Acta Cryst. (1953). **6**, 553

The Crystallography of Acridine. I

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(*Received* 13 *December* 1952 *and in revised form* 6 *February* 1953)

Three crystalline forms of acridine are described. The previously known orthorhombic form (now called acridine I) is shown to be a hydrate. The other two forms are monoclinic.

	a (Å)	*b* (Å)	*c* (Å)	β	Molecules/unit cell	Space group
Acridine I	17·55	26·60	8·93	—	16	*Pnca*
Acridine II	16·34	18·90	6·08	95° 5′	8	$P2_1/a$
Acridine III	11·41	5·99	13·69	98° 48′	4	$P2_1/n$

The spacings are accurate within ±0·5% and the angles within ±10′.

1. Introduction

Acridine, $C_{13}H_9N$, was first prepared by Graebe & Caro (1871), who obtained crystals from solution in dilute alcohol. Several crystalline forms were noticed, but of these the orthorhombic prisms only were examined by Groth (1919). Further measurements, very similar to those of Groth, were later made by Negri (1890). We have obtained three forms from dilute alcohol; one identical with that of Groth and Negri, and two monoclinic. All three forms crystallize together at about 20° C., but at lower temperatures the orthorhombic form predominates. For historical reasons the orthorhombic form has been called acridine I and the others acridine II and III.

Groth commented on the lack of resemblance between his crystals and those of anthracene; in fact, as we shall show, acridine I is a hydrate. Acridine II and III are anhydrous, and the latter exhibits the expected similarity to anthracene.

Neither of the forms II or III appears to have been described previously, except in the structure determination of acridine III published by one of us (Phillips, 1950). Kofler (1943) has reported the existence of five modifications of acridine distinguished microscopically by their appearance, optical properties and melting points, but the data given are insufficient to permit comparison with our specimens. A form grown by sublimation and different from any of ours has been observed by Halla (1952).

2. Acridine I

Crystals of acridine I (Fig. 1) are orthorhombic holosymmetric; the usual habit consists of prisms elongated along [001] with the form {100} most prominent. An alternative habit, consisting of rectangular plates elongated along [001] but with the form {010} most prominent, occurs occasionally.

Single-crystal photographs taken with a Buerger (1944) precession camera using copper radiation gave

$$a = 17{\cdot}55\pm0{\cdot}05,\ b = 26{\cdot}60\pm0{\cdot}08,\ c = 8{\cdot}93\pm0{\cdot}025\ \text{Å};$$
$$a:b:c = 0{\cdot}660:1:0{\cdot}336\ .$$

They show reflexions $\{hkl\}$ present in all orders, reflexions $\{0kl\}$ present only when $k+l = 2n$, reflexions $\{h0l\}$ present only when $l = 2n$, and reflexions $\{hk0\}$ present only when $h = 2n$. These results characterize the space group *Pnca*.

Powder photographs of acridine I in a state of purity have been obtained from specimens ground in the mother liquor and sucked, together with liquid, into a thin-walled capillary. Measurements of the diffraction pattern are given in Table 1.

Table 1. *Powder photograph of acridine I*

Intensity	*d* (obs.) (Å)	*d* (calc.) (Å)	*hkl*
20	13·21	13·30	020
40	8·46	8·47	011
100	7·34	7·33	220
30	6·65	6·65	040
50	6·13	6·09	211
3	5·65	5·66	221
15	5·32	5·30	240
3	5·09	5·11 5·10	231 141
50	4·80	4·81	311
3	4·60	4·59	321
75	4·41	4·44 4·42 4·39	060 151 400
5	4·19	4·17	420
70	3·92	3·94 3·93	341, 212 430
30	3·61	3·63 3·60	232 351, 431
30	3·53	3·55 3·52	302 312
30	3·43	3·43	322

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Crystals of acridine I deteriorate rapidly after removal from the mother liquor, the appearance of the faces suggesting efflorescence. X-ray single-crystal photographs of acridine I taken after a few hours exposure to air show well developed powder rings characteristic of a mixture of acridine II and III. Specimens may, however, be preserved indefinitely under water at room temperature, or in water-saturated air below 10° C.

