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Defects and Fluorescence of 9-Cyanoanthracene

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Abstract—The fluorescence of 9-cyanoanthracene (9-CNA) crystals analysed in polarized light was found to change under irradiation with the light of mercury lamp. Intensity changes of fluorescence maxima for crystals and powders (microcrystals) are reported.

Crystals of 9-CNA examined on the stage of a microscope were found to re-emit light from defects at beginning of irradiation whereas additional emitting centres were created as the irradiation proceeded. The green fluorescence (beginning of irradiation) is now correlated with defects and the blue one (after $\simeq$ 60 min. of irradiation) is thought to be due to monomer in dimer matrix formed under irradiation with a mercury light.

1. Introduction

In a previous paper[1] we reported the fluorescence spectrum of the crystal of 9-cyanoanthracene (9-CNA) and noted the progressive change in intensity of the spectrum with increasing irradiation time. A change with time had also observed for anthracene[2] when irradiated with a mercury light.

In both cases the effect may be correlated with a solid-state photodimerization reaction. Anthracene and anthracene derivatives have been reported to dimerize both in solution[3] and in the solid state.[4] The importance of defects as sites of reaction has been pointed out.[4] Zones of disorder have been suggested to be responsible for the reaction involved. The energy required may be concentrated at such sites by an exciton mechanism and used for the dimerization reaction.

Recent studies on anthracene[5] and 9-CNA[6] have supported the role of the defects in organic crystals as reaction sites. The alternative

explanation proposed,[7] based on the formation of trans-dimers in the gas phase and recondensation on the solid, remains unconfirmed. In fact the trans-dimers (9-CNA dimer) and (9-CHO dimer) reported in Ref. (4) were obtained from crystals grown from melts between silica discs, where the gas-phase mechanism seems implausible.

We have now analysed, under the microscope, crystals of 9-CNA excited under the conditions used to obtain fluorescence, and have followed the course of gross structural change. The growth of defects, in number and in size, was followed and photographed. In addition the fluorescence of a number of masked 9-CNA crystals was also analysed by taking exposures at different time of excitation. The growth of defects can be correlated with intensity changes of the green band. Fluorescence emission was also recorded from microcrystals; in this case the results were found very sensitive to the method used for growing samples. Good results were obtained by using microcrystals prepared by depolymerization of the dimer[8] with the differential scanning calorimeter system (DSC). Lipsett *et al.*[9] reported a study on anthracene defects correlated with the fluorescence process.

2. Microscopic examination of 9-CNA

Crystals of 9-CNA were examined on the stage of a microscope under front-face irradiation using the light of medium pressure (Mazda 250 W) mercury lamp. Photographs taken at different irradiation time show, at beginning of irradiation, fluorescence light reemitted only from defects. After a few minutes of exposure more defects appear in the irradiated area; they grow as the irradiation proceeds. After 50 minutes the irradiated area is completely disrupted and the extinction directions are different from the original ones. Cracks parallel to the elongation direction of crystals also appeared.

3. Fluorescence of 9-cyanoanthracene

The fluorescence was recorded on plates at different irradiation time by front illumination of samples (crystals or powders) with a set-up similar to that described in Ref. (1). During the experiments

we found it convenient to use samples prepared by the following methods:

(a) crystals obtained by sublimation in a metal crucible near 170 °C.

(b) powder (microcrystals) prepared from decomposition of the 9-CNA dimer with a differential calorimeter stopping the heating before the melting point of monomer.[8]

(c) Powder prepared by vacuum sublimation and by sublimation at 170° were also used. Polarized fluorescence from masked crystals was recorded by using a Wollaston prism and by separating the two beams respectively in the upper and lower part of the plate by moving in the proper position the plate holder; each beam was recorded separately and not at the same time as the other. We used this procedure because we found it difficult to correlate the intensities of two or more plates even by using step filters for calibration. By this procedure up to 60 spectra divided in two polarizations were recorded on the same plate. The fluorescence was taken by irradiation of a central part (away from edges) of a well formed crystal[1]; referred to as " masked crystal ".

