with the urea or acetamide oxygen atoms. There are also weak hydrogen bonds involving the amide amino group as donor and barbital oxygen atoms as acceptor, but these have no counterpart in the *N*-methyl-2-pyridone complex because of *N*-methylation. Thus, the mode of hydrogen bonding in each of these complexes is consistent with the barbital oxygen atoms being relatively poor hydrogen-bonding acceptors.

This work was supported by Grant No. NS-02763 from the U. S. Publich Health Service, National Institutes of Health. We thank Dr R. Shiono for the use of computer programs.

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The Crystal and Molecular Structure of Methyl 3,3,4-Trichloro-5-methoxyindolenine-2-carboxylate

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(*Received* 8 *December* 1973; *accepted* 10 *December* 1973)

The structure of a trichlorinated intermediate in the synthesis of isatin compounds by a new pathway has been determined by X-ray crystallography. The compound crystallizes in the orthorhombic system with $a=22{\cdot}450$, $b=13{\cdot}292$, $c=8{\cdot}558$ Å, space group $Pna2_1$, and two molecules of $C_{11}H_8NO_3Cl_3$ in the asymmetric unit. The structure was solved by the symbolic addition method, the phases of the 150 strongest $|E|$'s being found close to 0 or π. This is probably due to the near centrosymmetric distribution of the chlorine atoms. The structure, based on 1297 diffractometer intensities, has been refined to $R=0{\cdot}036$.

Introduction

Recent investigations of the products and mechanism of attack by the positive chlorine ion (Cl^+) on indole-2-carboxylic acid (Hinman & Bauman, 1964; Foglio & Swern, 1968; Muchowski, 1970) have provided a novel route for the synthesis of substituted isatins. R. J. Bass of Pfizer (U.K.) Ltd., who aroused our interest in this matter, proposed a reaction sequence (Fig. 1) involving an unstable 'intermediate compound' [Fig. 1 (I)]. Later, Muchowski (1970) suggested that this intermediate consists rather of a sequence of reactions (Fig. 2) leading to the formation of a trichloro species [Fig. 2 (7)] which subsequently loses the elements of hydrogen chloride and carbon dioxide before tautomerizing to an oxindole [Fig. 2 (8)]. Attack by a further Cl^+ ion then yields the 3,3,4-trichloro-oxindole shown in Fig. 2 (2).

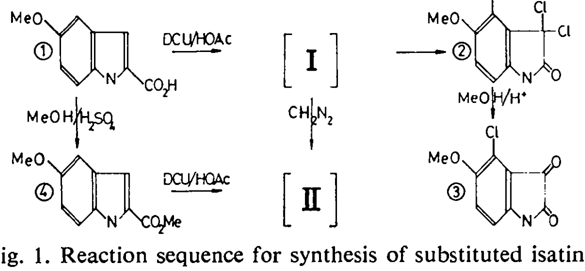

Fig. 1. Reaction sequence for synthesis of substituted isatins.

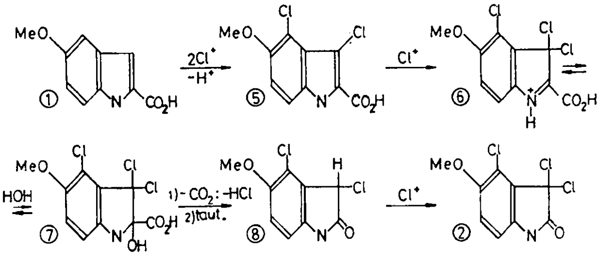

Fig. 2. Sequence of reactions comprising intermediate in Fig. 1 (I).

Bass found that treatment of the intermediate with diazomethane yielded a more stable and isolable com-

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pound [Fig. 1 (II)] of formula $C_{11}H_8NO_3Cl_3$ which could also be obtained from indole-2-carboxylic acid *via* its methyl ester. Spectroscopic data were compatible with two possible structures for this compound [Fig. 3 (*A*) and (*B*)]. The present crystal structure determination was undertaken to resolve the ambiguity.

Experimental

The title compound crystallizes from isopropyl alcohol, diethyl ether or benzene as fibrous yellow needles exhibiting parallel extinction.

*Crystallographic data**

$C_{11}H_8NO_3Cl_3$; $M=308{\cdot}5$; m.p. 185–190°C; orthorhombic; $a=22{\cdot}450$ (5); $b=13{\cdot}292$ (3); $c=8{\cdot}558$ (2) Å; $U=2554$ Å^3; $D_m=1{\cdot}60$ (5), $D_c=1{\cdot}605$ g cm^{-3} for $Z=8$; space group $Pna2_1$; $F(000)=1248$; μ(Cu $K\alpha$ radiation) $=41{\cdot}3$ cm^{-1}.

The absent spectra ($0kl$, $k+l=2n+1$; $h0l$, $h=2n+1$) are consistent with the space groups *Pnam* and $Pna2_1$. Difficulty was experienced in measuring the density of the compound owing to its high solubility in non-polar liquids and its apparent reactivity with polar liquids. The crystals were observed to have approximately neutral buoyancy in carbon tetrachloride, suggesting a density of about 1·6 g cm^{-3}. This implies a unit-cell occupancy of 8 molecules and the presence of two molecules in the asymmetric unit if the space group proves to be $Pna2_1$.

