BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (1), 52—56 (1977) [Vol. 50, No. 1

Emission Spectra of the Vinyl Polymers with Pendant Phenanthryl Groups

Akira Itaya, Ken-ichi Okamoto, and Shigekazu Kusabayashi

Department of Chemical Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755

(Received June 30, 1976)

The emission properties of 9-ethylphenanthrene (EPh), poly(9-vinylphenanthrene) (PVPh), poly(9-phenanthryl methacrylate) (PPhMA), and poly[2-(9-phenanthryl)ethyl vinyl ether] were investigated in solution. These vinyl polymers showed no clear excimer fluorescence in the longer-wavelength region. Both the fluorescence quantum yield and the lifetime of PVPh decreased largely with an increase in temperature at higher temperatures. This suggests that PVPh forms an excimer which has a low fluorescence quantum yield. The fluorescence properties of PPhMA and PPhEVE, in which Ph chromophores are widely spaced on the skeletal chains, indicated little interaction between neighboring Ph chromophores in the singlet state. This results from the nature of Ph, in whith it is difficult to form an excimer. The phosphorescence spectrum and its lifetime of PPhEVE indicated a presence of a weak interaction between neighboring Ph chromophores in the triplet state. PVPh and PPhEVE showed a delayed fluorescence resulting from a T-T annihilation between two migrating triplet excitons.

Recently, emission spectra of aromatic vinyl polymers have been extensively investigated. It is known that aromatic vinyl polymers exhibit excimer fluorescences in dilute solutions due to the interaction between neighboring chromophores.

1-Ethylpyrene and 1-ethylnaphthalene show the excimer fluorescence in concentrated fluid solutions at room temperature. Poly(1-vinylpyrene)[1,2] and poly(1-vinylnaphthalene)[3-5] show almost exclusively the excimer fluorescence in dilute solutions. Poly(1-pyrenylmethyl vinyl ether) (PPyMVE),[1,6] poly(1-naphthylmethyl vinyl ether) (PNMVE),[6] and poly(1-naphthyl methacrylate) (PNMA),[7] in which the pyrenyl and naphthyl chromophores are widely spaced on the skeletal chains by –O–CH$_2$– and –CO–O– bonds, show both the structured monomer fluorescence and the excimer one in dilute solutions. On the other hand, *N*-ethylcarbazole (ECz) and 9-ethylacridine (EAcr) show no excimer fluorescence in concentrated solutions.[1,8] Poly(*N*-vinylcarbazole) (PVCz)[8] and poly(9-vinylacridine) (PVAcr),[1] however, show the excimer fluorescence. Poly[2-(*N*-carbazolyl)ethyl vinyl ether] (PCzEVE), in which the carbazolyl chromophores are widely spaced on a skeletal chain by –O–CH$_2$–CH$_2$– bonds, shows a structureless fluorescence, which is different from both the monomeric structured fluorescence and the sandwich-like excimer one observed for the model compounds and PVCz respectively. This implies the presence of the excited-state interactions among the carbazolyl chromophores in PCzEVE.[9]

Phenanthrene crystal has only two molecules per unit cell arranged with their molecular planes almost perpendicular. It does not normally exhibit an excimer emission. However, this crystal under a high pressure does exhibit a broad emission with a peak at *ca.* 440 nm. This emission is assigned to the excimer fluorescence.[10] Despite extensive studies of the prompt and delayed fluorescence of phenanthrene, no excimer fluorescence has been observed in this compound at room temperature.[11] Studies of the emission of a phenanthrene sandwich dimer prepared by photolytic dissociation have also shown that phenanthrene does not form an excimer even under favorable condition.[12] Therefore, it is of interest to investigate the emission spectra of the vinyl polymers, where the phenanthryl (Ph) chromophores are directly connected to or widely spaced on the skeletal chains.

In the present paper, we have investigated the spectroscopic behaviors of poly(9-vinylphenanthrene) (PVPh), poly(9-phenanthryl methacrylate) (PPhMA), and poly[2-(9-phenanthryl)ethyl vinyl ether] (PPhEVE); in the latter two polymers, the phenanthryl chromophores are widely spaced on the skeletal chains by –CO–O– and –O–CH$_2$–CH$_2$– bonds respectively.