In Fig. 1 spectra taken at different irradiation time of a 9-CNA crystal is reported. At beginning of exposure (upper part) green

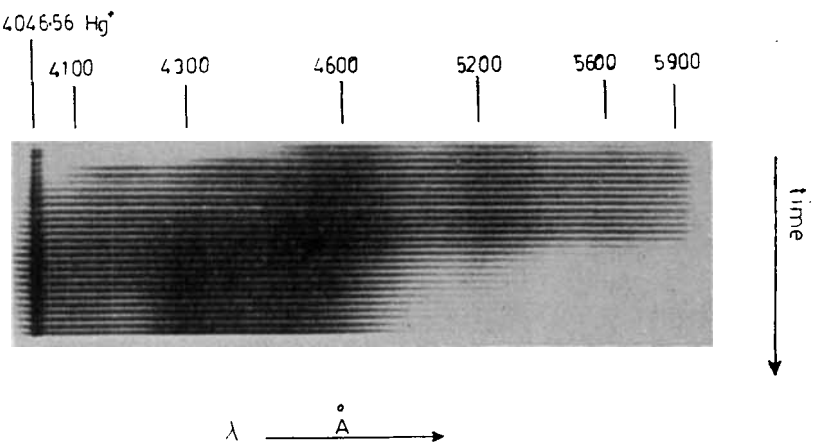
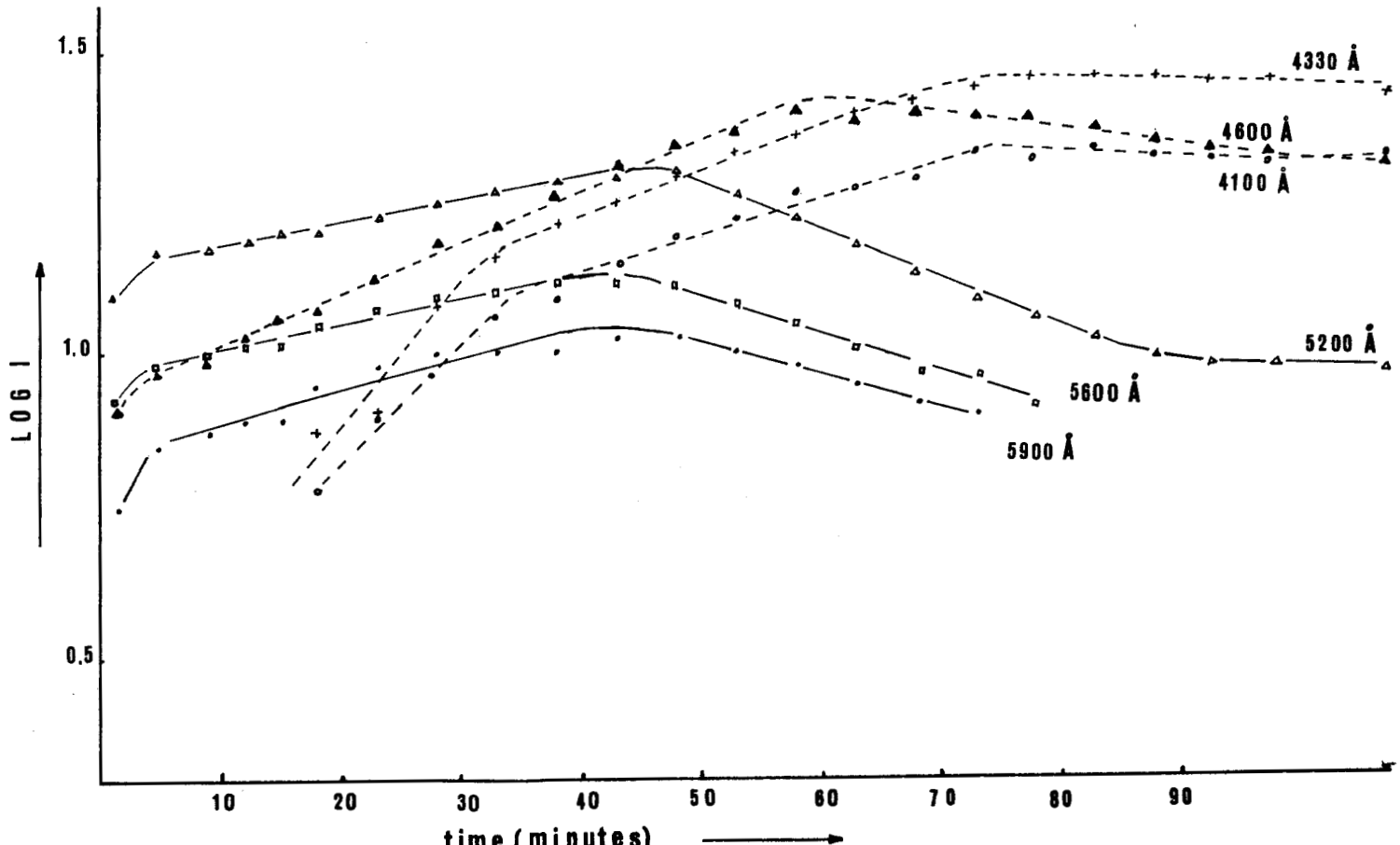


Figure 1. Plate with fluorescence spectra taken at different irradiation time.



