Two Crystal Forms and the Fluorescence Spectra of 9, 10-Dichloroanthracene

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It has been pointed out by Stevens(1) that the fluorescence spectra of aromatic hydrocarbons in the solid state have a close relationship to their crystal structures. According to him, aromatic hydrocarbons of type A show slightly red-shifted emission spectra, preserving molecular vibrational structures, whereas crystals of type B exhibit broad, structureless emission bands at considerably longer wavelengths than the corresponding molecular fluorescence in solutions.

Bock et al.(2) reported the fluorescence spectrum of 9, 10-dichloroanthracene (DClA) at various temperatures. They reported that, at room temperature, the spectrum exhibits a broad band with something of a structure and with peaks at about 470 and 490 mμ. On the other hand, Stevens and Dickinson(3) reported a single green-fluorescence band, with a peak about 540 mμ, for sublimed DClA. This fact has stimulated us to verify the existence of the two crystal forms of DClA.

Results and Discussion

Materials.—DClA was purified by column chromatography through alumina and recrystallized from benzene. Crystal-form α was obtained as long, yellow plates from benzene, alcohol or carbon tetrachloride. Form β was obtained as greenish-yellow plates on sublimation or by heating the α-form crystal above 180°C.

Lattice Constants and Crystal Structures.—The lattice constants of the α and β forms of DClA were determined by the usual X-ray technique. The crystal data for the α and β forms are summarized in Table I, together with the values reported by Trotter.(4)

The lattice constants of the α form agree excellently with those reported by Trotter. This leads to the conclusion that the α form is identical with that analyzed by Trotter.(5) According to his result, molecules are stacked along the a-axis, with their molecular planes nearly perpendicular to the a-axis. Adjacent molecules in the stacked column are separated by about 3.5 Å. In the projection along the a-axis, the long axes of two adjacent molecules are seen to be at an angle of about 60° to each other.

A crystal structure analysis of the β form is now in progress. Preliminary results reveal that the molecular stacking along the a-axis resembles the 9, 10-dibromoanthracene crystal, the structure of which has been analyzed by Trotter.(6) Namely, as can be seen from the value of the a-axis, the molecular planes are nearly parallel to the bc plane and the molecules in a stacking column are completely superposable on the bc plane when they are projected along the a-axis. In this regard, the β form is in sharp contrast to the α form, although both α and β forms belong to the type B.

Fluorescence Spectra. — The fluorescence spectra were recorded with a Shimadzu model SV-50 AL spectrophotometer equipped with an accessory for measuring the emission spectra of solid samples.

The fluorescence spectra measured on polycrystalline powders of the α and β forms of DClA at room temperature are shown in Fig. 1, together with that measured in a cyclohexane solution.

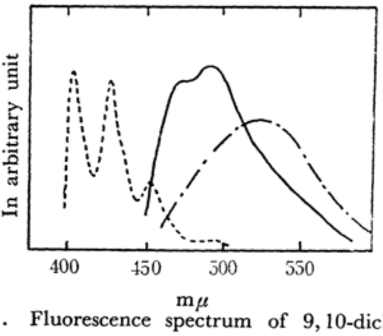

Fig. 1. Fluorescence spectrum of 9, 10-dichloroanthracene.

- - - -: in cyclohexane ——: α form
— — —: β form

Emission bands in the crystalline state are at longer wavelengths than that in the solution. The α form exhibits a broad spectrum with peaks at about 470 and 490 mμ, whereas the β form shows a broad structureless band, with a peak at about

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1) B. Stevens, *Spectrochim. Acta,* **18**, 439 (1962).
2) E. Bock, J. Ferguson and W. G. Schneider, *Can. J. Chem.,* **36**, 507 (1958).
3) B. Stevens and T. Dickinson, *Spectrochim. Acta,* **19**, 1865 (1963).
4) J. Trotter, *Acta Cryst.,* **11**, 564 (1958).
5) J. Trotter, ibid., **12**, 54 (1959).
6) J. Trotter, ibid., **11**, 803 (1958).

TABLE I. CRYSTAL DATA OF TWO CRYSTAL FORMS OF 9,10-DICHLOROANTHRACENE

	α Form		β Form
	Present work	Trotter	
a	7.04 Å	7.04 Å	3.87 Å
b	17.95 Å	17.93 Å	8.58 Å
c	8.60 Å	8.63 Å	16.98 Å
α	90°	90°	106°31′
β	103°06′	102°56′	94°56′
γ	90°	90°	95°04′
Space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$ or $P1$
V	1059 Å^3	1062.3 Å^3	535 Å^3
Z	4	4	2
$d_{\text{calcd.}}$	1.549 g. cm^{-3}	1.545* g. cm^{-3}	1.535 g. cm^{-3}
$d_{\text{obsd.}}$	1.549 g. cm^{-3}	1.525 g. cm^{-3}	1.532 g. cm^{-3}

* A value recalculated from their lattice constants.

525 mμ.* The spectrum reported by Bock et al. resembles the present one on the α form, but the emission band reported by Stevens and Dickinson is located at a slightly longer wavelength than that of the β form reported herein.

As has been mentioned, the α and β forms of DClA both belong to the type B. These closely-stacked structures with interplanar distances of about 3.5 Å seem to be favorable for the formation of excimers. The broad structureless emission of the β form is separated from the 0–0 band of the emission spectrum in a cyclohexane solution by about 5800 cm^{-1}. For aromatic hydrocarbons in solutions, it has been pointed out that the excimer fluorescence spectra are located at positions lower than the 0–0 bands of monomer emissions by about 6000 cm^{-1}.7) Furthermore, pyrene, a typical crystal with a dimer structure, shows a structureless emission band quite similar to the excimer fluorescence observed in solutions of moderately-high concentrations (10^{-2} mol./l.) as regards its shape and its position.1) Therefore, the fluorescence spectrum of the β form can be regarded as being due to the excimer state.

On the other hand, it is not easy to explain the structure of the emission band of the α form. This band has a frequency lower than that of the 0–0 band of the monomer emission by about 3600 cm^{-1}. This band may be explained by; (a)"a weak excimer state" or (b) "a unimolecular degradation of an excited state strongly perturbed in crystals." Recently, it has been reported8) that anthracene in cyclohexane at a low temperature (20°K) shows an excimer fluorescence with some structure located at a position lower than the 0–0 band of monomer emission by only about 2000 cm^{-1}. This fact seems to suggest the superiority of the explanation (a) over (b), but the possibility of (b) cannot be ruled out. Therefore, a more satisfactory explanation should be obtained from studies of the temperature dependence of the fluorescence spectra of the α and β forms of DClA.

Many theortical papers9) have appeared on the excimer configuration, but no definite conclusion has yet been obtained. The present results will at least throw some light on this problem.

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* The excitation spectra of the α and β forms were only a little different. This means that the absorption spectra of the α and β forms are essentially indentical.

7) J. B. Birks, M. D. Lumb and I. H. Munro, *Proc. Roy. Soc.*, **A280**, 289 (1964).

8) J. Ferguson, *J. Chem. Phys.*, **43**, 306 (1965).

9) T. Azumi and S. P. McGlynn, ibid., **42**, 1675 (1965), and references cited therein.