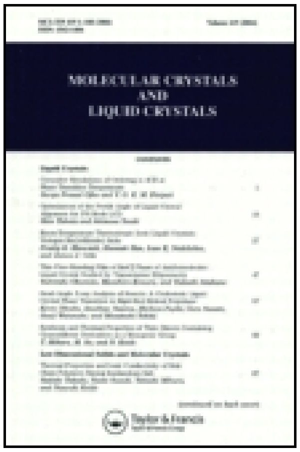

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Crystal Absorption Spectrum of 9-Cyanoanthracene at 4.2°K in the Region 4210-3240 Å

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Crystal Absorption Spectrum of 9-Cyanoanthracene at 4.2°K in the Region 4210–3240 Å

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Abstract—The polarized UV absorption spectrum of 9-cyanonanthracene crystal at 4.2°K is reported. The absorption polarization ratio for light polarized along the *c*- and *a*-axes is compatible with the assignment of the long wave system to a short axis transition as in the case of anthracene itself.

A few years ago it was noted[1] that there is a change in the fluorescence spectrum of crystalline 9-cyanoanthracene under irradiation by a mercury lamp. The disappearance of the green fluorescence after several hours irradiation and the appearance of the blue emission was correlated with the removal of excimers by the formation of chemical dimers. The excimers were thought to be responsible for the green fluorescence and the unreacted monomer responsible for the blue. Later Stevens *et al.*[2] suggested that crystalline 9-cyanoanthracene undergoes photodimerization under the exposure of the product to light of 366 mμ of a mercury lamp.

Recently[3] there has been renewed interest in the product formed in the irradiated solid. It has been shown to have *trans*-structure as in the dimer prepared by irradiation of a solution of 9-cyanoanthracene in benzene,[4] whereas the arrangement of molecules in the crystal of the monomer[5] suggests that a dimer,

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if formed, would have a *cis*-configuration. Spectroscopic studies in polarized light have now been undertaken to support more detailed analysis of the photochemical processes involved. In this paper the absorption spectrum at 4.2°K in the region 4210–3240 Å is reported.

The Crystal Absorption Spectrum near 4.2°K

9-Cyanoanthracene crystallizes in the orthorombic system with four molecules per unit cell.[5] The X-ray structure shows that crystals grown by sublimation are developed in the *ac*-plane; *c* being the direction of elongation of the crystals.

The UV spectrum was recorded with the light path perpendicular to the *ac*-face. The spectrum of 9-cyanoanthracene crystal is reported in Fig. 1 and compared with the spectrum in solution from which it is red-shifted by 1304 ± 17 cm^{-1}; in solution the first maximum is at 24 990 ± 10 cm^{-1} and in the solid at 23 686 ± 7 cm^{-1}. In addition the crystal spectrum in this region shows two maxima with polarized components along both *a*- and *c*-axes. The values for the absorption maxima of 9-cyanoanthracene at 4.2°K in the region 4210–3240 Å (corrected to vacuum) are given in Table 1.

TABLE 1 Absorption maxima (cm^{-1}) for crystalline 9-cyanoanthracene

pol. *c*	pol. *a*
23 686 ± 7	23 736 ± 8
23 986 ± 7	23 970 ± 8
25 014 ± 15	24 982 ± 20
26 208 ± 8	26 298 ± 20 sh.
	26 820 ± 20
27 828 ± 30	27 665 ± 35 sh.
	29 010 ± 30
	30 727 ± 50 sh.

Figure 1 shows three maxima for polarization in the *c*-direction whereas in the *a*-direction there are four maxima and two shoulders. Two of them are split but for that at 25 014 ± 15 cm^{-1} (pol. *c*) the splitting, if any, is within experimental error. In addition, two maxima at 26 820 ± 20 cm^{-1} and 29 010 ± 30 cm^{-1} appear with *a*-polarization only.