Intensities for the 1383 reflexions out to $\theta=50°$ were collected on an off-line Siemens automatic four-circle diffractometer operated in the coupled $\omega/2\theta$ scan mode with filtered Cu $K\alpha$ radiation. The crystal was mounted on a quartz fibre to rotate about the needle axis (c) and the data were processed in the normal way with the 800 reflexion as intensity reference. Four reflexions were discarded because of paper-tape errors and 1297 of the measured data were classified as observed with a net count greater than $2{\cdot}58\sigma(I)$. Details of the standard procedures used in this laboratory have been published by Allen, Rogers & Troughton (1971).

Table 1. *The starting set for phase determination*

h	k	l	$\lvert E\rvert$	φ	
8	1	0	2·67	0	Define the origin
7	8	0	2·50	0	
2	4	1	2·43	0	
14	4	0	2·42	0	$\sum_1$
10	8	0	2·21	π	
12	6	0	1·92	π	
6	6	0	1·84	0	
14	2	0	1·59	π	
0	4	0	2·38	π	$\sum_2$
16	0	0	1·61	π	
2	11	0	2·37	0	
7	1	7	2·93	a	$\pi/4$
5	4	5	2·70	b	$3\pi/4$, π, $5\pi/4$
6	3	7	2·32	c	$3\pi/4$, π, $5\pi/4$

Solution and refinement of the structure

A 'DATFIX' (Stewart, 1964) calculation, carried out in an attempt to resolve the space-group ambiguity, gave statistics which are compared with the theoretical values in the following table and favour the non-centrosymmetric space group $Pna2_1$.

	$\langle\lvert E\rvert\rangle$	$\langle E^2\rangle$	$\langle\lvert E^2-1\rvert\rangle$
Observed	0·833	0·929	0·773
Acentric	0·866	1·000	0·736
Centric	0·798	1·000	0·968

An attempt was therefore made to solve the structure by the symbolic addition method (Karle & Karle, 1966) with a local version of the Drew, Templeton & Zalkin (1969) *PHASEM* program.

The phases of five *ee*0 reflexions with probabilities (Cochran & Woolfson, 1955) greater than 0·94 were obtained from the $\sum_1$ equation (Hauptman & Karle, 1953). Also, the phases of two one-dimensional reflexions with satisfactory variances (Karle & Karle, 1966) were derived from $\sum_2$ relationships, and the origin was defined by assignment of arbitrary phases to two linearly independent $hk0$ and one $hk1$ reflexion. A preliminary application of the $\sum_2$ formula, however, gave numerous indications that the 2,11,0 reflexion (phase 'c') should have a phase of 0. It was therefore given this value and a new reflexion, 637, given the phase c. Table 1 shows the final starting set with the phases used in tangent refinement.

The $\sum_2$ formula was applied with the requirement that $\sum_{kr}\lvert E_h\,.\,E_k\,.\,E_{h-k}\rvert$ (Karle & Karle, 1966) should be greater than 10·0 if a phase indication was to be accepted. This gave unambiguous phases for 84 reflexions and indications that $a\simeq 0$ and $b\simeq c\simeq\pi$. Use of these values increased the number of known phases to 116. Although this meant that none of the symbolic reflexions was ideally suitable for fixing the enantiomorph, it was decided to try tangent refinement, the 717 reflexion being restricted for this purpose. Tangent refinement was carried out for the 9 combinations of the phases listed in Table 1 and it was found that the average consistency, t_h (Karle & Karle, 1966) and the Q factor (Drew, Templeton & Zalkin, 1969) generally converged in less than 5 cycles.

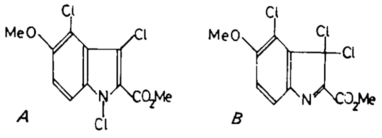

Fig. 3. Two possible structures of $C_{11}H_8NO_3Cl_3$.

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* In practice the data collection was carried out assuming the space group *Pnma* and the refinement in the non-standard space group $Pn2_1a$. All cell, position and thermal parameters and the symbolic addition are reported in space group $Pna2_1$. The final structure amplitudes, however, retain their original Miller indices.

Examination of the resulting sets of phases revealed close similarities between them despite the different starting values of the symbols. This illustrates the power of tangent refinement to 'pull' a set of phases into a general pattern despite wide differences in the starting values, provided one starts with a longish list of well connected $|E|$'s. The statistics obtained for almost every starting set were:

$\bar{t}_h$ = 0·826
Q_h = 0·17
R_{Karle} = 20·5 (Karle & Karle, 1966)

and in general the phases refined to values which were within ± 50 m cycles of 0 or π, a strong indication that the structure was centrosymmetric or nearly so. Only two phases lay far outside this range and they had very low consistencies:

	$\|E\|$	φ (m cycles)	t_h
10,7,0	1·52	262	0·28
10,4,6	1·76	811	0·28

In view of this, the two reflexions with low consistencies were dropped and a 3-dimensional Fourier map for *Pnam* was computed with the 148 $|E|$'s whose phases were known. The map contained 8 large peaks:

Peak	x	y	z
1	0·133	0·413	0·250
2	0·177	0·608	0·250
3	0·410	0·545	0·250
4	0·423	0·758	0·250
5	0·037	0·615	0·040
5′	0·037	0·615	0·460
6	0·297	0·668	0·046
6′	0·297	0·668	0·454

