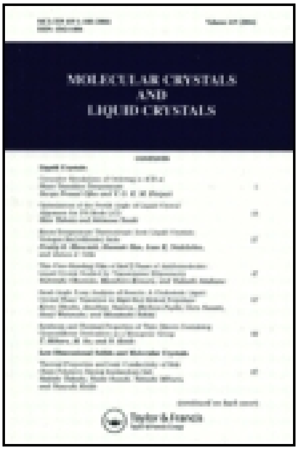

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Purification and Single Crystal Growth of N-ethylcarbazole

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Version of record first published: 21 Mar 2007.

To cite this article: Keishi Kato, Masaaki Yokoyama, Kenichi Okamoto, Shigekazu Kusabayashi, Hiroshi Mikawa, Keitaro Yoshihara & Saburo Nagakura (1974): Purification and Single Crystal Growth of N-ethylcarbazole, Molecular Crystals and Liquid Crystals, 28:1-2, 37-49

To link to this article: http://dx.doi.org/10.1080/15421407408083151

Mol. Cryst. Liq. Cryst., Vol. 28, pp. 37-49
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Printed in Dordrecht, Holland

Purification and Single Crystal Growth of N-ethylcarbazole

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(*Received February 2, 1974*)

N-ethylcarbazole of high purity, free from anthracene and sufficient for optical and electrical measurements, was obtained by the purification of synthesized N-ethylcarbazole. Purity was confirmed by the fluorescence lifetime in crystalline state being independent of the fluorescence wavelength. Single crystal growth of N-ethylcarbazole was successfully carried out according to the Bridgman method with very slow lowering speed of growth-vessel. N-ethylcarbazole of commercially available grade contains anthracene as a main impurity at more than 10^{-3} mole/mole, which is impossible to remove by the usual methods of purification including zone melting. No excimer fluorescence was observed in N-ethylcarbazole either in concentrated solution or in the molten or crystalline state, contrary to poly-N-vinylcarbazole.

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INTRODUCTION

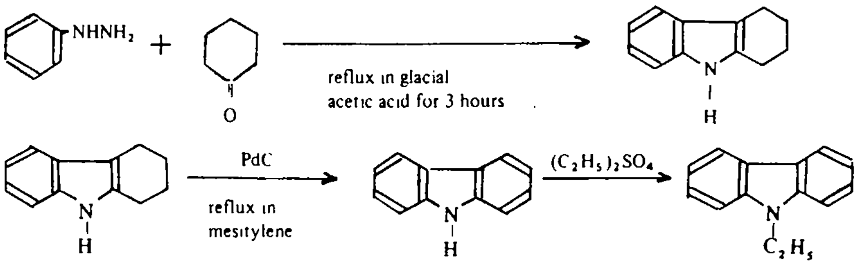
Purification and single crystal growth of condensed aromatic hydrocarbons such as anthracene have been investigated[1] rather well to study their optical and electrical properties. There are very few reports on the extreme purification and single crystal growth of heterocyclic aromatic compounds, although single crystal growth of phenazine and 9,10-dichloroanthracene was recently carried out.[2] The present paper deals with the method of purification and single crystal growth of N-ethylcarbazole (EtCz), which is a model compound of a well-known photoconductive polymer, i.e., poly-N-vinylcarbazole (PVCz). At the earlier stage of this study, it was found that commercially available EtCz contains anthracene (An) as a major impurity, more than 10^{-3} mole/mole, and that a small amount of An gives rise to a considerable influence on the fluorescence spectrum due to the energy transfer from EtCz to An molecules in the crystalline state as well as in concentrated solution. This impurity was impossible to remove completely by the usual methods of purification including zone melting. Therefore, in order to prepare EtCz free from An, synthesis of this compound was required, say starting from phenylhydrazine and cyclohexanone. The synthesized EtCz was purified by the ordinary methods of purification and finally by zone melting method. The material thus obtained showed correct fluorescence spectrum even in crystalline solid. The purity was estimated from the measurements of the fluorescence lifetime and its spectral dependence. Absence of the spectral dependence of the fluorescence lifetime is currently recognized as one of the most sensitive test for the presence of a trace of impurity.[3,4] Purified EtCz showed no excimer fluorescence even in concentrated solution and in molten or crystalline state, although PVCz is reported to exhibit excimer fluorescence in solution as well as in solid film.[5]

Single crystal growth of EtCz thus obtained, was tried according to the conventional Bridgman method and was found to be successful with a very slow lowering speed of growth-vessel.