Experimental

Syntheses of 9-Ethylphenanthrene(EPh) and PVPh. EPh and 9-vinylphenanthrene(VPh) were prepared according to the literature.[13,14] The EPh was purified by recrystallization from methanol and sublimation *in vacuo*. The VPh was purified by recrystallization from ethanol and sublimation *in vacuo*. The PVPh was prepared by the polymerization of a 0.4 M benzene solution of the purified VPh in the presence of 0.2 mol% azobisisobutyronitrile in an evacuated sealed tube at 80 °C for 20 h and was reprecipitated three times from the benzene solution with methanol or hexane. The molecular weight measured by a vapor pressure osmometer was 3600. The degree of polymerization($\overline{DP}$) is about 18.

Synthesis and Polymerization of 2-(9-Phenanthryl)ethyl Vinyl Ether(PhEVE). 2-(9-Phenanthryl)ethanol(PhEtOH) was prepared from purified phenanthrene according to the literature[15] and purified by recrystallization from cyclohexane. The PhEVE was synthesized from the PhEtOH by the route similar to 2-(*N*-carbazolyl) ethyl vinyl ether[16] and was purified by recrystallization from ligroin and sublimation *in vacuo*. Yield, 30%; mp 82.0—84.0 °C, IR(KBr-disk): δ_{CH} of vinyl ether 960 and 820 cm^{-1}, NMR (CDCl$_3$): 1.4—1.6 τ (multiplet, two ring protons); 2.0—2.2 τ (multiplet, one ring proton); 2.3—2.7 τ (multiplet, six ring protons); 3.5—3.8 τ (quartet, –O–C$\underline{H}$=CH$_2$); 5.8—6.2 τ (multiplet, –C$\underline{H}_2$–CH$_2$–O–CH=C$\underline{H}_2$); 6.5—6.7 τ (triplet, –CH$_2$–C$\underline{H}_2$–O–). Found: C, 87.07; H, 6.52%. Calcd for C$_{18}$H$_{16}$O: C, 87.05; H, 6.51%.

The polymerization conditions are summarized in Table 1. The solvents were purified by ordinary methods.

Synthesis and Polymerization of Phenanthryl Methacrylate(PhMA). 9-Phenanthrol was prepared from the purified phenanthrene according to the literature.[17] The PhMA was synthesized by reacting methacryl chloride with the 9-phenanthrol by the route similar to naphthyl methacrylate.[18] The monomer was extracted with benzene, washed with water, and dried over Na$_2$SO$_4$. The PhMA was isolated by column chromatography (silica gel, benzene); mp 53.5—55.0 °C, IR (KBr-disk); 1715 ($\nu_{C=O}$), 1615 ($\nu_{C=C}$), 920 ($\delta_{C=CH_2}$) cm^{-1}, NMR ($CDCl_3$); 1.35—1.61 τ (quartet, two ring protons); 2.03—2.32 τ (multiplet, two ring protons); 2.03—2.32 τ (multiplet, two ring protons); 2.36—2.62 τ (multiplet, five ring protons); 3.54 τ (singlet, terminal vinyl proton(*cis*)); 4.22 τ (singlet, terminal vinyl proton(*trans*)); 7.86 τ (singlet, methyl protons). This monomer was very labile and was polymerized often during the purification. The PPhMA used for spectral measurements was prepared by a thermal polymerization and was reprecipitated from the chloroform solution with methanol. This polymer was insoluble in some organic solvents, but soluble in chloroform. Found: C, 81.31; H, 5.40%. Calcd for $C_{18}H_{14}O_2$; C, 82.41; H, 5.39%.

Method. The sample of PPhEVE (No. 5 in Table 1), which had the highest value of $\overline{DP}$(87) was used for spectral measurements. All of the solvents used (tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), chloroform, and 1,4-dioxane) were purified by the usual methods. Solutions were completely degassed by freeze-pump-thaw cycles. The emission spectra and fluorescence decay times were measured with the apparatus described in the previous paper.[8]

Results and Discussion

Polymerization of PhEVE. The cationic polymerization results are shown in Table 1. The PPhEVE is obtained in fairly good yields at or below 0 °C. The yield decreases with an increase in the polymerization temperature above 0 °C. PhEVE is also polymerized by $AlEtCl_2$ in high yields. The PPhEVE is soluble in some organic solvents, such as tetrahydrofuran and 1,2-dichloroethane.