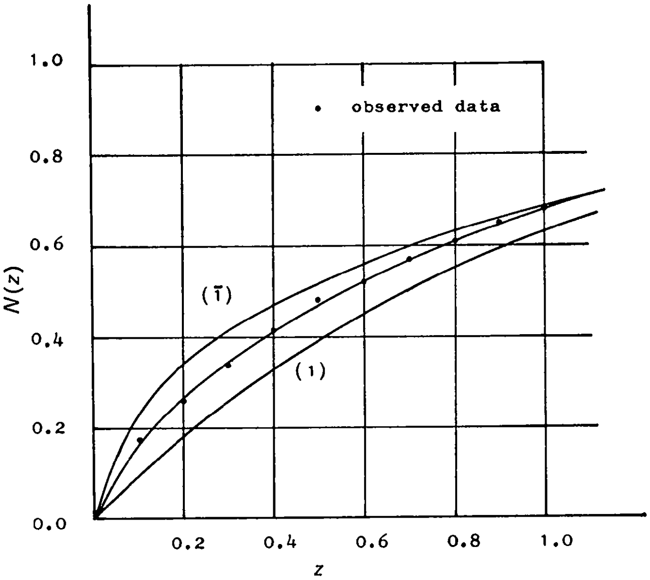

Fig. 4. The distribution of observed normalized intensities compared with the theoretical curves for centro- and non-centrosymmetric structures.

The first four peaks lay in crystallographically independent positions on the mirror plane at $z=\frac{1}{4}$, and peaks 5 and 6 occurred as approximately half-weight peaks, reproduced by the space group in the mirrored positions 5′ and 6′.

Calculation showed that this arrangement could be regarded as four identical near-equilateral triangles occurring as two crystallographically independent pairs with one member of each pair of triangles arising either from disorder, or more likely, from the use of the space group *Pnam*. To comply with space group $Pna2_1$ one must transfer 5 (or 5′) and 6 (or 6′) across the mirror plane. There are clearly two possibilities for this, such that the full-weight 'atoms' produced could be either *cis* or *trans* relative to the pseudo-mirror plane. Both possibilities were considered.

It was at this stage possible to reject the *N*-chloroindole structure [Fig. 3(*A*)], first because the shape and size of the triangles found in the *E*-map did not match that expected from this molecule, and secondly because, if the triangles found did represent the molecular plane, no acceptable mode of packing could be envisaged, especially in view of the shortness of *b* (8·6 Å).

On the other hand, the observed triangles agreed well with that expected from the *gem*-dichloroindole structure [Fig. 3(*B*)] and an acceptable packing could be visualized with the plane of the molecule lying approximately perpendicular to **c**. In addition to this, it was observed that the intramolecular vector set linking the 6 peaks agreed well with the set observed around the origin in the Patterson map, provided that peaks 5 and 6 were taken *cis* to the pseudo-mirror plane.

It was therefore decided to reject peaks 5′ and 6′ and to attempt least-squares refinement of the other peaks, treating them as full-weight chlorine atoms and reverting to space group $Pna2_1$.

The result was encouraging, R being 0·355 after four cycles of refinement and the temperature factors of all the chlorine atoms less than 4·9 Å^2. A difference map contained no sign of the mirror images of peaks 5 and 6. The remaining atoms in the structure were located by a series of difference syntheses giving an asymmetric unit consisting of two crystallographically independent molecules of the 3,3,4-trichloroindolenine structure shown in Fig. 3(*B*). With all the atoms correctly identified and after assignment of anisotropic temperature factors to the chlorine atoms, refinement reduced R to 0·07.

A correction for absorption was then applied with a program written in this laboratory based on the work of Coppens, Leiserowitz & Rabinovich (1965), after which a difference map was computed and found to contain peaks of the order of 0·7 to 1·5 eÅ^{-3} in the regions of all the side chains. These were refined anisotropically and R fell to 0·048.

As there are six chlorine atoms in the asymmetric unit, the correction for anomalous dispersion by chlorine is considerable for reflexions having a large contribution from these atoms. Unfortunately the

X-RAY 63 full-matrix and block-diagonal refinement programs are unable to apply correctly the correction in polar space groups. However, several workers (*e.g.* Ohrt, Haner, Cooper & Norton, 1968) have reported the successful use of atomic form factors corrected only for the real part of the anomalous scattering, so modified chlorine form factors were used for subsequent calculations. This produced a small improvement, R falling to 0·046, but the change in the chlorine form factors [$\Delta f' = +0{\cdot}3$ (*International Tables for X-ray Crystallography*, 1968)] seems to have been largely compensated by a 5·8% increase in the overall scale factor and a small increase in the chlorine temperature factors.

From a further difference map the positions of all 16 hydrogen atoms in the structure were identified as peaks of height 0·3 to 0·7 eÅ^{-3}. These atoms were given temperature factors of 4·0 Å^2 while the non-hydrogen atoms were subjected to 3 cycles of refinement, R falling to 0·038. The hydrogen positional parameters were then refined holding their temperature factors and the rest of the structure fixed. Finally six reflexions were removed for suspected extinction and all the structural parameters except the hydrogen temperature factors were refined to convergence at $R = 0{\cdot}036$. A difference map computed with the final parameters was very flat, mostly in the range ±0·1 eÅ^{-3} but it contained two peaks of height 0·2 eÅ^{-3}, neither of which could be related to any aspect of the structure.