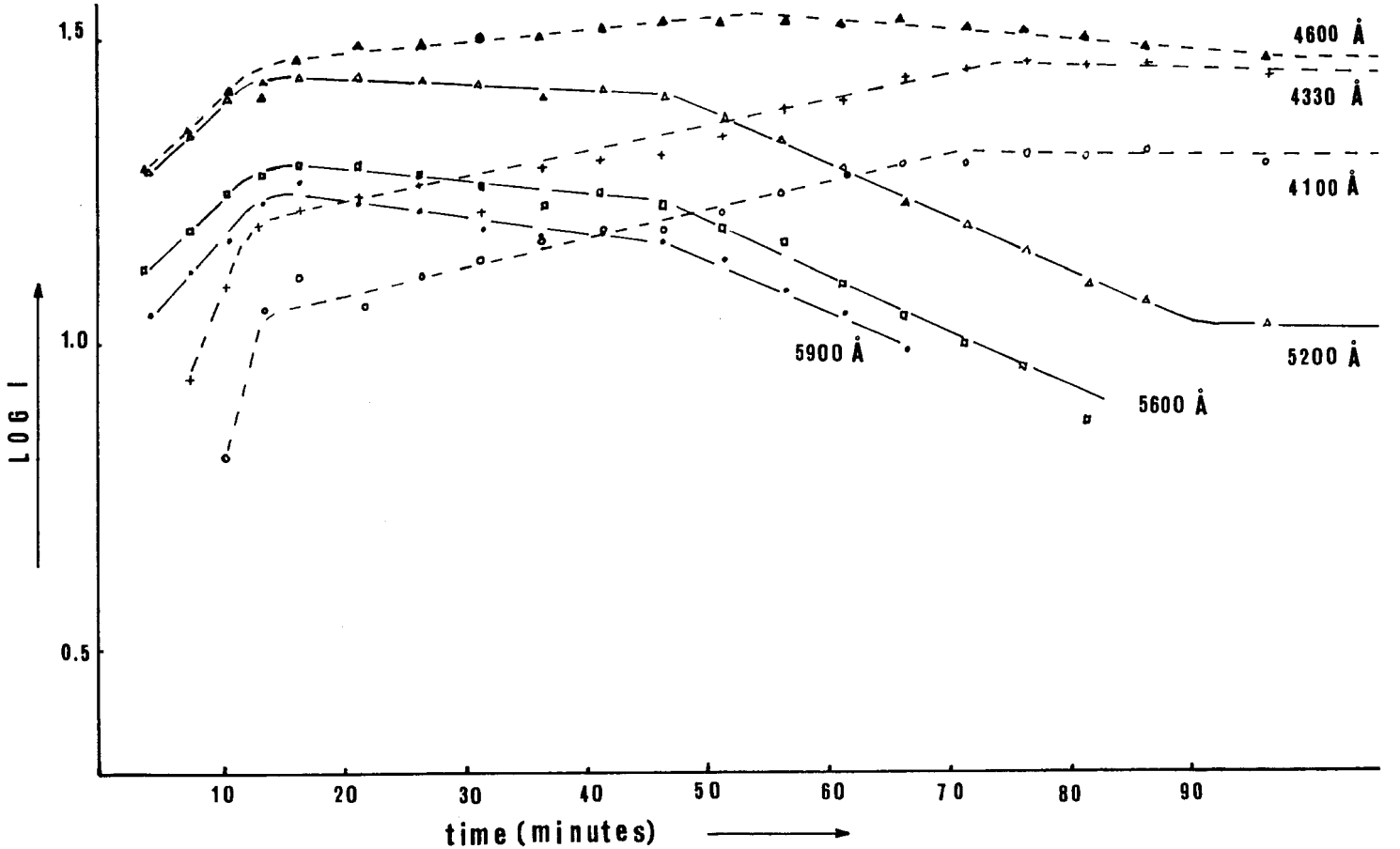


Figure 2. Intensities of singular points (maxima and shoulders) of fluorescence of 9-CNA crystal against time of irradiation. Top: polarization parallel to c axis. Bottom: polarization parallel to a axis.