The melting point of acridine I, observed in a sealed capillary, is about 85° C. Crystals heated in an open capillary to the temperature range 85°–90° C. exude liquid, leaving a solid residue which, like acridine II, melts near 109° C. Furthermore, acridine II heated with distilled water forms a liquid layer of material below its melting point, fragments of which on cooling behave like acridine I.

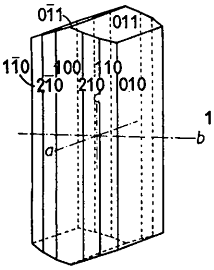


Fig. 1.

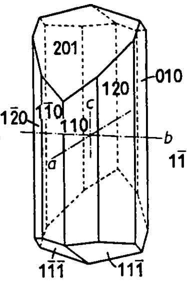


Fig. 2.

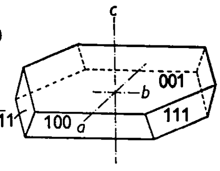


Fig. 3.

Fig. 1. Crystal of acridine I. Measured angles:
$(100):(110)$ 33° 22′; $(011):(0\bar{1}1)$ 36° 52′;
$(011):(110)$ 80° 4′; $(100):(210)$ 18° 27′.

Fig. 2. Crystal of acridine II. Measured angles:
$(010):(110)$ 49° 7′; $(010):(120)$ 29° 54′;
$(201):(120)$ 71° 8′; $(010):(\bar{1}11)$ 73° 21′;
$(120):(11\bar{1})$ 67° 35′; $(120):(\bar{1}11)$ 82° 50′.

Fig. 3. Crystal of acridine III (axes non-primitive). Measured angles:
$(001):(100)$ 79° 37′; $(100):(111)$ 67° 39′;
$(111):(\bar{1}1\bar{1})$ 56° 3′; $(001):(111)$ 70° 5′;
$[010]:[110]$ 110° 2′.

These facts are all consistent with the view that acridine I is a hydrate which decomposes with loss of water into the anhydrous acridine II. Mr J. H. Purnell, of the Chemistry Department of this College, has kindly examined a sample of acridine I using the Karl Fischer reagent, and confirmed that water is present. There is some evidence, however, that the water content may vary from specimen to specimen.

The density of crystals from one crop was measured by flotation in both potassium bromide and zinc chloride solutions, and found to be $1{\cdot}238 \pm 0{\cdot}002$ g.ml.$^{-1}$. Assuming that water of crystallization is present, the observed symmetry and density show that this specimen is a monohydrate. The calculated number of molecules of $C_{13}H_9N.H_2O$ per unit cell is $15{\cdot}75 \pm 0{\cdot}15$.

3. Acridine II

The monoclinic holosymmetric crystals of acridine II (Fig. 2) usually take the form of prisms elongated along [001] and with {010}, {110} and {120} faces. Less often they develop as parallelepipedal wafers elongated along the same direction with principal face {010} or {120}. Some twins with composition plane (100) have been observed.

Single-crystal precession photographs gave:

$$a = 16{\cdot}34 \pm 0{\cdot}06, \quad b = 18{\cdot}90 \pm 0{\cdot}08, \quad c = 6{\cdot}08 \pm 0{\cdot}02\ \text{Å},$$
$$\beta = 95°\ 5' \pm 10'; \quad a:b:c = 0{\cdot}865:1:0{\cdot}322\,.$$

The unit cell is shown in Fig. 4. The reflexions $\{hkl\}$ are present in all orders, $\{h0l\}$ only when $h = 2n$, and $\{0k0\}$ only when $k = 2n$, results which characterize the space group $P2_1/a$. The density, measured by

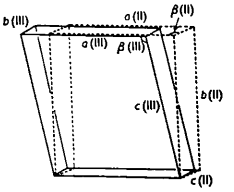
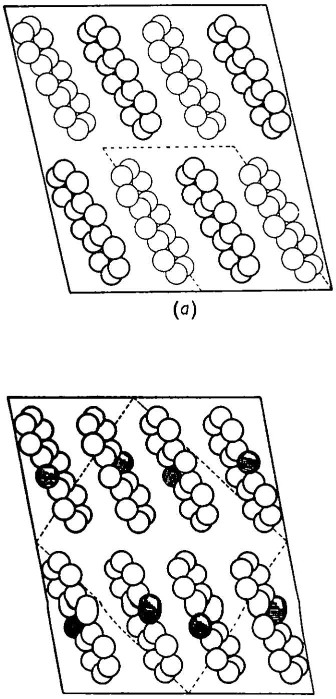


Fig. 4. Unit cells of acridine II, broken line; and acridine III (non-primitive), full line.