The successful refinement of the structure in the non-centrosymmetric space group $Pna2_1$ resolved the space-group ambiguity and confirmed the indications from the intensity statistics in spite of the preponderance of near real phases among the 150 strongest $|E|$'s. The distribution of normalized intensities is shown in Fig. 4, an $N(z)$ plot (Howells, Phillips & Rogers, 1950) for $z < 1{\cdot}0$. The distribution of the lower intensities is about half-way between the theoretical centro- and non-centrosymmetric distributions but reflexions with normalized intensity greater than $0{\cdot}9\langle I\rangle$ show a distribution coincident with the theoretical values for a centrosymmetric structure. Since the phase determination utilizes the strongest $|E|$'s it is not surprising that the phases from tangent refinement were close to 0 or π.

The centrosymmetric character of many of the reflexions may be attributed to the positions of the chlorine atoms in the structure. If, in the space group $Pna2_1$, all the atoms in a structure lie on the planes $z = 0{\cdot}25$ and 0·75, centres of symmetry will be induced on the screw axes at $z = 0{\cdot}0$ and 0·5. In the present structure 4 of the 6 chlorine atoms and several of the lighter atoms lie close to $z = 0{\cdot}25$ and 0·75. This means that many of the vectors in the phase/amplitude diagram will conform approximately to $\bar{1}$ symmetry and this will be apparent in the final phases.

Camerman & Camerman (1971) have reported a remarkably similar situation, in which a partial structure lying on the mirror planes in the space group *Pnam* was determined by iterative application of the Sayre (1952) equation, but the remaining parts of the structure were only located after changing to $Pna2_1$.

Tables 2, 3 & 4 contain the positional and thermal parameters of the non-hydrogen atoms, Fig. 5 shows the two molecules of the structural asymmetric unit in their true relative positions and the atom numbering scheme and Table 5 contains the hydrogen positions.*

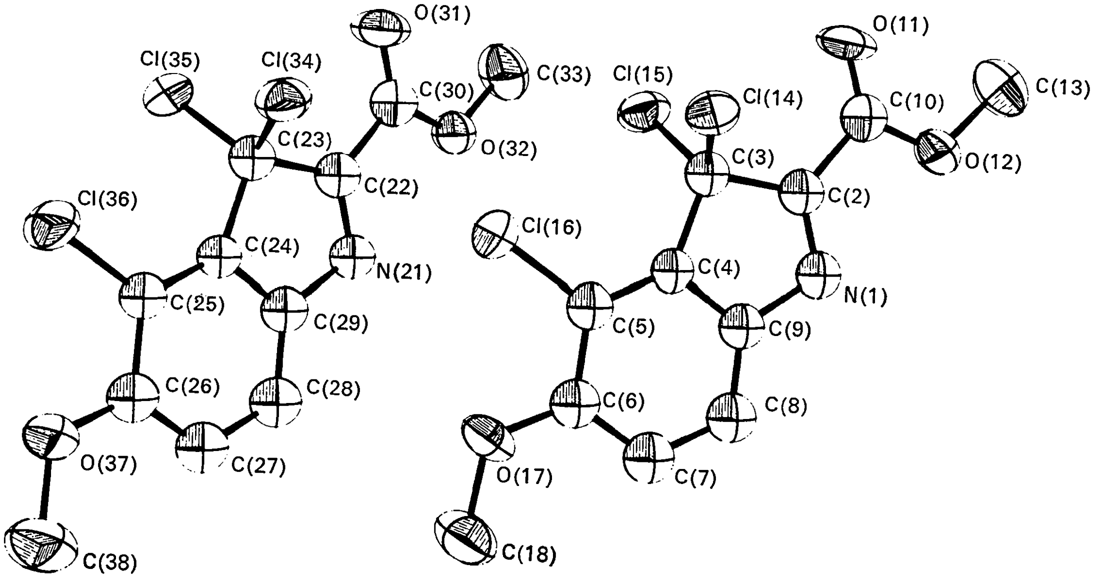

Fig. 5 The structural asymmetric unit.

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* The final structure-factor data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30311 (5 pp.). Copies may be obtained through the Excecutive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic positions (fractional coordinates* $\times 10^4$)