EXPERIMENTAL

Materials and Purification

Commercial EtCz was obtained from Maruwaka Chemical Industry. Synthesis of EtCz was performed according to the literatures.[6,7,8]



Overall yield of EtCz, melting at 70°C, was 32.5% of the theoretical value. On each step of the syntheses, materials and solvents were used after sufficient purification.

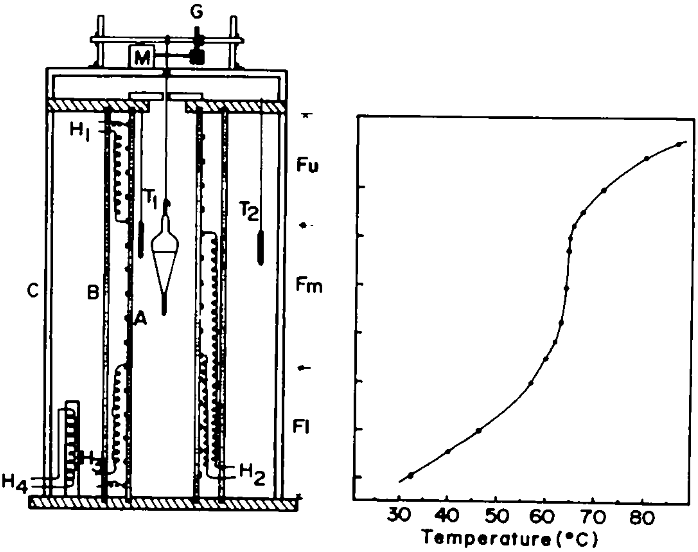
Conventional purification procedures used in the present investigation are as follows: (1) recrystallization, from methanol more than five times, (2) Diels-Alder chemical reaction with maleic anhydride by which only An reacts to give the adduct, (3) chromatographic separation, on alumina or silica column with *n*-hexane, (4) sublimation, under 1 mmHg, (5) vacuum distillation under 10^{-3}mmHg, and (6) zone melting, more than 50 passes of melt-zone with a Shimadzu Cryogenic Zone Refiner CZ-1.

Absorption and Emission Measurements

Absorption spectra in solution were measured with a Hitachi 124 Spectrophotometer. Fluorescence spectra of solutions and of the solid were recorded with a Hitachi MPF-3 Spectrofluorometer equipped with a 150W Xe excitation lamp and a HTV R446 photomultiplier tube. For the measurements in crystalline state at room temperature, a quartz plate was used on which about 10μ thick samples were adhered, and the fluorescence spectra were measured with right-angle reflection method to eliminate reabsorption effects. Both for the measurements of fluorescence spectra at liquid nitrogen temperature and for the fluorescence measurements, pyrex-tubes were used in which samples were sealed under high vacuum. Fluorescence decay curves were obtained by employing the pulsed method using a nitrogen gas laser (halfwidth3~5nsec,10kW, 337 nm) and an RCA 1P28 photomultiplier.

Single Crystal Growth

A Bridgman type crystal growing furnace is shown in Figure 1. A vertical furnace is made with a pyrex glass tube (2.7cm in diameter), and three Nichrome heating coils are wound on the tube separately in three sections (Figure 1(a), H_1, H_2, H_3). The appropriate temperature gradient in the furnace is obtained by indi-



(a) (b)

FIGURE 1 (a) Crystal-growing furnace; A, B, Pyrex glass tube; C, acril plate; H_1, H_2, H_3, H_4, heating coils; T_1, T_2, thermistor; M, a synchronous motor (1 round/day); G, a gear wheel.