The PPhEVE prepared in the present study has a comparatively high molecular weight (22000, $\overline{DP}$=87). This value of $\overline{DP}$ for PPhEVE is higher than the values for PCzEVE, PPyMVE, and PNMVE (33, 10, and 22, respectively).[16,19] The rather low softening point (SP) of the PPhEVE suggests the enhanced flexibility of the skeletal chain as compared with the cases of PVPh (SP: 209—218 °C, $\overline{DP}$=18), PPyMVE (SP: 220—230 °C, $\overline{DP}$=10) and PCzEVE (SP: 137—148 °C, DP=33).[16,19] The reason why the PPhEVE with the comparatively high $\overline{DP}$ has the low SP value is that phenanthryl chromophores, being less bulky than carbazolyl and pyrenyl chromophores, are widely spaced on the skeletal chain.

Emission Spectra. 1,3-Di(*N*-carbazolyl)propane and *N*-vinylcarbazole oligomer ($\overline{DP}$=4), of which the monomer compound (ECz) shows no excimer fluorescence, show excimer fluorescence in dilute solution at room temperature.[7,20-22] Therefore, the PVPh(DP=18) sample has sufficient molecular weight to be used in order to examine the possibility of excimer formation.

Fluorescence spectra of PVPh, PPhMA, PPhEVE, and EPh in solutions at room temperature are shown in Fig. 1. The fluorescence spectrum of the concentrated EPh solution indicated that EPh does not form an excimer, as is the case of phenanthrene. The fluorescence spectrum of PPhEVE is similar to that of EPh. Although the fluorescence spectra of PVPh and PPhMA are broad as compared with those of EPh and PPhEVE, no clear excimer fluorescence in the longer-wavelength region is observed for PVPh and PPhMA. Therefore, it is suggested that the interaction between neighboring chromophores in these polymers is much weaker than that observed for other aromatic vinyl polymers.

Fluorescence spectra of PVPh, PPhEVE, and EPh in rigid glasses at 77 K are shown in Fig. 2. The fluorescence band shifts to lower frequencies in the order of EPh, PPhEVE, and PVPh. The clear vibrational structure bands observed for PVPh and PPhEVE are similar to that for EPh and the fluorescence lifetimes of PVPh and PPhEVE are also much the same as that of

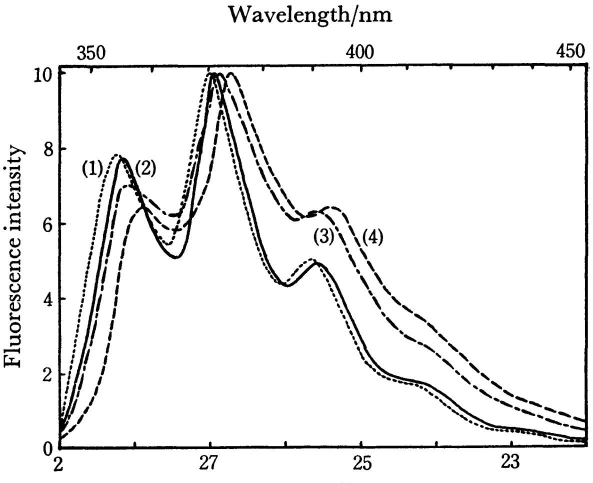

Fig. 1. Normalized fluorescence spectra of (1) ······; EPh, (2) ——; PPhEVE, (3) ·–·–; PPhMA, and (4) ------; PVPh in solutions at room temperature. Solvents; (1), (2), (3); MTHF-THF (3:2) mixture, (3); chloroform containing 1.0% ethanol. Excitation wavelength; 345 nm.

Table 1. Polymerization of PhEVE[a)]

No.	Cat. (BF_3OEt_2) mol % to monomer	Temp °C	Time h	Conversion %	SP[b)] °C	Mol wt[c)]
1	1	55	9	28	115—125	
2	1	20	9	52	88—100	
3	1	0	9	73	103—110	
4	1	−15	4	88	100—110	
5	1	−40	4	92	115—120	22000
6	5	−45	4	87	100—118	
7	2	−60	4	90	110—115	18000
8	1	−78	9	84	100—110	

a) PhEVE, 0.2—0.5 g; monomer concentration, No. 6: 0.16 M, the others: 0.2 M; solvent, toluene. b) SP, softening point. c) Measured by a vapor pressure osmometer.

