1-Acetylskatole, a Compound Crystallizing with an Unusual Perfection

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The crystal and molecular structure of $C_{11}H_{11}NO$ has been determined by single-crystal X-ray diffraction analysis. The crystals are monoclinic, space group $P2_1/a$, with $a = 8.502$ (4), $b = 15.935$ (6), $c = 7.318$ (4) Å, $\beta = 110.40$ (5)°, and $Z = 4$. The structure has been solved by direct methods. The parameters have been refined by full-matrix least squares using 1617 observed reflexions. The H atoms have been included in the calculations. Isotropic secondary-extinction corrections have been made neglecting primary extinction. This treatment is justified by separate X-ray transmission topography studies and an adequate model for the crystal. The refinement converges at $R = 0.068$ and $R_w = 0.079$. The different bond lengths and angles are in good agreement with the expected values. The molecule shows a planar conformation.

Introduction

1-Acetylskatole belongs to the benzazole family. The crystal structure analysis has been undertaken in order to establish the stereochemistry (E/Z) of the molecule (Sauvaitre, Teysseyre & Elguero, 1976; Fayet, Vertut, Mauret, Claramunt & Elguero, 1977).

(*E*)　　　　　(*Z*)
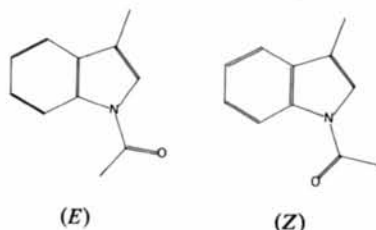
Intensity data were collected on a Philips PW 1100 diffractometer. Cu radiation was used. The background was established by a unique set of data measured for several values of θ.

Structure determination and refinement

The structure of this compound has been easily resolved with the program *MULTAN*. A difference synthesis gave the positions of all the H atoms.

Inserting these H atoms in the structure factor calculation led, after a first set of least-squares refinement cycles (scale factor, positional parameters and anisotropic temperature factors for the non-hydrogen atoms), to residual R and R_w values of 0.136 and 0.184 respectively. The interatomic distances and angles show no anomalies.

A few sets of intensity data were collected with a second crystal and led to similar values of R and R_w.

A detailed analysis of the values of the residual R for different values of $\sin\theta/\lambda$ showed that R is high for those reflexions for which $\sin\theta/\lambda < 0.38$ Å^{-1}. Large discrepancies between the values of F_o and F_c have been observed for many strong reflexions. Some have been studied by the step-scanning technique using the diffractometer and were found to have very sharp rocking curves.

These remarks suggested that the crystals of 1-acetylskatole used were of unusual crystalline perfection. In order to test the crystal quality, Lang (1958) transmission topographs of the sample were then obtained. Fig. 1 shows topographs from two different
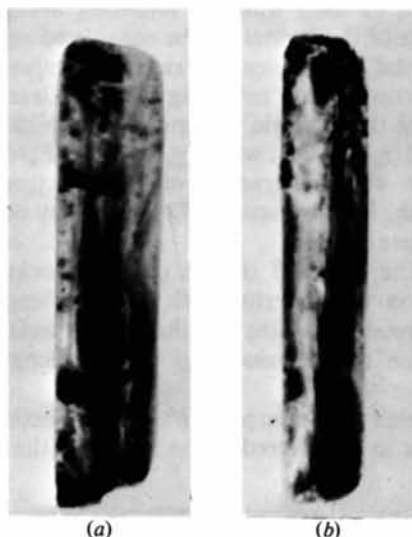

(*a*)　　　　　(*b*)

Fig. 1. X-ray transmission topographs (Cu $K\beta$ radiation, magnification ×65). (*a*) Reflexion 110; (*b*) reflexion 020.

reflexions (020 and 110). The following points should be noted:

(a) the whole crystal image exhibits local distortions and equal deformation contours, an indication that the quality of the crystal is quite good;

(b) on the other hand, the local defect density is too high to obtain images of isolated defects;

(c) the angular position of the maximum of the 'experimental rocking curve' varies slightly from point to point when the crystal is translated. This misorientation of the corresponding reflecting planes has been measured. It is equal to about $10''$ for a 100 μm translation.

From (a) one can deduce that X-ray kinematical theory cannot be applied to such a crystal, but (b) and (c) imply that the crystal is not good enough to use perfect-crystal dynamical theory.

The exact calculation of the intensity diffracted by such a crystal which is neither perfect nor ideally imperfect cannot be performed at the present time.

The only theories available at the moment rely on the mosaic model of imperfect crystals and thus on the distinction between primary and secondary extinctions (Zachariasen, 1967; Coppens & Hamilton, 1970; Becker & Coppens, 1974).