Standard deviations in parentheses

	x	y	z
N(1)	2271 (3)	4201 (5)	−307 (8)
C(2)	2156 (3)	4350 (6)	1158 (9)
C(3)	1576 (3)	4937 (6)	1438 (9)
C(4)	1378 (3)	5107 (7)	−243 (9)
C(5)	911 (3)	5589 (6)	−852 (9)
C(6)	863 (3)	5662 (5)	−2501 (11)
C(7)	1295 (3)	5213 (6)	−3426 (10)
C(8)	1769 (3)	4687 (6)	−2769 (11)
C(9)	1814 (3)	4662 (6)	−1172 (10)
C(10)	2543 (3)	4004 (5)	2467 (12)
O(11)	2430 (3)	4196 (5)	3786 (7)
O(12)	3008 (2)	3470 (4)	1948 (6)
C(13)	3381 (4)	3060 (8)	3127 (12)
Cl(14)	1061 (1)	4187 (2)	2500
Cl(15)	1715 (1)	6090 (1)	2424 (3)
Cl(16)	364 (1)	6142 (2)	320 (3)
O(17)	386 (2)	6191 (5)	−3028 (6)
C(18)	343 (4)	6367 (7)	−4685 (12)
N(21)	5192 (3)	6300 (5)	−4114 (8)
C(22)	5052 (3)	6351 (6)	1043 (10)
C(23)	4385 (3)	6484 (6)	1341 (9)
C(24)	4161 (3)	6498 (5)	−327 (9)
C(25)	3612 (3)	6617 (6)	−912 (9)
C(26)	3532 (3)	6588 (5)	−2542 (11)
C(27)	4037 (4)	6459 (6)	−3513 (11)
C(28)	4602 (3)	6353 (6)	−2873 (11)
C(29)	4656 (3)	6388 (6)	−1283 (10)
C(30)	5490 (3)	6298 (5)	2366 (12)
O(31)	5352 (3)	6319 (5)	3672 (7)
O(32)	6038 (2)	6234 (5)	1794 (6)
C(33)	6506 (4)	6160 (8)	2965 (12)
Cl(34)	4097 (1)	5440 (2)	2396 (3)
Cl(35)	4239 (1)	7628 (1)	2358 (3)
Cl(36)	3985 (1)	6737 (2)	276 (3)
O(37)	2972 (2)	6702 (5)	−3074 (6)
C(38)	2856 (4)	6572 (8)	−4732 (12)

Table 3. *Anisotropic temperature factors* ($\times 10^4$)

Standard deviations in parentheses

The anisotropic temperature factor is given by

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\right].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(11)	30 (2)	129 (6)	9 (1)	20 (3)	−4 (3)	−14 (5)
O(12)	18 (1)	86 (4)	13 (1)	9 (2)	−2 (3)	−2 (5)
C(13)	24 (2)	101 (7)	23 (2)	14 (4)	−1 (1)	1 (1)
Cl(14)	20 (1)	76 (1)	115 (3)	−3 (1)	10 (1)	8 (2)
Cl(15)	24 (1)	67 (1)	111 (3)	−2 (1)	6 (1)	−18 (2)
Cl(16)	22 (1)	84 (2)	134 (3)	16 (1)	10 (1)	−1 (2)
O(17)	22 (1)	95 (5)	12 (1)	8 (2)	−3 (3)	22 (5)
C(18)	36 (3)	10 (1)	16 (1)	8 (4)	−13 (6)	4 (1)
O(21)	30 (2)	144 (6)	8 (1)	7 (3)	−10 (3)	−18 (6)
O(22)	18 (1)	112 (5)	13 (1)	3 (2)	−10 (3)	6 (6)
C(33)	27 (2)	11 (1)	22 (2)	5 (4)	−26 (6)	6 (6)
Cl(34)	27 (1)	107 (3)	69 (3)	−3 (1)	7 (1)	16 (2)
Cl(35)	23 (1)	66 (1)	115 (3)	3 (1)	8 (1)	−23 (2)
Cl(36)	16 (1)	118 (2)	134 (3)	1 (1)	6 (1)	−5 (3)
O(37)	30 (2)	129 (6)	9 (1)	20 (3)	−4 (3)	−14 (7)
C(38)	30 (3)	11 (1)	15 (2)	6 (4)	−22 (6)	−2 (1)

Discussion

The structure

Figs. 6 and 7 contain the bond lengths and angles in the two molecules comprising the asymmetric unit.

Table 4. *Isotropic temperature factors*

	B (Å^2)		B (Å^2)
N(1)	3·71 (13)	N(21)	3·82 (14)
C(2)	3·71 (16)	C(22)	3·83 (17)
C(3)	3·53 (16)	C(23)	3·55 (16)
C(4)	3·17 (15)	C(24)	3·19 (15)
C(5)	3·35 (16)	C(25)	3·61 (17)
C(6)	4·00 (16)	C(26)	4·11 (16)
C(7)	4·32 (18)	C(27)	4·54 (18)
C(8)	4·51 (17)	C(28)	4·50 (18)
C(9)	3·73 (16)	C(29)	3·77 (16)
C(10)	4·23 (16)	C(30)	4·21 (16)

Table 5. *Hydrogen positions (fractional coordinates* $\times 10^3$)

	x	y	z
H(1)	118 (3)	518 (6)	−460 (10)
H(2)	199 (3)	398 (6)	−346 (10)
H(3)	68 (3)	675 (6)	−504 (10)
H(4)	35 (3)	585 (6)	−512 (10)
H(5)	−1 (3)	678 (6)	−480 (10)
H(6)	370 (3)	272 (6)	284 (10)
H(7)	308 (3)	249 (6)	353 (11)
H(8)	351 (3)	358 (6)	366 (11)
H(21)	384 (3)	608 (6)	−359 (10)
H(22)	501 (3)	623 (6)	−462 (10)
H(23)	313 (4)	712 (6)	−538 (10)
H(24)	245 (4)	665 (6)	−480 (11)
H(25)	295 (3)	586 (6)	−488 (11)
H(26)	650 (3)	548 (6)	316 (10)
H(27)	685 (3)	624 (5)	248 (12)
H(28)	646 (3)	675 (6)	353 (11)

The two molecules are virtually identical and, with one exception, the small differences between them are confined to the side chains and are probably attributable to packing forces. The exception is also the largest difference, the C(6)–C(7) bond being 0·03 Å shorter than C(26)–C(27). The close similarity between the two molecules also extends to the temperature factors (Tables 3 and 4).