TABLE 2. SPECTROSCOPIC DATA OF VINYL POLYMERS WITH PENDANT PHENANTHRYL CHROMOPHORES IN MTHF–THF

Polymer	Relative yield at 20°C	Fluorescence lifetime[b] /ns				Phosphorescence lifetime/s
		77 K	−40°C	24 °C	50 °C	
EPh	1.00	59	50	50	48	4.4
PPhEVE	0.85	59	49	47	46	3.4
PPhMA[a]	0.15	—	—	16[c]	15[c]	—
PVPh	0.17	58	40	21[c]	20[c]	2.8

a) Solvent: chloroform containing 1.0% ethanol. b) The fluorescence was observed through Toshiba UV-DIC and UV-35 filters. Error is ±2 ns. c) The initial fast decay component was observed.

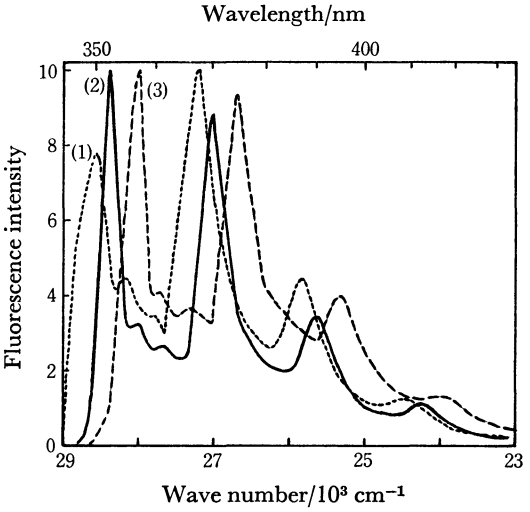

Fig. 2. Normalized fluorescence spectra of (1) EPh, (2) PPhEVE, and (3) PVPh in MTHF–THF rigid glasses at 77 K. Excitation wavelength; 330 nm.

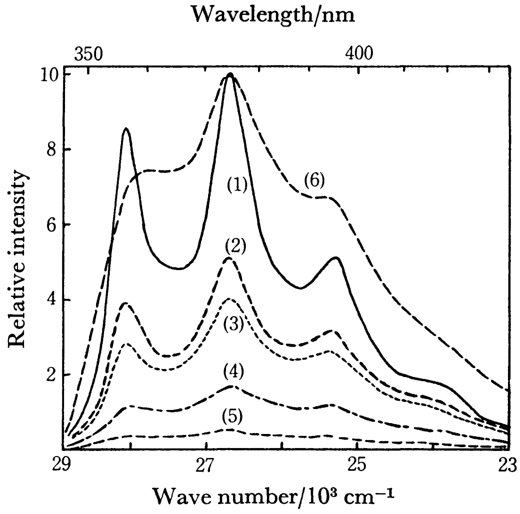

Fig. 3. Temperature dependence of fluorescence spectra of PVPh (5.1×10^{-4} M) in MTHF–THF solution. Excitation wavelength; 310 nm. (1) −130, (2) −86.5, (3) −37.7, (4) 6, and (5) 63.5 °C. The fluorescence (6) is 1.95 times the fluorescence (5).

EPh at 77 K (Table 2). These facts suggest that there is little interaction between neighboring Ph chromophores in PPhEVE and PVPh in rigid glasses at 77 K.

Table 2 shows the relative fluorescence quantum yields, taking the value of EPh as unity, and the fluorescence lifetimes. The fluorescence quantum yields and lifetimes of PVPh and PPhMA at room temperature are much lower than those of EPh and PPhEVE. The decay curve of PVPh has an initial fast component. The fluorescence spectra of PVPh in MTHF–THF solution at various temperatures are shown in Fig. 3. The fluorescence intensity decreases and the vibrational bands broaden with an increase in temperature. Temperature dependences of the fluorescence yields are shown in Fig. 4. The changes observed for EPh, PPhEVE, and PPhMA are small and they show a similar tendency. On the other hand, only PVPh shows a large decrease. The same tendency is observed for the temperature dependence of the fluorescence lifetimes (Table 2). Namely, the fluorescence lifetimes of EPh, PPhEVE, and PVPh in rigid glasses at 77 K are all equal. Only the lifetime of PVPh, however, decreases unusually with an increase in temperature.