light of low intensity is reemitted from the crystal. By increasing the irradiation time (central and lower part of the plate) the spectrum changes either in intensity or in wavelength, and eventually the green emission is replaced by the blue one. The intensities of each singular point (shoulders or maxima) are reported in Fig. 2 as a function of time exposure. The general pattern of the fluorescence of crystals may be divided into two sets of bands: the green one centred at 5200 Å and the blue one centred at 4300 Å. The behaviour of these two emissions is different; all the maxima correlate to the green band are weak at the beginning of the exposure, then they increase to a maximum value within 20–25 minutes under our conditions and then decrease as the irradiation time increases. The maxima due to the blue band appeared after $\simeq$ 10 minutes and increased in intensity with time up $\simeq$ 60 minutes.

The fluorescence was recorded over 150 minutes of irradiation. The plot of the fluorescence maxima of 9-CNA powders (DSC-method) against time of irradiation is reported in Fig. 3. Also in this case the maxima of the green band has a different pattern from that of the blue one.

In addition the green emission band is at maximum of intensity at the beginning of the irradiation and then decreases to zero value within $\simeq$ 100 min. The blue band however maintain the same pattern found for the crystal; the only difference being the beginning of the emission below 5 min. of irradiation.

In Fig. 4 a fluorescence spectrum of 9-CNA crystal with an intermediate situation is reported. All the maxima correlate both to the green emission and to the blue one are shown. Table 1 refers to wave number in cm^{-1} (converted *in vacuo*) for the maxima of fluorescence of crystal.

4. Discussion

By following the fluorescence emission of 9-CNA it is possible to have information on the solid state reaction of dimerization involved under irradiation with a mercury light. From the results obtained it is possible to conclude that green fluorescence is emitted at near defects from the excited sample. Pictures taken at increasing irradiation times show an increasing number of emitting centres. In