Table 6 contains details of the least-squares planes through the indole nuclei, the aromatic and heterocyclic rings, and the diene system N(1)–C(2)–C(10)–O(11).

The indolenine nucleus can be accurately described as two planes intersecting at the ring bridgehead [C(4)–C(9) and C(24)–C(29)] at a mean angle of 1·85°. The only atoms, apart from the chlorine atoms in the 3 positions, which deviate to a significant extent from the overall molecular planes are the methyl carbon atoms C(18) and C(38). The structure is considered in detail below.

(*a*) *The indolenine nucleus*

Many determinations of structures containing the indole nucleus, in various oxidation states, have been reported, but none contains the indole nucleus in the indolenine form. This work, therefore, contributes to the completion of the series shown in Fig. 8.

The structure of the indole nucleus found in the present determination is entirely consistent with the

Table 6. *Least-squares planes in the structure*

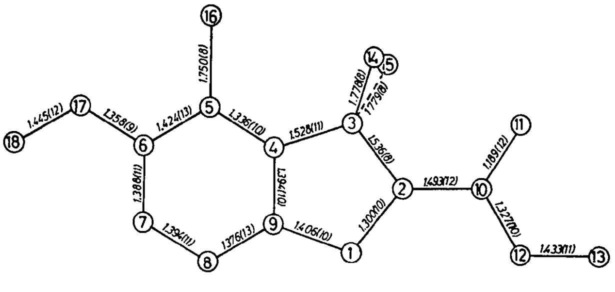
Planes are expressed in the form $Px+Qy+Rz+S=0$, referred to the crystallographic axes (x, y and z in Å). Deviations of atoms from the planes are tabulated in Å ($\times 10^3$).

The indole nuclei			
$P=11{\cdot}72$	$Q=11{\cdot}34$	$R=-0{\cdot}07$	$S=-7{\cdot}43$
N(1)	−1	C(6)	20
C(2)	22	C(7)	23
C(3)	7	C(8)	−22
C(4)	−21	C(9)	−9
C(5)	−17		
$P=2{\cdot}38$	$Q=13{\cdot}21$	$R=-0{\cdot}17$	$S=-9{\cdot}59$
N(21)	47	C(26)	5
C(22)	−7	C(27)	−28
C(23)	5	C(28)	−44
C(24)	−2	C(29)	−12
C(25	35		
The six-membered rings			
$P=11{\cdot}88$	$Q=11{\cdot}28$	$R=0{\cdot}04$	$S=-7{\cdot}39$
C(4)	2	C(7)	9
C(5)	−11	C(8)	−19
C(6)	6	C(9)	14
$P=2{\cdot}79$	$Q=13{\cdot}18$	$R=-0{\cdot}31$	$S=-9{\cdot}75$
C(24)	−13	C(27)	−1
C(25)	9	C(28)	−3
C(26)	−2	C(29)	10
The pyrrole rings			
$P=11{\cdot}53$	$Q=11{\cdot}40$	$R=-0{\cdot}18$	$S=7{\cdot}42$
N(1)	−1	C(4)	0
C(2)	0	C(9)	1
C(3)	0	C(10)*	32
$P=2{\cdot}29$	$Q=13{\cdot}22$	$R=-0{\cdot}10$	$S=-9{\cdot}55$
N(21)	11	C(24)	0
C(22)	−4	C(29)	−23
C(23)	16	C(30)*	13
The 1,4-diene systems			
$P=11{\cdot}63$	$Q=11{\cdot}35$	$R=-0{\cdot}44$	$S=7{\cdot}41$
N(1)	14	O(12)*	−56
C(2)	−15	C(13)*	−139
C(10)	−14	C(3)*	−36
O(11)	15		
$P=1{\cdot}85$	$Q=13{\cdot}25$	$R=-0{\cdot}07$	$S=-9{\cdot}34$
N(21)	−1	O(32)*	24
C(22)	2	C(33)*	4
C(30)	3	C(23)*	53
O(31)	−4		

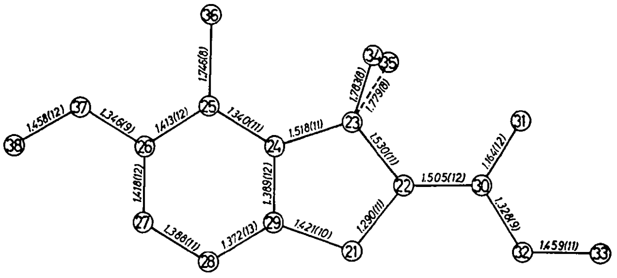
breakdown of aromaticity of the pyrrole ring. The nucleus is somewhat larger than might be expected, but this is partly attributable to repulsion forces between the side chains and partly to coordination with the methoxycarbonyl side chain.

The average of the N(1)–C(2) bond lengths [1·295 (7) Å] is significantly longer than a simple C–N double bond (1·26 Å), (Bayer & Häfelinger, 1966), but is well within the range of values reported for C–N double bonds in coordinated systems by Karlsson (1972) and Rao & Sundaralingam (1970). The C(9)–N(1) bond is significantly longer than the accepted $Csp^2{}_{\text{arom}}$–Nsp^2 bond, 1·39 Å (Bayer & Häfelinger, 1966; Dupont & Dideberg, 1972). This may arise from the participation of the nitrogen atom in the conjugated diene system N(1)–C(2)–C(10)–O(11) (see below).