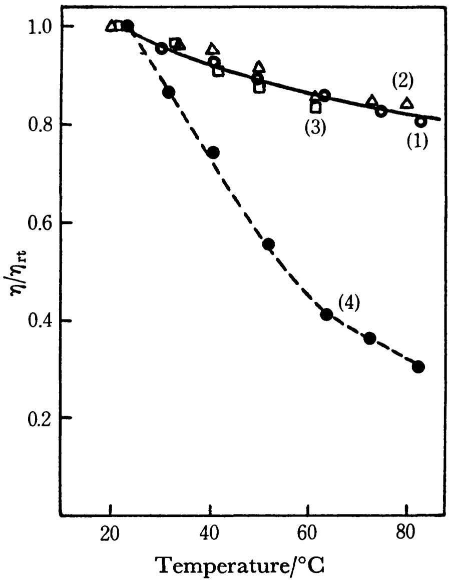

Fig. 4. Temperature dependence of the fluorescence yields. The value of η/η_{rt} exhibits the ratio of the fluorescence yield at some temperature to that at room temperature. (1) ○; EPh, (2) △; PPhEVE, (3) □; PPhMA, and (4) ●; PVPh. Solvent: (1), (2), (4); 1,4-dioxane, (3); chloroform containing 1.0% ethanol. These values were uncorrected for decrease in density of solvents with an increase in temperature.

As mentioned above, the vibrational structure of fluorescence and its lifetimes of PVPh and PPhEVE are similar to those of EPh in rigid solutions at 77 K. However, the phosphorescence of PVPh and PPhEVE is markedly different from that of EPh, as is shown in Fig. 5. The phosphorescence band shifts to lower frequency and the vibrational structure broadens in the order of EPh, PPhEVE, and PVPh. The phosphorescence lifetime shortens in the same order (Table 2). The red shift of the phosphorescence band is much larger than that of the fluorescence. These facts indicate that an interaction between neighboring Ph chromophores in the triplet state is much larger than that in the singlet state in rigid glasses at 77 K.

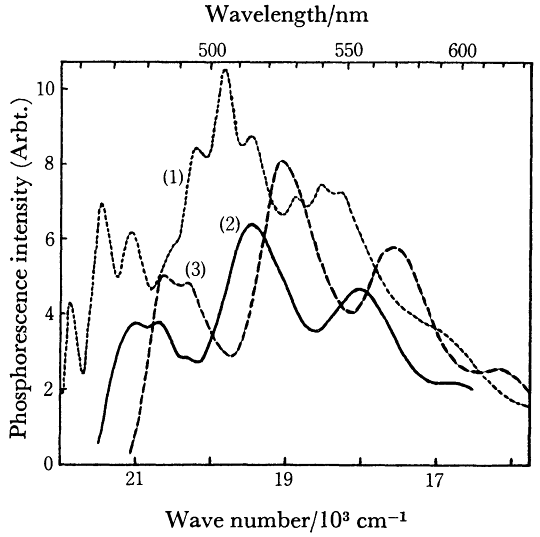

Fig. 5. Phosphorescence spectra of (1) EPh, (2) PPhEVE, and (3) PVPh in MTHF–THF rigid glasses at 77 K. Excitation wavelength; 310 nm.

The delayed emission, of which the position and profile are the same as those observed for the normal fluorescence at 77 K, is observed for PVPh and PPhEVE in rigid glasses at 77 K. The emission intensity depends quadratically on the phosphorescence intensity. The lifetime of this emission of PPhEVE is about 30 ms, while that of PVPh could not be determined because of the extremely low intensity. These facts indicate that this emission band can be assigned to the delayed fluorescence resulting from a T-T annihilation between two migrating triplet excitons.

PPhEVE resembles EPh very closely in fluorescence properties, forms no excimer, and does not show the anomalous fluorescence observed for PCzEVE.9) The fluorescence spectra of PPhMA is markedly different from that of EPh and its lifetime is very short. The temperature dependence of the fluorescence yield, however, is similar to those of EPh and PPhEVE. This indicate that PPhMA forms no excimer. The fluorescence properties observed for PPhMA seems to be more likely to be affected by the substituent groups (-O-CO-). On the other hand, PPyMVE, PNMVE, and PNMA show the excimer fluorescence in dilute solutions at room temperature. Therefore, the failure of PPhEVE and PPhMA to form an excimer is considered to be attributable to the nature of Ph, which forms an excimer only with difficulty.