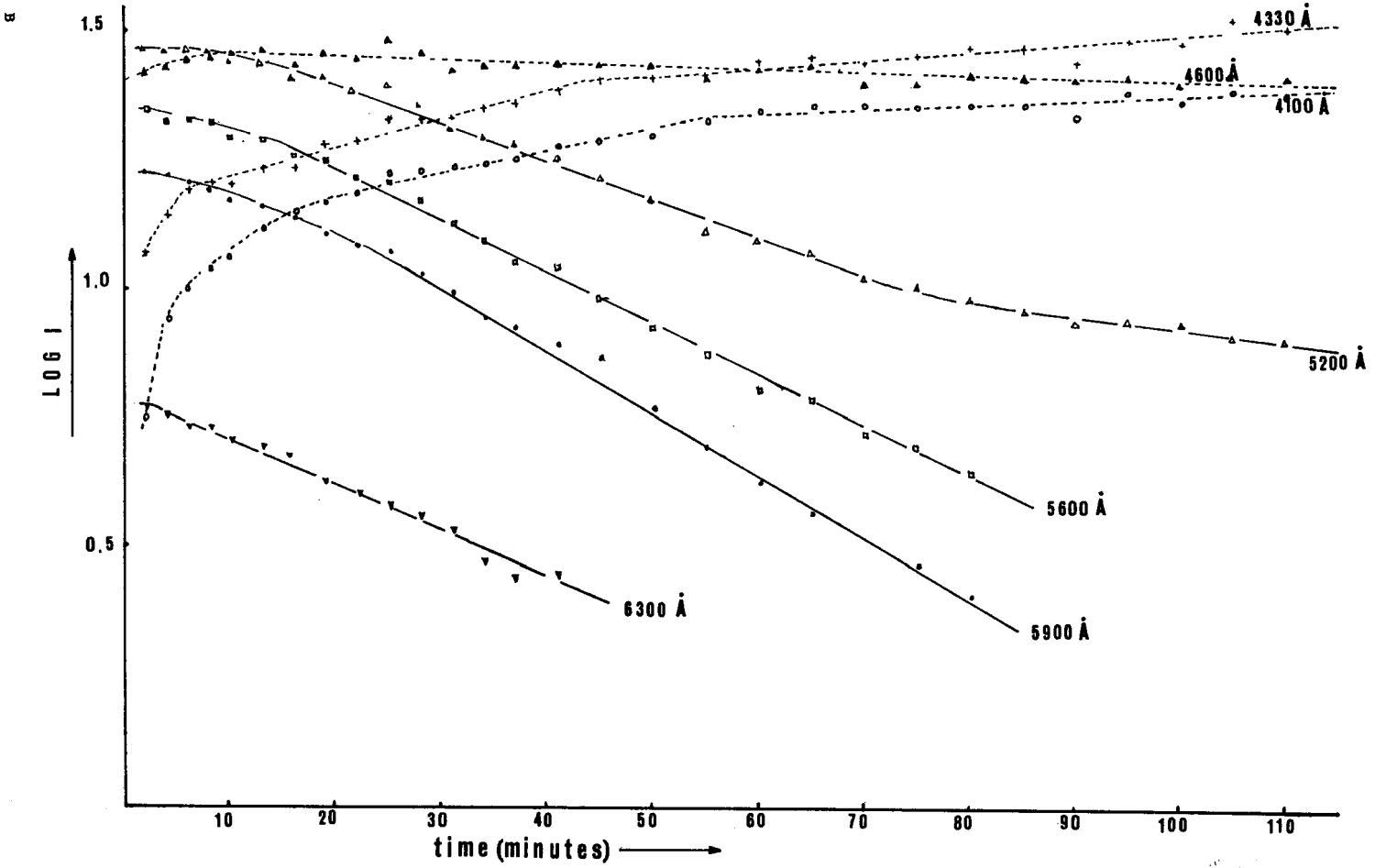


Figure 3. Intensities of singular points (maxima and shoulders) of fluorescence of 9-CNA powders against time of irradiation.

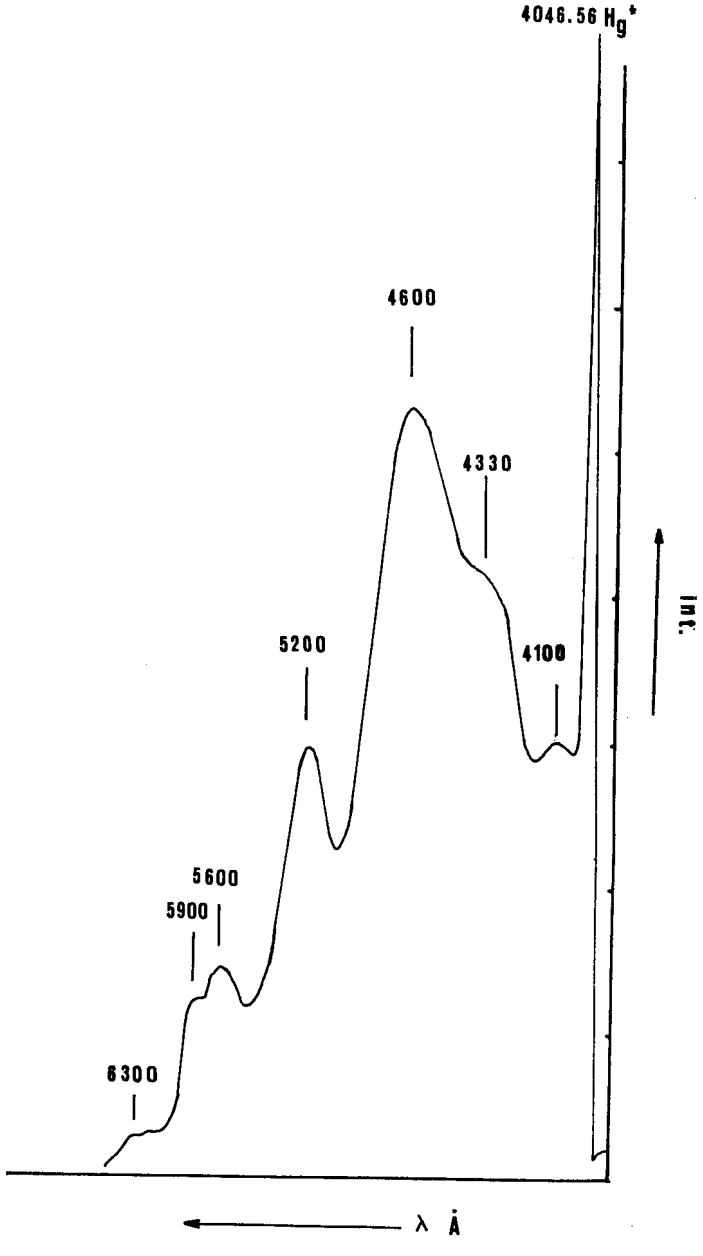


Figure 4. Fluorescence spectrum of 9-CNA crystal. Intermediate irradiation time. All bands are shown.