The C(2)–C(3) bond [mean 1·534 (6) Å] and the C(3)–C(4) bond [mean 1·523 (6) Å] are both longer than the accepted values (Sutton, 1964), an effect which is probably due to repulsive forces between the substituent groups (see below).

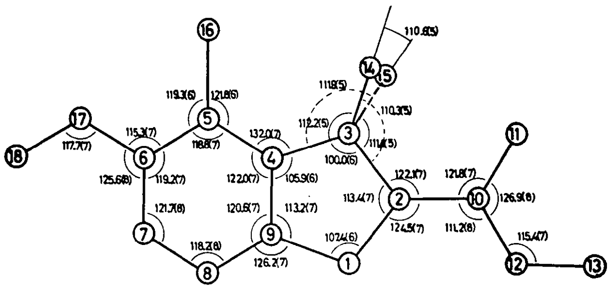


MOLECULE 1

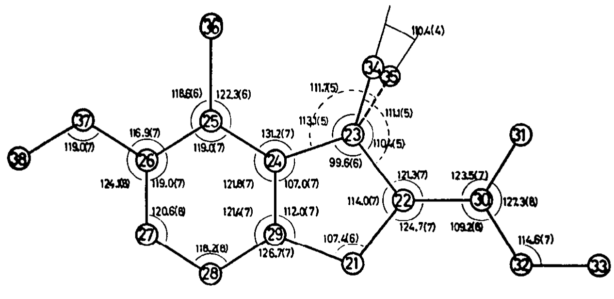


MOLECULE 2

Fig. 6. Bond lengths with e.s.d.'s in parentheses.



MOLECULE 1

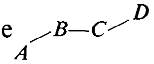


MOLECULE 2

Fig. 7. Bond angles with e.s.d.'s in parentheses.

(*b*) *The substituent groups*

(1) *The 2-methoxycarbonyl group*

The system N(1)–C(2)–C(10)–O(11) may best be considered as a *trans*-1,4-diene of the type  and as such its geometry can be explained in terms of π-electron delocalization.

In butadiene ($A=D=CH_2$) the single-bond length is 1·463 (3) Å (Haugen & Trætteberg, 1966), in acrolein ($A=CH_2$, D=oxygen) the bond length is 1·478 (5) Å (Cherniak & Costain, 1966) and in glyoxal ($A=D=$ oxygen) the bond is further lengthened to 1·525 (3) Å (Kuchitsu, Fukuyama & Morino, 1968). Qualitatively, the lengthening is related to the electronegativity of the groups A and D. On this basis, the C(2)–C(10) bond in the present structure should lie between those of acrolein and glyoxal. This is, in fact, the case, the mean bond length being 1·499 (8) Å. The overall planarity of the diene system in this structure (the torsion angle about the C(2)–C(10) bond is less than 0·1°) is also consistent with the presence of π–π interaction.

The mean carbonyl bond length is 1·177 (8) Å, considerably shorter than that summarized by Sutton (1964) for esters and ketones (1·23 and 1·22 Å respectively). It is also shorter than the value used by Hahn (1957) in his paper on the structural characteristics of amino acids. Several structures (Hahn, 1957) have been reported with C=O bonds of approximately 1·19 Å and in L-tryptophan hydrochloride (Takigawa, Ashida, Sasada & Kakudo, 1966) a value of 1·147 Å was found. The geometry of the carboxyl group found in the latter structure closely resembles that found in this work. The shortness of the carbonyl bond may be partly attributable to the inductive effect of the terminal methyl group [C(13)] as the C(10)–O(12) bond is also rather short.

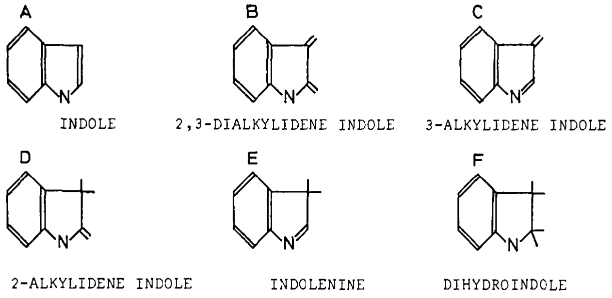


Fig. 8. Formulae.

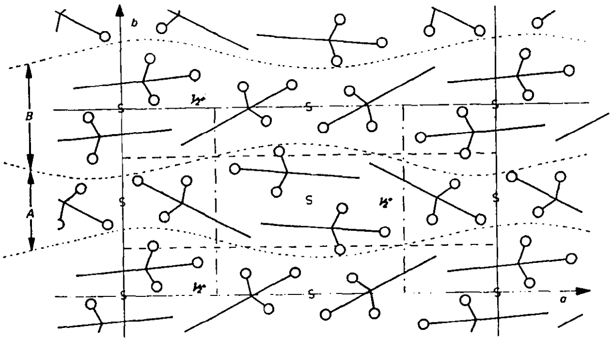


Fig. 9. Stylized (001) projection showing layering of the structure.