Emission properties of PVPh indicate clearly that interaction between neighboring Ph chromophores in PVPh is strongest in these polymers studied. It has been reported, from fluorescence yield and decay curve measurements, that phenanthrene does not show concentration quenching of fluorescence at room temperature.23,24) Therefore, if PVPh forms no excimer, the fluorescence yield of PVPh is expected to be as large as that observed for EPh. The present result is not so. Namely, the fluorescence yield of PVPh is much lower than that of EPh (Table 2) and decreases largely with an increase in temperature (Fig. 4). These facts suggest that PVPh forms an excimer which has a low fluorescence quantum yield. This is reasonable from the fact that the phenanthrene excimer in the crystal state under a high pressure has a low fluorescence quantum yield.10)

As mentioned above, ECz, EAcr, and EPh show no excimer fluorescence in concentrated solutions at room temperature. PVCz and PVAcr, however, show the excimer fluorescence in dilute solutions at room temperature. It is suggested from the above mentioned results that PVPh forms an excimer, although it does not show clearly an excimer fluorescence. Thus, the following conclusions were drawn: in the case of the vinyl polymers with the aromatic chromophores which form no excimer, an excimer is formed in the vinyl polymers in which the aromatic chromophores are directly connected to the skeletal chains, but it is not formed in the vinyl polymers in which the aromatic chromophores are widely spaced on the skeletal chains. PCzEVE is considered to be rather a special case.

References

1) M. Yokoyama, T. Tamamura, T. Nakano, and H. Mikawa, *Chem. Lett.*, **1972**, 499.

2) J. R. McDonald, W. E. Echols, T. R. Price, and R. B. Fox, *J. Chem. Phys.*, **57**, 1746 (1972).

3) M. T. Vala, J. Haebig, and S. R. Rice, *J. Chem. Phys.*, **43**, 886 (1965).

4) R. B. Fox, T. R. Price, R. F. Cozzens, and J. R. McDonald, *J. Chem. Phys.*, **57**, 534 (1972).

5) Y. Nishijima, M. Yamamoto, S. Katayama, K. Hirata, Y. Sasaki, and M. Tsujisaki, *Rep. Prog. Polym. Phys. Jpn.*, **15**, 445 (1972).

6) T. Yano, M. Yokoyama, and H. Mikawa, 22nd Annual Meeting on Macromolecules, Kyoto, 29C09, May 1973.

7) A. C. Sommersall and J. B. Guillet, *Macromolecules*, **6**, 218 (1973).

8) M. Yokoyama, T. Tamamura, M. Atsumi, M. Yoshimura, Y. Shirota, and H. Mikawa, *Macromolecules*, **8**, 101 (1975).

9) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **49**, 2082 (1976).

10) P. F. Jones and M. Nicol, *J. Chem. Phys.*, **48**, 5440 (1968).

11) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York (1970), p. 341.

12) E. A. Chandross and H. T. Thomas, *J. Am. Chem. Soc.*, **94**, 2421 (1972).

13) C. K. Bradsher and S. T. Amore, *J. Am. Chem. Soc.*, **63**, 493 (1941).

14) C. C. Price and B. D. Halpern, *J. Am. Chem. Soc.*, **73**, 818 (1951).

15) E. Bergmann and O. Blum-Bergmann, *J. Am. Chem.*

Soc., **58**, 1678 (1936).

16) K. Okamoto, A. Itaya, and S. Kusabayashi, *Polym. J.*, **7**, 662 (1975).

17) E. Ohta and A. Takemasa, *Yūki Gōsei Kagaku*, **29**, 183 (1971).

18) S. Patai, M. Bentor, and M. E. Reichmann, *J. Am. Chem. Soc.*, **74**, 845 (1952).

19) S. Yoshimoto, K. Okamoto, H. Hirata, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **46**, 358 (1973).

20) W. Klöpffer, *Chem. Phys. Lett.*, **4**, 193 (1969).

21) W. Klöpffer and W. Liptay, *Z. Naturforsh.*, **25a**, 1091 (1970).

22) G. E. Johnson, *J. Chem. Phys.*, **61**, 3002 (1974).

23) B. Stevens and J. T. Dubois, *Trans. Faraday Soc.*, **62**, 1525 (1966).

24) J. B. Birks and S. Georghiov, *J. Phys. B*, **1**, 958 (1968).