We show that for the 1-acetylskatole crystal* considered here primary extinction can be neglected. Therefore it is necessary to correct the observed intensities for secondary extinction only, since we do not aim at accurate electronic densities but only at the correct structure of the crystal.

In all the existing theories mentioned above, the crystal is considered to be made of successive small perfect crystals slightly misoriented one from the other. This model is, in fact, fairly poor for most crystals (including ours) which present continuous distortions.

We suggest that, for such crystals, the mosaic-crystal model can be used with the following assumption: a given zone of the crystal can be considered as a perfect small crystal for a given reflexion if the misorientation of the corresponding reflecting planes is less than the width δ of the intrinsic rocking curve which is of the order of $2|\chi_h|/\sin 2\theta_B$, where $\chi_h = -r_e[\lambda^2 F_h/(\pi V)]$ and r_e is the classical radius of the electron, λ the wavelength, V the volume of the elementary cell, and F_h the structure factor.

Since the width δ of the intrinsic rocking curve depends on the reflexion and the wavelength, for a given crystal, the size of the 'quasi-perfect' areas depends on the reflexion and the wavelength of the radiation.

This result is not surprising as the perfection of any device has to be referred to the nature of the means of

analysis used to test the perfection (here λ) and to the strength of the coupling between this analysis tool and the device (here F_h).

Using the value of the misorientation as given above [see (c)], one can calculate the size of the quasi-perfect areas for those reflexions which are very sensitive to the extinction effect (Table 1).

The thickness thus obtained has to be compared with a characteristic length which can be estimated to be roughly $\frac{1}{5}$ of the so-called Pendellösung or extinction length Λ ($\Lambda = \lambda \cos \theta/|\chi_h|$ for transmission symmetrical reflexion).

Several calculations or measurements justify this value of $\Lambda/5$. It is well known that dynamical and kinematical results become identical when the thickness of the sample tends to zero. The value of the thickness under which kinematical results can be used even for perfect crystals depends on both the nature of the property to be measured and the accuracy which is required. Three examples may be given: (1) the values of the integrated reflected intensity calculated for non-absorbing crystals with both theories show a relative difference of 10% for a thickness equal to or less than $\Lambda/5$ and 5% for a thickness equal to or less than $\Lambda/8$; (2) the contrast of defect images obtained in X-ray transmission topography vanishes when the thickness of the crystal becomes less than a certain value which is something between $\Lambda/3$ and $\Lambda/6$ (Penning & Goemans, 1968; Tanner, 1972); (3) the positions of the subsidiary peaks on the kinematical and dynamical rocking curves become identical for crystal thicknesses which are equal to or less than $\Lambda/3$ (Lefeld-Sosnowska & Malgrange, 1969).

We have considered here only the case of transmission topographs. The results are listed in Table 1. The shape of the crystal under study is nearly that of a square-based parallelepiped ($\sim$400 $\times$ 400 μm), the basal surface being a (001) plane.

Table 1. *Values of the Pendellösung length Λ and the thickness e of quasi-perfect domains for the 1-acetylskatole crystal studied here and for different reflexions (with Cu Kα radiation)*

The Pendellösung or extinction lengths Λ given here are calculated for symmetrical cases for which $\Lambda = \lambda \cos \theta/|\chi_h|$.

Reflexion	F_h	Λ (μm)	δ ($''$)	e (μm)	$\dfrac{\Lambda}{5}$	y
110	87·2	82	3·5	35	16	–
020	73	97	3·3	33	19	–
040	34·5	204	0·8	8	41	0·82
031	24·9	207	0·6	6	41·5	0·89
1̄31	33	204	0·75	7·5	41	0·83
1̄32	41·3	158	0·7	7	31·6	0·82
022	69·9	95	1·3	13	19	0·63
2̄51	48·6	131	0·6	6	26	0·80

* Other crystals have been tested on the diffractometer. The results for the intensities show the same features. All the as-grown crystals are thus quite good.

During the measurements on the diffractometer, the X-ray incident beam covers the whole crystal so that the rays of the diffracted beam mainly correspond to transmission cases since the Bragg angle remains small for nearly all the spots undergoing a strong extinction.

Table 1 shows that (except for 110 and 020 reflexions which, in fact, have not been taken into account because of experimental inaccuracy due to geometrical conditions) primary extinction can be neglected.

The structure was refined on the basis of these results, taking into account only the isotropic secondary extinction, with *ORXFLS*3. This program uses the results of Coppens & Hamilton (1970) which have been shown to be valid for values of the parameter 'y' larger than 0·8 (Becker & Coppens, 1974).

This new refinement lowered the residual *R* to 0·068.* The final atomic parameters are given in Table 2. Fig. 2 shows a view of the molecule.