TABLE 1 Fluorescence Maxima (cm^{-1}) for Crystalline 9-CNA

	pol. c	pol. a
Green band	20850 ± 50	20850 ± 50
	19240 ± 50	19240 ± 50
	17700 ± 50	17700 ± 50
	17020 ± 50	17020 ± 50
Blue band	24340 ± 20	24340 ± 20
	23100 ± 20	23200 ± 20
	22000 ± 20	22000 ± 20

The values reported refer to fluorescence taken at beginning of irradiation (green band) and at the end of irradiation (blue band).

addition, at the beginning of the irradiation, emission is seen only from edges or from zones containing a high number of preformed imperfections. As a result of increasing of the emitting centres the green fluorescence of crystals also increases to a maximum and then decreases because the dimerization process may become dominant.

In the case of powders (DSC method) the number of emitting centres is very high even at the beginning and this is shown by the green fluorescence which is intense even at the beginning of irradiation.

An intermediate situation is obtained by using microcrystals (prepared with method c). The green emission increases in intensity under exposure to the light, but reaches a maximum at shorter times than in the crystal. This suggests that a higher number of imperfections is present initially but can still increase somewhat under irradiation.

It is not necessary to invoke exciton fluorescence in 9-CNA to explain any of these results. The major part of the green fluorescence is thus attributed to defect emission from the sample.

By comparison of the maxima of the blue emission band with the maxima of crystal absorption[10] no mirror image symmetry is found; however there is a good correlation between the blue emission and the solution absorption spectrum (Fig. 5). This fact reinforces the hypothesis[11] that the blue emission is due to monomer of 9-CNA in dimer matrix.

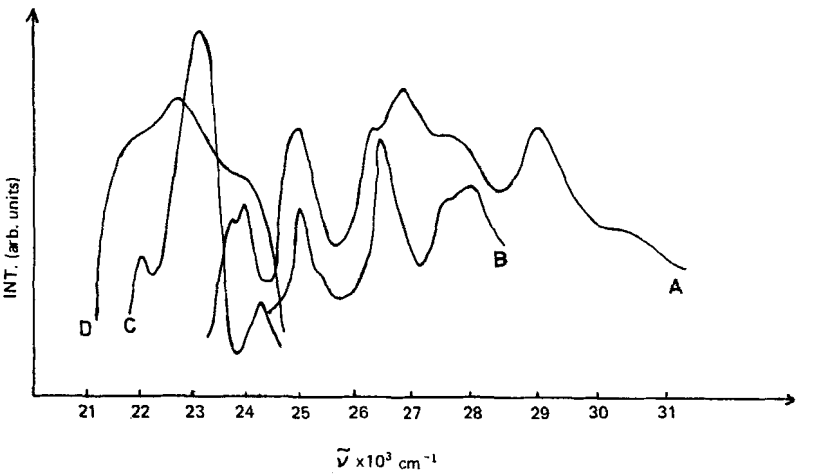


Figure 5. A: UV absorption spectrum of 9-CNA (4°K) parallel to the *a* axis. B: UV solution spectrum (methylcyclohexane). C: Blue fluorescence of 9-CNA crystal. D: Fluorescence of 9-CNA in solution (methanol).

5. Experimental

Crystals were prepared as described in Ref. (1). Plates (Ilford R 30) were recorded on a Hilger-Watts E 742 spectrometer.

The light of a Mazda (250 W) lamp was filtered with a Chance Pilkington OX1 filter and focused with a silica lens on the sample. Fluorescence light passed through a Wollaston prism was collected on the slit of the spectrometer. For each plate the proper γ value was calculated by means of a step filter (Hilger-Watts). A Hilger-Watts microphotometer was used to measure the plates. The exposure time was 1 min. for crystals and 30 sec. for powders. A Leitz (Laborlux) microscope equipped with an orthomat camera was also used.

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