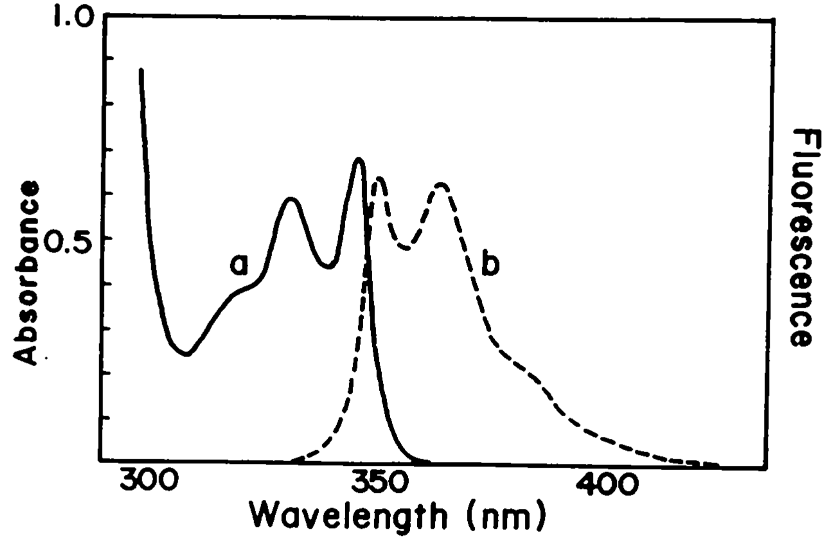


FIGURE 2 The absorption (a) and fluorescence (b) spectra of EtCz in 3.59×10^{-4} mole/l. benzene solution.

vidual control of the supply currents to these three heating coils, an isothermal point in the middle part of the furnace being regulated by a thermistor. In order to prevent the outflow of heat and the disturbance of the temperature gradient, the furnace is surrounded by another concentric pyrex glass tube (Figure 1(a), B) wound with asbestos, and the temperature in the whole box made of plastic plates was maintained constant at about 30°C.

The samples were distilled into a crystal-growing vessel of pyrex glass under 10^{-4} torr, and sealed off. This vessel was suspended first in the upper part of the furnace, where the temperature was above the melting point, and then lowered slowly down through the temperature gradient by means of a synchronous motor set at the top of the furnace. When the tip of the crystal-growing vessel passed the isothermal point, 70°C, crystallization began.

RESULTS AND DISCUSSION

As already stated briefly, commercial EtCz contains An as a main impuity. In the case of low concentration solution (10^{-3}mole/l) of commercial EtCz purified by the usual methods of purification, the fluorescence spectrum gave a good mirror-image relationship with its absorption spectrum and apparently did not show any fluorescence due to An as shown in Figure 2. In concentrated solution as well as in the crystalline state, however, the fluorescence spectra showed the presence of An, which was impossible to remove by further purification. Therefore, in order to prepare highly pure EtCz, synthetic material had to be used as the starting material of purification.

Highly pure EtCz

Synthesized EtCz was recrystallized twice from methanol, and then purified by zone melting or sublimation. Figure 3 shows the fluorescence spectra at 77°K of zone-refined samples. The EtCz from the upper part of the zoning-tube showed a correct fluorescence spectrum of EtCz even in crystalline state, while that from the bottom part exhibited a different fluorescence spectrum with a maximum at about 390 nm, probably due to the concentrated impurity. Thus, the synthesized EtCz also contained some fluorescent impurity, which segregated at the bottom of the zoning-tube. The sample purified by sublimation gave a similar correct spectrum to that of the sample in the upper part of the zoning-tube. This suggests that the fluorescent impurity in the synthesized EtCz can be also removed by sublimation. The excitation spectrum of the 390 nm emission showed a peak at about 372 nm, in addition to the peaks corresponding to the absorption of EtCz. The impurity absorbing at 372 nm and fluorescing at about 390 nm, seems to be a by-product, probably 3,4-benzocarbazole or its deriva-