Discussion

In Fig. 3 the numerical values which characterize the molecular geometry are given. The bond lengths and interbond angles are in good agreement with the expected values.

Table 2. *Atomic parameters* ($\times 10^4$)

Standard deviations are given in parentheses.

	x	y	z	B_{eq} or B (Å²)
N(1)	4846 (3)	9488 (2)	7870 (3)	2·7
C(2)	6572 (4)	9646 (2)	8371 (5)	3·0
C(3)	6831 (4)	10429 (2)	7876 (5)	3·1
C(4)	5206 (4)	10809 (2)	6986 (4)	2·7
C(5)	4711 (5)	11604 (2)	6169 (5)	3·6
C(6)	3010 (5)	11780 (2)	5396 (5)	4·0
C(7)	1814 (5)	11197 (2)	5458 (5)	3·8
C(8)	2274 (4)	10401 (2)	6269 (5)	3·2
C(9)	3985 (4)	10224 (2)	6999 (4)	2·6
C(10)	8481 (5)	10851 (3)	8163 (8)	5·0
C(11)	4107 (4)	8728 (2)	8041 (5)	3·2
C(12)	5289 (6)	8017 (2)	8982 (6)	4·2
O(13)	2602 (3)	8642 (2)	7464 (4)	4·4
H(2)	7371 (43)	9248 (22)	9017 (51)	0·7
H(5)	5549 (43)	11973 (23)	6141 (50)	0·7
H(6)	2727 (55)	12317 (29)	4751 (66)	2·7
H(7)	654 (49)	11358 (24)	4919 (55)	1·3
H(8)	1369 (42)	10035 (21)	6279 (49)	0·5
H(10A)	9383 (62)	10466 (30)	8584 (69)	3·1
H(10B)	8577 (0)	10988 (0)	6959 (0)	5·0
H(10C)	8732 (0)	11101 (0)	9308 (0)	5·0
H(12A)	5980 (67)	7803 (34)	8270 (80)	4·4
H(12B)	4682 (56)	7586 (31)	9297 (66)	2·8
H(12C)	6180 (56)	8178 (27)	10161 (66)	2·3
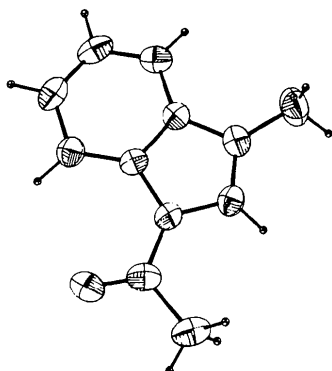
Fig. 2. View of the molecule as obtained by *ORTEP*. Ellipsoids are at the 50% probability level.
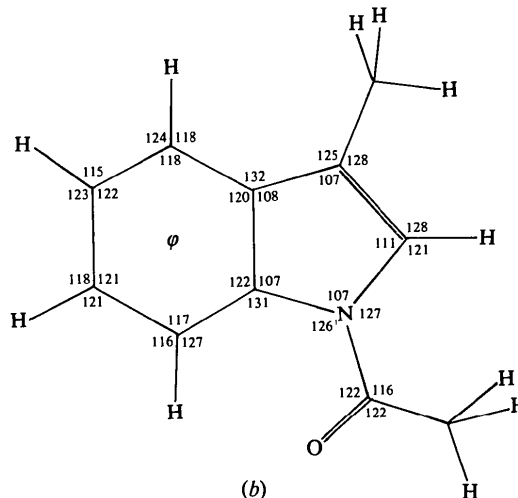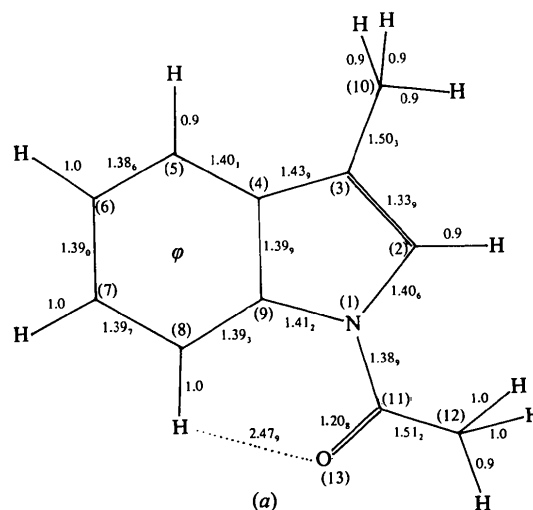
Fig. 3. Schematic views showing (*a*) bond lengths (Å), $\bar{\sigma} \simeq 0.005$ Å, and (*b*) interbond angles (°), $\bar{\sigma} \simeq 0.4°$.

