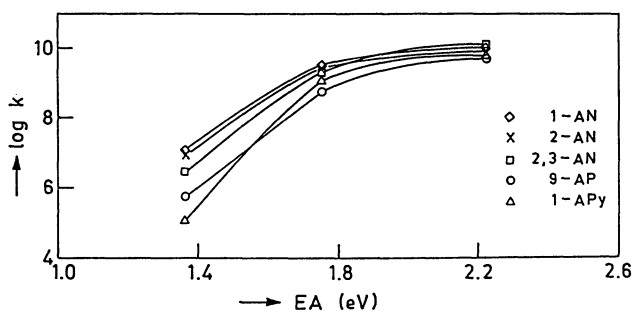

Fig. 2. Plot of $\log k_q$ vs. electron affinity of the quencher, in cyclohexane.

Unfortunately no charge-transfer bands were observed with these acceptor molecules, though simple empirical relations are available to relate the energy of the CT band and *I.P.* of donor molecule. With the limited data available, it is clear that we cannot assume that *I.P.*'s are constant for these amines. However in the absence of *I.P.* values, $\log k_q$ versus singlet state energy of the fluorophores, for CH_2Cl_2, $CHCl_3$, and CCl_4 as quenchers, in cyclohexane and acetonitrile are depicted in Fig. 3. The plots are linear for CH_2Cl_2 and $CHCl_3$ in cyclohexane and acetonitrile, with slopes 3.5 and 2.5 in the former solvent and 2.0 and 1.5 eV^{-1} in the latter solvent, whereas for CCl_4, the plots are horizontal to *x*-axis. The linear correlation suggests that *C* and *P* values are practically constant. The above results further suggest that the *I.P.* of these aromatic amines are proportional to the singlet state energy (i.e. $I.P.-S_1$), thus leading ($S_1-I.P.$) to $(1-a)$ S_1 where '*a*' is a constant of proportionality. The above results are consistent with the fact that the values of the quenching rate constants are limited by the singlet state energy of the fluorophore so long these are less than k_{diff}. Once the value of k_q is equal to k_{diff}, k_q will be independent of either E_S or *E.A.* The values of slopes obtained in case of CH_2Cl_2 or $CHCl_3$ are much less than the theoretical value [i.e. $1/(2.303\ k_bT)=16.78\ ev^{-1}$].

Thus the above results suggest that fluorescence quenching for these aromatic amines does not occur via charge-transferred state. As said earlier quenching could proceed via an intermediate donor-acceptor (DA)* complex formed between the excited aromatic amine and quencher.

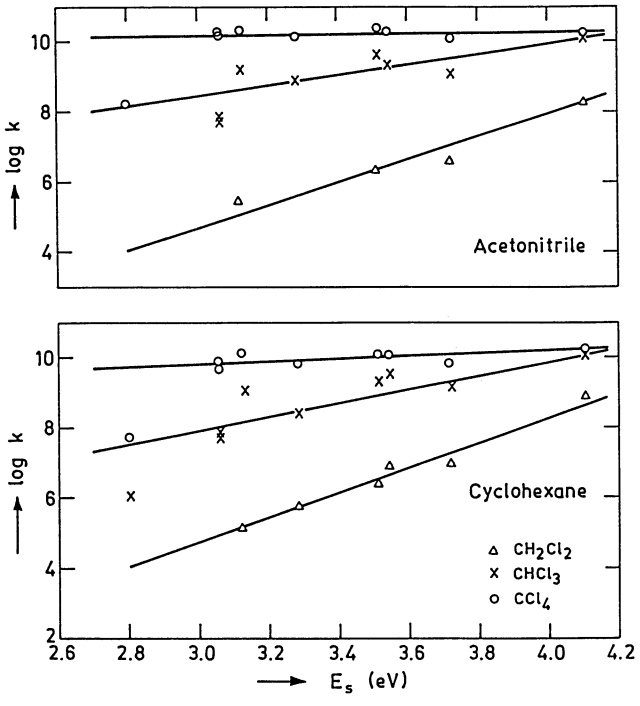

Fig. 3. Plot of log k_q vs. singlet state energy of aromatic amines. (a) Cyclohexane (b) Acetonitrile.

The value of k_q observed for 3-AF is much less than that can be predicted from the $\log k_q$ vs. S_1 plot. Our earlier results[23] have indicated that proton-induced fluorescence quenching of neutral 3-AF is much less than that generally observed in other aromatic amines,[24-28] with few exceptions.[29,30] This indicates that charge transfer character in S_1 state of 3-AF is very less and thus the transfer of charge from 3-AF to chlorinated methanes will not be efficient process.