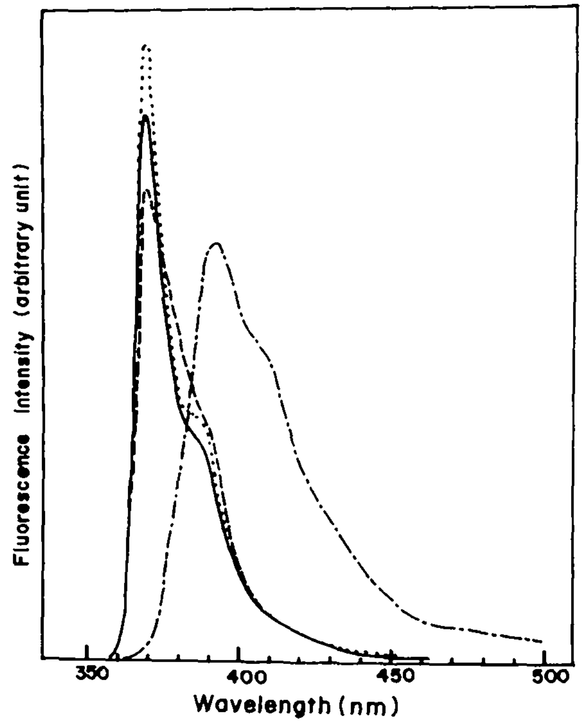


FIGURE 3 The fluorescence spectra of the zone-refined synthesized EtCz in crystalline state at 77° K: (– – –); upper part, (———); middle part, (———); lower part of the tube. The dashed curve (———) indicates the fluorescence spectrum of synthetic EtCz purified by sublimation.

tives, which was reported to have such absorption and fluorescence spectra.[9], [10]

The purity was monitored further by the fluorescence lifetime and its spectral dependence. Table 1 shows the fluorescence lifetimes of several samples purified by various methods. The zone-refined sample has the longest lifetime, about 20 nsec, and the sample in the bottom of the zoning-tube shows much shorter decay because of the energy transfer from EtCz to the impurity. Since the fluorescence lifetime should be constant through the whole fluorescent region when the emission is due to only one chromophore, the measurement of the spectral dependence of the fluorescence lifetime can give one of the most reliable criterion for purity. The results for EtCz purified by sublimation and zone melting are shown in Table 2. Highly purified synthesized EtCz in the upper part of the zoning-tube showed no dependence on the fluorescence wavelength within the limit of experimental error. In the case of the sample purified by sublimation, however, some derivations could be seen with respect to the

TABLE 1

Fluorescence lifetimes (nsec) of several samples of N-ethylcarbazole purified by various methods at room temperature.

Sample[a]	Purification[b]	375 nm	385 nm	405 nm	430 nm
Com.	column chromatography	6	–	8	–
Com.	zone melting (1)	9	–	8	–
Com.	zone melting (2)	9	–	18	20
Com.	zone melting (3)	6	–	15	26
Syn.	recrystallization	7	13	11	12
Syn.	sublimation	19	21	21	18
Syn.	zone melting (1)	20	23	20	18
Syn.	zone melting (2)	19	21	17	–
Syn.	zone melting (3)	8	–	8	9

[a] The samples designated by *Com.* and *Syn.* are the commercial and synthesized N-ethylcarbazole (EtCz).

[b] Zone melting (1), (2) and (3) indicate the samples of the upper, middle and bottom part of the zoning-tube.

wavelength and the fluorescence decay was somewhat shorter than that of the zone-refined sample. Thus, synthesized EtCz contained a certain amount of impurity but this impurity could be easily removed by zone melting. The fluorescence lifetime of the sample thus obtained was found to be independent on the wavelength and to be about 20 nsec in crystalline state.

Single Crystal Growth of EtCz

Single crystal growth from the melt is most suitable to prepare a single crystal for the optical and electrical measurements, since no solvent is occluded and large crystals can be obtained.[1] Crystal growth by the Bridgman method requires initiation of a single crystal nucleus in the capillary of the growing-vessel and its propagation over a large volume of the material.