$c \sin \beta$

(a)

(b)

$a \sin \beta$

(c)
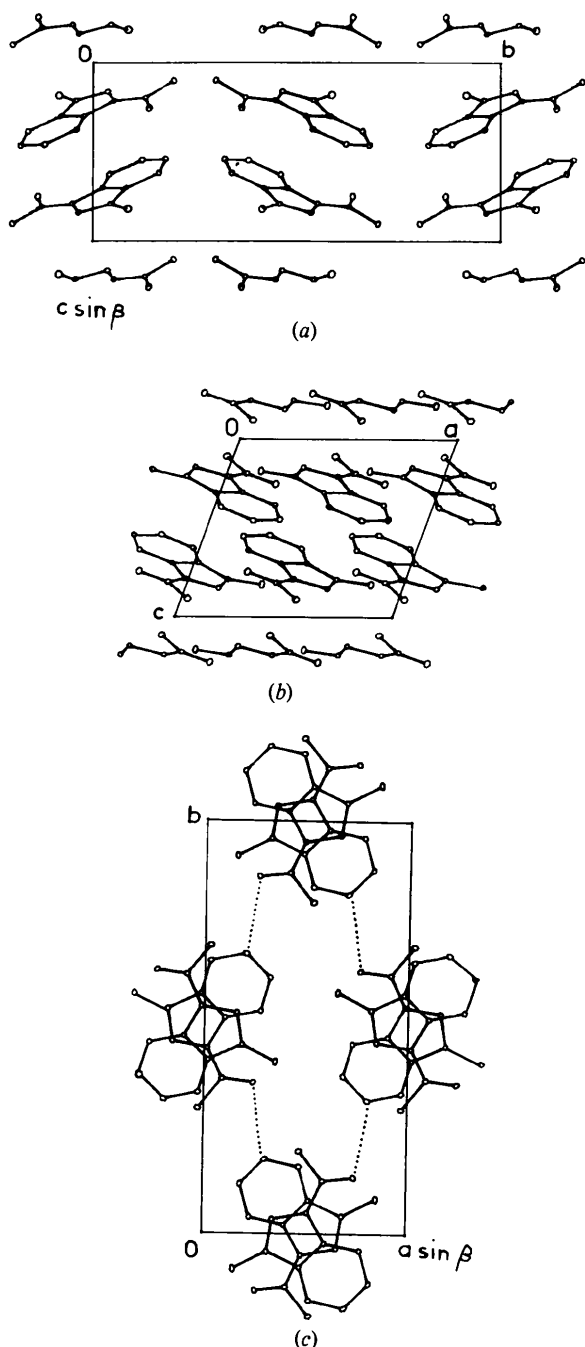
Fig. 4. Projections of the crystal structure (a) down a, (b) down b and (c) down c; broken lines indicate van der Waals short contacts.

In the crystalline state, the molecule may be considered as nearly planar and the configuration is Z, in good agreement with studies on N-acetylbenzazole molecules (Sauvaitre, Teysseyre & Elguero, 1976). There is a close intramolecular contact: $C(8)-H(8)\cdots O(13)$ with a distance of $2\cdot47_9$ Å for $H(8)\cdots O(13)$.

The group $COCH_3$ is inclined to the molecular plane of the skatole part $(0\cdot2939x - 0\cdot3385y - 0\cdot8939z + 9\cdot3344 = 0)$ by $4\cdot7°$.

Fig. 4 shows the crystalline organization.

The molecules are stacked in infinite columns parallel to the c axis. The molecular planes are nearly normal to this axis. Along each column, the molecules, which are related by inversion, may be associated by pairs and the distance between $N(1)(x,y,z)$ and $N'(1)(1-x, 2-y, 2-z)$ is $3\cdot44_8$ Å; the $N(1)N'(1)$ direction is nearly normal to the molecular planes: $N'(1)\cdots N(1)-C(2)\ 86°$, $N'(1)\cdots N(1)-C(9)\ 83°$.

Van der Waals contacts provide the crystalline cohesion. The shortest of these contacts is $C(11)-O(13)(x,y,z)\cdots H(6)-C(6)(\frac{1}{2}-x,\ y-\frac{1}{2},\ 1-z)$ with $O(13)\cdots H(6)\ 2\cdot61_6$ Å, $C(11)-O(13)\cdots H(6)\ 100°$, and $O(13)\cdots H(6)-C(6)\ 166°$.

Within experimental errors, cell parameters are related by the simple relation $b = 2a \sin \beta$ [$15\cdot935$ (6), $15\cdot938$ (5) Å]. We could not find any reasonable explanation for this.

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