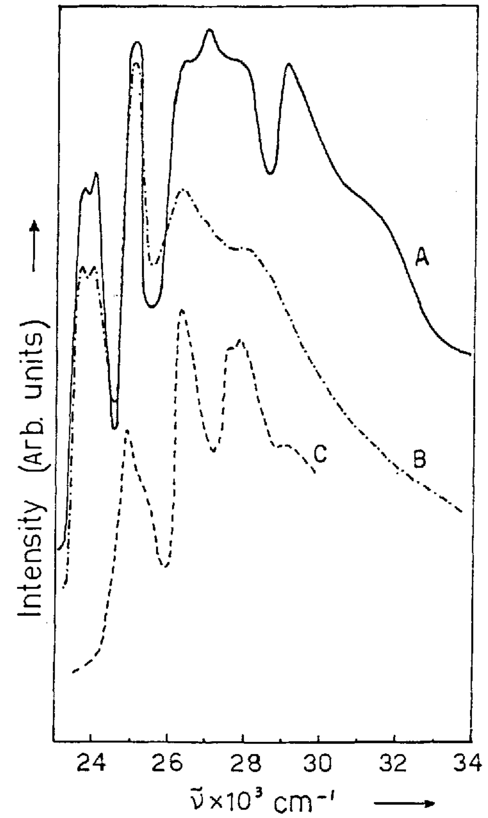

Figure 1. Crystal (4.2°K) and solution absorption spectra of 9-cyanoanthracene.

Curve A: polarized absorption parallel to the *a*-axis.
Curve B: parallel to the *c*-axis.
Curve C: solution spectrum in methyl-cyclohexane (room temp.).

On the question of the polarization direction of this absorption system in the free molecule one notes that the absorption almost certainly corresponds to the same electronic transition as the long wave system of anthracene itself near 3800 Å, in which it is known for both the free molecule[6] and the solid state[7] that the assignment is to a short axis transition. From the spectroscopic point of view the presence of $-\mathrm{CN}$ group in the 9 position of anthracene has an effect intermediate between that of an alkyl group and that of a group which conjugates with the anthracene ring.[8] This argument suggests that the low frequency band is short axis polarized for the 9-cyanoanthracene free molecules also. There is, as in anthracene itself a shift to the red between the solution and crystal absorption.

The experimentally found polarization ratio is 1.3:1 (a/c) compared with 5.0:1 for long-axis and 3.2:1 for short-axis molecular axes in the oriented gas model. The result is thus inconclusive, but a reduction from 3.2:1 to 1.3:1 implied by a short axis assignment is compatible with the known influence of second-order crystal interactions on polarization ratios.[9]

Experimental

9-Cyanoanthracene was prepared by the literature method.[10] The product was recrystallized from alcohol (twice) and then sublimed (twice) in a nickel crucible at 170°; m.p. 178°. Sublimation was also used to prepare thin crystals for the measurement of absorption spectra, the specimens prepared being elongated in the c-direction.

Typical dimensions were 3×1.5 mm. The thickness could not be measured accurately because the birefringence is unknown; however the retardations for the crystals used were 250–150 mμ. This would suggest that the thickness was of the order of 1 μ or less. The samples were mounted over a pinhole (0.33 mm dia) drilled in a brass disc using a trace of stopcock grease as cement. In order to avoid fracturing when the temperature was lowered, the crystal was secured at one point only. After locating the crystal axes by microscopic examinations, the crystal holder was placed into a block in the cryostat. The spectra were recorded with a Hilger Littrow E 492 on photographic plates and measured on the Joyce microdensitometer. The wavelength calibration was provided by an iron arc spectrum. The set-up used was similar to that described in the literature[11] except that a xenon arc was used as light source. In one case, after recording the spectrum, the crystal used was allowed to warm up at room temperature. The crystal holder was rotated through 90° and then cooled down to 4.2°K, following which the spectrum recorded was found to be unchanged within experimental error. The samples used for absorption spectra at low temperature could be recovered undamaged.

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