Three types of vessels used are shown in Figure 4. Two of these vessels (a) and (b) have an ordinary narrow capillary about 1.5 cm long and 1 to 2 mm in diameter. The other has a constricted bulb, which was reported to give the highest probability of initiating single crystal growth.[11] However, in our case none of these vessels could achive a initiation of single crystal growth in so far as the whole material was once melted and lowering was started, because of the tendency of supercooling of the material. Therefore, we had to use a method similar to the seeding method as follows. The growing-vessel containing EtCz was first suspended in the lower part of the furnace, where the temperature was below the melting point, and then raised gradually to the upper part of the

TABLE 2

Wavelength dependence of the fluorescence lifetime (nsec).

Sample	370nm	380	390	400	410	420	430	440	450
Com-Z	10	12	14	17	17	17	17	17	17
Syn-S	13	15	16	15	16	15	14	13	13
Syn-V	15	18	18	18	17	18	20	18	18
Syn-Z	19	22	22	19	19	19	18	17	15

Com-Z, commercial EtCz purified by zone melting; *Syn-S*, *Syn-V*, and *Syn-Z* are synthetic EtCz purified by sublimation, vacuum distillation and zone melting, respectively.

furnace, EtCz was melted from the top of the vessel, leaving a small amount of multi-crystals at the tip of the capillary. After being so arranged, the vessel was gradually lowered. Thus, supercooling was avoided and the initiation of single crystal growth could be accomplished.

When the vessel shown in Figure 4(b) was used, multi-crystals were formed at the upper end of the capillary. The vessel shown in Figure 4(a) was successful. Thus, the wall of the vessel should not have a sharp corner, which often acts as a point of spurious nucleation. Figure 1(b) shows the temperature gradient in the furnace for the successful single crystal growth. Lowering speed of the growing-vessel greater than 0.4 mm/h always resulted in a bundle of needle-like single crystals growing parallel to the direction of lowering, whereas the speed slower than 0.2 mm/h resulted in successful growth. This suggests that the rate of crystal growth in the vertical direction is much larger than that in diametric direction. Large single crystals were grown in 15 to 20 days with this lowering speed. After complete solidification, the single crystal should be brought slowly to room temperature to anneal out thermal strains; otherwise, many cracks

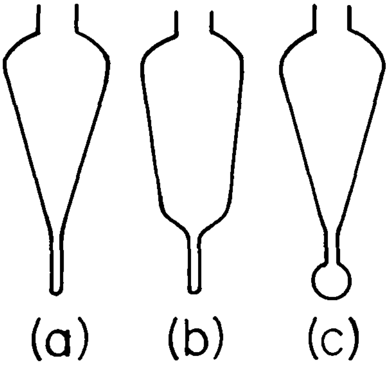


FIGURE 4 Crystal-growing vessels.

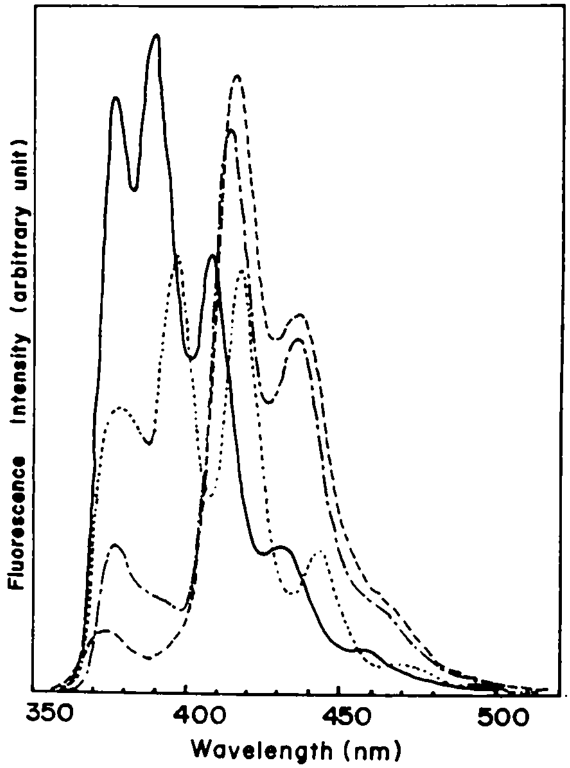


FIGURE 5 The fluorescence spectra of commercial EtCz solids purified by various methods at room temperature: (———), chromatography; (———), zone melting; (———), chemical reaction; (– – – –), sublimation.

would be produced in the crystal. Therefore, the temperature in the furnace was lowered to room temperature with about 2°C/h.