(a)

(b)

Fig. 5. Comparison of anthracene and acridine III. Primitive unit cells in broken line.
(a) Structure of anthracene in projection on (010). Heavily and lightly drawn molecules belong to different levels in the unit cell.
(b) Structure of acridine III in projection on (010). No distinction is made between the molecules since the vertical distribution is not yet determined. Nitrogen atoms shaded.

Table 2. *Powder photographs of acridine II and acridine III*

Acridine II				Acridine III			
hkl	*d* (calc.) (Å)	*d* (obs.) (Å)	Intensity	Intensity	*d* (obs.) (Å)	*d* (calc.) (Å)	*hkl**
110	12·33	12·30	50				
020	9·45	9·42	80	100	9·35	9·40	002
120 200	8·17 8·14	8·20	80	2	8·10	8·07	200
210	7·47	7·54	5				
130	5·88	5·87	20				
$11\bar{1}$	5·59	5·58	80	25	5·50	5·51 5·48	103 $11\bar{1}$
111	5·30	5·31	80	75	5·26	5·29	111
021 $20\bar{1}$	5·10 5·08	5·06	10	5	5·08	5·05	012
201	4·66	4·66	60	20	4·70	4·70	004
$22\bar{1}$	4·47	4·49	60	3	4·48	4·48	$21\bar{2}$
$13\bar{1}$	4·29	4·29	2	2	4·35	4·32	$11\bar{3}$
$31\bar{1}$ 330 240	4·13 4·11 4·09	4·11	30	80	4·05	4·06 4·04 4·03	113 400 $31\bar{1}$
410 $23\bar{1}$	3·98 3·95	3·98	30				
301 $32\bar{1}$	3·87 3·86	3·84	10	80	3·83	3·81	311
231 420 041	3·75 3·74 3·73	3·75	100				
141 321 340	3·59 3·58 3·56	3·58	5				
$33\bar{1}$ $41\bar{1}$ $24\bar{1}$	3·51 3·47 3·46	3·49	5	80	3·46	3·49	402
430	3·42	3·40	60				
241 331; $42\bar{1}$	3·32 3·30	3·30	50	75	3·32	3·35 3·32	410 $41\bar{2}$
411	3·20	3·19	20				
440; $43\bar{1}$ 421	3·08 3·07	3·07	90	80	2·99	3·01	412

* Indices referred to the non-primitive unit cell quoted in the text.

flotation in potassium bromide solution, is 1·278±0·002 g.ml.$^{-1}$, corresponding to 8·04±0·10 molecules of $C_{13}H_9N$ in the unit cell. Measurements of a powder photograph of acridine II are given in Table 2.

4. Acridine III

The monoclinic holosymmetric crystals of acridine III (Fig. 3) take the form of roughly hexagonal flat plates elongated in the [010] direction. The principal forms are {001} and {100}; {111} is developed occasionally.

Single-crystal precession photographs gave:

$$a = 16{\cdot}42\pm0{\cdot}06,\quad b = 5{\cdot}99\pm0{\cdot}02,\quad c = 19{\cdot}11\pm0{\cdot}08\ \text{Å},\quad \beta = 100^\circ\ 30'\pm10'\ .$$