The results of dichloromethane using as an electron acceptor have indicated that the fluorescence intensity as well as shift in fluorescence band maximum of the donor molecule is observed when the concentration of CH_2Cl_2 is more than 5 M and thus can be explained in term of a change in the rate of unimolecular photoprocesses induced by the change in solvent. At very high concentration of CH_2Cl_2 its effect as a solvent (and the decrease in k_q due to the decrease in the polarity) is more significant than the change in the quencher concentration (i.e. $k_q[Q]$ decreases with increase in [Q]). Similar dependence has also been observed in other systems.[22]

Conclusion. In conclusion, we consider that the dominant quenching pathway involves an intermediate donor-acceptor (DA)* complex formed between the excited aromatic amine and quencher molecules.

The authors are thankful to the Department of Science and Technology, New Delhi for financial support.

References

1) S. Mazumdar, R. Manoharan, and Sneh K. Dogra *J. Photochem. Photobiol. A,* **46**, 301 (1989).

2) a) C. Lewis and W. R. Ware, *Chem. Phys. Lett.,* **15**, 290 (1972). b) W. R. Ware and C. Lewis, *J. Chem. Phys.,* **57**, 3546 (1972).

3) J. Klein, V. P. Plazanet, and G. Laustriat, *J. Chim. Phys. Physiochim. Biol.,* **67**, 302 (1970).

4) D. Saperstein and E. Levine, *J. Chem. Phys.,* **62**, 3560 (1975).

5) M. V. Encinas, M. A. Rubio, and E. A. Lissi, *J. Photochem.,* **18**, 137 (1982).

6) J. O. Pavlik, P. I. Plogard, A. C. Sommsall, and J. E. Guillet, *Can. J. Chem.,* **51**, 1435 (1973).

7) R. O. Loutfy and A. C. Somersall, *Can. J. Chem.,* **54**, 760 (1976).

8) G. E. Johnson, *J. Phys. Chem.,* **84**, 2940 (1980).

9) T. Takahashi, K. Kikuchi, and H. Kokubun, *J. Photochem.,* **14**, 67 (1980).

10) J. A. Riddick and W. Bunger, "Organic Solvents," Wiley Interscience, New York (1970), pp. 632, 695, 801.

11) M. Swaminathan and S. K. Dogra, *Indian J. Chem., Sect. A,* **22**, 853 (1983).

12) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York (1966), p. 627.

13) F. W. Billmeyer, "Textbook of Polymer Science," Wiley, New York (1971), pp. 293—301.

14) H. Shizuka, T. Saito, and T. Morita, *Chem. Phys. Lett.,* **56**, 519 (1976).

15) H. Shizuka, M. Nakamura, and T. Morita, *J. Phys.*

Chem., **84**, 989 (1980).
16) T. Moriya, *Bull. Chem. Soc. Jpn.*, **57**, 1723 (1984); **59**, 961 (1986).
17) K. A. Addullah and T. J. Kemp., *J. Chem. Soc., Perkin Trans. 2*, **1985**, 1279.
18) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, New York (1970), p. 408.
19) J. C. Scanio, *J. Am. Chem. Soc.*, **102**, 7747 (1980).
20) H. Leonhardt and A. Weller, *Z. Physik. Chem., N. F.*, **29**, 277 (1961); *Ber. Bunsen-Ges. Physik. Chem.*, **61**, 791 (1963).
21) T. Miwa and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **38**, 529 (1965).
22) T. Miwa and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **39**, 2588 (1966).
23) A. K. Mishra and S. K. Dogra, *J. Chem. Soc., Perkin Trans. 2*, **1984**, 943.
24) H. Shizuka and K. Tsutsumi, *J. Photochem.*, **9**, 304 (1978).
25) K. Tsutsumi, S. Setaguchi, and H. Shizuka, *J. Chem. Soc., Faraday Trans. 2*, **78**, 1087 (1982).
26) K. Tsutsumi and H. Shizuka, *Z. Phys. Chem.* (*Munich*), **111**, 129 (1978).
27) H. Shizuka, *Acc. Chem. Res.*, **18**, 141 (1985).
28) A. K. Mishra and S. K. Dogra, *J. Photochem.*, **23**, 163 (1983); A. K. Mishra and S. K. Dogra, *Bull. Chem. Soc. Jpn.*, **58**, 3587 (1985).
29) H. Shizuka, T. Ogiwara, and E. Kimuea, *J. Phys. Chem.*, **89**, 4302 (1985).
30) A. K. Mishra and S. K. Dogra, *Indian J. Chem., Sect. A*, **24**, 364 (1985).