The quality of the crystal depends on the purity of the material. Crystals grown from commercial samples have a tendency of producing many cracks and striations during annealing, whereas the crystal grown from the synthesized EtCz were free from visible cracks and striations.

The analysis of crystal structure is now in progress, and the preliminary crystallographic data are given here. All observed reflections in the X-ray pattern could be indexed with orthorhombic unit cell; $a = 7.99$ Å, $b = 24.611$ Å, $c = 56.57$ Å. The space group is *Pbca*, determined from systematic absence of reflections. The observed density of 1.165g/cm^3 was consistent with the calculated value of 1.165g/cm^3 by assuming that 40 formula units are contained in a

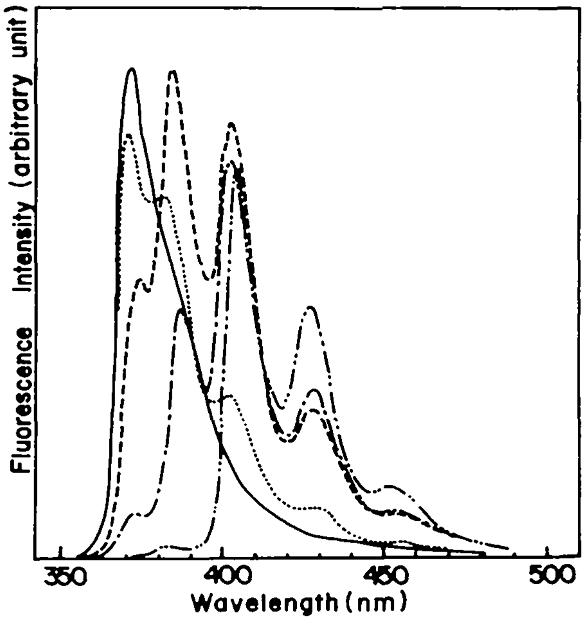


FIGURE 6 The fluorescence spectra of An (guest)-EtCz (host) mixed crystals at room temperature: The concentration (mole/mole) of An in mixed crystals is: 2×10^{-2} (— - —), 10^{-3} (—-—), 1.4×10^{-4} (- - - -) and 3.1×10^{-5} (———). The fluorescence spectrum of pure EtCz (———) is also shown.

unit cell. Single crystals of EtCz show no apparent cleavage plane, and the crystal grows in the growing-vessel to *a*-direction.

Purification of Commercial EtCz

In this section is described briefly the difficulty of removing a trace of An from commercial EtCz. Figure 5 shows the fluorescence spectra of solid commercial samples purified by various purifications. The spectra of these samples consisted of the fluorescence of EtCz with a maximum at 376 nm and the fluorescence of An in the longer wavelength region than 390 nm. The latter emission is due to the efficient energy transfer from excited EtCz to An. In order to estimate the concentration of An, the fluorescence spectra of An-EtCz mixed crystals were measured by changing the concentration of An in zone-refined synthesized EtCz. The results are shown in Figure 6. The relative fluorescence intensity ratio of guest (An) to host (EtCz) is plotted against the concentration of An in EtCz from 10^{-6} mole/mole to 10^{-3} mole/mole in Figure 7. The relative fluorescence

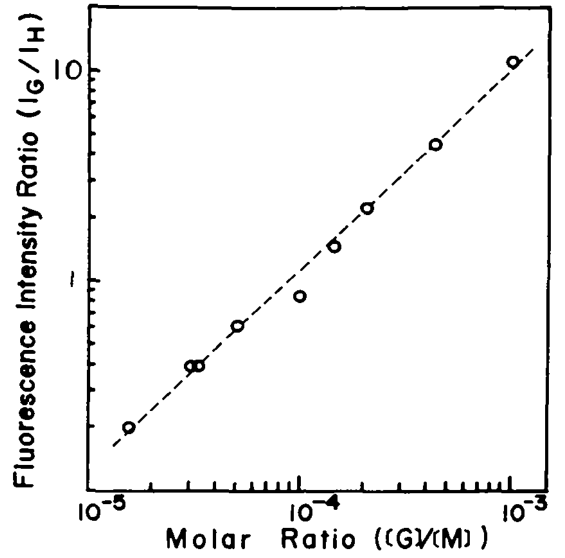


FIGURE 7 Intensity ratio of guest (An) to host (EtCz) fluorescence as a function of guest concentration (mole/mole).