This unit cell is shown in Figs. 4 and 5(*b*). It is convenient when comparing acridine III with anthracene and with acridine II, but it is not in fact the simplest unit cell. A primitive unit cell may be derived by the transformations

$$\mathbf{a}' = \tfrac{1}{2}(\mathbf{a}+\mathbf{c}),\ \mathbf{b}' = \mathbf{b},\ \mathbf{c}' = \tfrac{1}{2}(\mathbf{a}-\mathbf{c})\ ,$$

giving dimensions

$$a' = 11{\cdot}41\pm0{\cdot}03,\quad b' = 5{\cdot}99\pm0{\cdot}02,\quad c' = 13{\cdot}69\pm0{\cdot}07\ \text{Å},\quad \beta' = 98^\circ\ 48'\pm10'\ .$$

This unit cell is indicated by the broken lines in Fig. 5(*b*). Referred to the corresponding primitive axes the photographs show reflexions {*hkl*} present in all orders, {*h*0*l*} only when $h+l = 2n$, and {0*k*0} only when $k = 2n$. These results characterize the space group $P2_1/n$. The density, measured by flotation in potassium bromide solution, is 1·293±0·003 g.ml.$^{-1}$ corresponding to 4·02±0·06 molecules per unit cell.

Measurements of a powder photograph of acridine

III are given in Table 2, where they may be compared with the corresponding data for acridine II.

5. The relationship of acridine III to anthracene

A detailed structure analysis of acridine III will be published shortly. In the meantime it is of interest to point out the relationship of its structure to that of anthracene (Mathieson, Robertson & Sinclair, 1950). The [010] projection of acridine III, as determined by Phillips (1950), is shown in Fig. 5(*b*) in the non-primitive unit cell of the preceding section. For comparison, Fig. 5(*a*) shows the [010] projection of anthracene in a unit cell derived from that of Robertson by the transformations

$$\mathbf{a}' = 2\mathbf{a},\ \mathbf{b}' = \mathbf{b},\ \mathbf{c}' = 2\mathbf{c}+\mathbf{a}\ .$$

The dimensions of this anthracene unit cell are

$$a' = 17{\cdot}12,\quad b' = 6{\cdot}04,\quad c' = 18{\cdot}80\ \text{Å},\quad \beta = 102^\circ\, 43'\ .$$

The similarity of the projections is immediately evident, though the vertical distribution of the acridine molecules has not yet been determined.

The differences between the two structures are due to the lesser symmetry of the acridine molecule, which gives rise to a dipole moment along its symmetry axis (Bergmann, Engel & Meyer, 1932). It is not difficult to see that any attempt to pack acridine molecules as in anthracene without enlarging the unit cell must result in a polarized crystal. Such structures are, however, generally avoided in nature in favour of electrically neutral configurations (Vousden, 1953). This is achieved in acridine III by the antiparallel orientation of molecular dipoles shown. The antiparallel arrangement of the molecules can in all probability be attributed solely to their dipolar interaction, and it appears that acridine III may be regarded as an antiferroelectric in that sense.

6. The relationship of acridine II and acridine III

A noticeable similarity between the unit cells of the forms II and III of acridine has been brought out in Fig. 4. It results in a certain resemblance between the powder photographs of the two forms which may be discerned from Table 2.

The two forms appear to have nearly the same free energies at room temperature, since neither shows any great tendency to transform into the other and both are produced by the decomposition of I. At higher temperatures, however, acridine II is the stable form, but it is not possible to state the range of stability, if any, of acridine III. Powder photographs have been taken of specimens maintained for several days at temperatures ranging from 20° C. to 100° C. They show that III is transformed into II with increasing rapidity as the temperature is raised above 45° C.

The similarity of the unit cells and the lattice energies, together with the fact that the volumes per molecule are almost equal, make it likely that acridine II has the same general type of packing as acridine III; the two forms thus appear as different antiferroelectric variants based on the anthracene type of packing.

Some of the earlier goniometric measurements were made by Mr P. C. Cliffe. In the development of the work, thanks are due to Dr A. J. C. Wilson for his interest and for the use of apparatus purchased with a Royal Society grant. One of us (D.C.P.) is indebted to the University of Wales and the Department of Scientific and Industrial Research for financial assistance. Thanks are due to Mr J. H. Purnell for his chemical investigations. We are also grateful to Dr W. H. Barnes of the National Research Council, Canada, for encouraging the continuation of the work in Ottawa, and to Mrs Helen Sheppard for taking the powder photographs.

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