TABLE 3

Estimated concentration of An in commercial EtCz purified by various methods.

Purification	I(An)/(EtCz)*	*concentration of An*
Sublimation	7.1	7.0×10^{-4} mole/mole
Chemical reaction	2.8	1.5×10^{-4}
Chromatography	0.7	6.0×10^{-5}
Zone melting	1.1	10^{-4}

* I(An)/I(EtCz) indicates the observed fluorescence intensity ratio of guest (An) to host (EtCz).

intensity ratio depends linearly on the concentration of An. Thus, the amounts of An in commercial samples purified by various methods were estimated, and are given in Table 3. The most effective method to remove An in commercial EtCz was column chromatographic separation, by which An in EtCz could be reduced to about 10^{-4} mole/mole. Even by zone melting we could not obtain EtCz completely free from An. These results were confirmed by the measurements of the fluorescence lifetime. As shown in Tables 1 and 2, the lifetimes of purified commercial EtCz were found to be much shorter than that of highly pure synthesized EtCz.

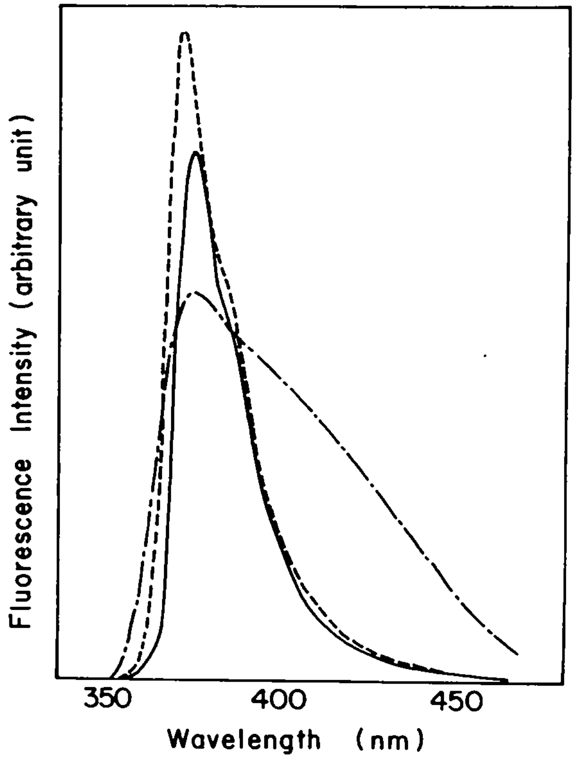


FIGURE 8 The fluorescence spectra of pure EtCz in concentrated solution, 3 mole/THF, liter, (– – –) and of crystalline state (———). The fluorescence spectrum of PVCz (– · – · –) in solution, 1.6 × 10^{-2} mole/THF, liter, is also shown for comparison.

Fluorescence Spectra of Pure EtCz

As in the case of aromatic vinylpolymers having the large pendant π-electron system such as polyvinylnaphthalene [12] and polyvinylpyrene [13, 14], PVCz exhibits excimer fluorescence in solution as well as in solid film.[5] Figure 8 shows the fluorescence spectra of pure EtCz in concentrated solution and in crystalline state together with PVCz. In the molten state of EtCz, the similar fluorescence pattern was observed to that of concentrated solution of EtCz. No excimer fluorescence was observed even in concentrated solution and in molten or crystalline state of EtCz, contrary to the case of PVCz. This was also confirmed by the experimental results that the fluorescence decays fitted to a single exponential curve with the lifetime of about 20 nsec over the whole spectral region.

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