(2) *The chlorine substituent atoms and the 5-methoxy side chain*

In the *gem*-dichloro system Cl(14), C(3), Cl(15), the bond lengths are close to those found in chloroform (van Soest & Peerdeman, 1970), (1·74 Å). The Cl–C–Cl bond angle is also normal. The aromatic C–Cl bond, C(5)–Cl(16), is rather longer (1·748 Å) than the mean value for the bond calculated by Palenik, Donohue & Trueblood (1968), (1·709 Å), and termed an 'isolated C_{arom}–Cl bond length' by Rudman (1971).

The mean length of C(4)–C(5) [1·338 (7) Å] is very short for an aromatic ring and is typical of a double bond, whereas the C(5)–C(6) bond [mean length 1·418 (9) Å] is rather longer than normal. Together with the elongation of the C(5)–Cl(16) bond this may arise from the closeness of the non-bonded contact between O(17) and Cl(17) [mean 2·877 (4) Å], a distance 0·31 Å shorter than the sum of the van der Waals radii of oxygen (1·40 Å) and chlorine (1·80 Å), (Pauling, 1960). However, the bond angles in the system tend to suggest that the opposite may be the case since Cl(16) leans towards O(17) and away from Cl(14) and Cl(15), although the latter contacts [mean 3·543 (2) Å] are considerably larger than any of the non-bonded Cl–Cl contacts tabulated by Rudman (1971) and are only slightly less than twice the van der Waals radius of chlorine, As there are no exceptionally short non-bonded contacts to C*l*(16) or to the methoxy side chain (Table 9) the effect cannot be attributed to packing forces. A similar effect is apparent in the bond angles around C(2) and C(10), although in this case the oxygen to chlorine distances [mean 3·239 (3) Å] are not remarkable.

(3) *The hydrogen atoms*

Tables 7 and 8 contain the C–H bond lengths and angles. Most of the figures lie within the normal range

Table 7. *The carbon–hydrogen bond lengths* (Å)

C(7)—H(1)	1·043 (87)	C(27)–H(21)	1·154 (81)
C(8)—H(2)	1·214 (82)	C(28)–H(22)	1·088 (87)
C(18)–H(3)	0·968 (80)	C(38)–H(23)	1·103 (77)
C(18)–H(4)	0·784 (83)	C(38)–H(24)	0·925 (84)
C(18)–H(5)	0·974 (80)	C(38)–H(25)	0·975 (81)
C(13)–H(6)	0·883 (75)	C(33)–H(26)	0·920 (78)
C(13)–H(7)	1·077 (78)	C(33)–H(27)	0·876 (80)
C(13)–H(8)	0·877 (83)	C(33)–H(28)	0·928 (83)

The mean C–H bond length = 0·987 Å.

found in X-ray crystallographic determinations of hydrogen positions. The C(8)–H(2) and C(27)–H(21) bonds are long but there is no evidence on the final difference map to suggest new positions for these hydrogen atoms. The geometry of the methyl groups is also quite acceptable, only one angle, H(28)–C(33)–H(26), being exceptionally large.

Table 8. *Bond angles involving hydrogen atoms* (°)

C(6)—C(7)—H(1)	114 (4)	C(26)–C(27)–H(21)	103 (4)
C(8)—C(7)—H(1)	124 (4)	C(28)–C(27)–H(21)	134 (4)
C(7)—C(8)—H(2)	120 (4)	C(27)–C(28)–H(22)	123 (4)
C(9)—C(8)—H(2)	116 (4)	C(29)–C(28)–H(22)	136 (2)
O(17)–C(18)–H(3)	110 (5)	O(37)–C(38)–H(23)	108 (5)
O(17)–C(18)–H(4)	109 (6)	O(37)–C(38)–H(24)	103 (6)
O(17)–C(18)–H(5)	102 (5)	O(37)–C(38)–H(25)	102 (5)
H(4)—C(18)–H(3)	108 (8)	H(24)–C(38)–H(23)	116 (7)
H(5)—C(18)–H(3)	109 (7)	H(24)–C(38)–H(25)	108 (7)
H(5)—C(18)–H(4)	117 (8)	H(25)–C(38)–H(23)	118 (7)
O(12)–C(13)–H(6)	119 (5)	O(32)–C(33)–H(26)	100 (5)
O(12)–C(13)–H(7)	97 (4)	O(32)–C(33)–H(27)	107 (6)
O(12)–C(13)–H(8)	105 (6)	O(32)–C(33)–H(28)	103 (5)
H(7)—C(13)–H(6)	104 (6)	H(27)–C(33)–H(26)	104 (7)
H(8)—C(13)–H(6)	106 (7)	H(28)–C(33)–H(26)	137 (8)
H(7)—C(13)–H(8)	126 (8)	H(28)–C(33)–H(27)	104 (7)

Molecular packing

From Fig. 9 it can be seen that the structure consists of molecular layers of varying thickness centred on the $x0z$ and $x\frac{1}{2}z$ planes and related to each other by the n and a glide planes. Fig. 10 shows the diad screw relationship of the molecules within a single layer and Table 9 contains the shorter intramolecular contact distances.

From these distances it is evident that the intramolecular binding forces within the crystal are solely of the van der Waals type. The van der Waals volume of the molecule determined by the addition of the appropriate increments from the table given by Bondi (1968) is 218 Å^3. The 'packing density' is thus 0·679, a value similar to that for benzene (0·697) (Kitaigorodskii, 1957), and typical of aromatic structures.

We are grateful to Mr R. J. Bass for the specimen and several helpful discussions, to the Science Research Council for equipment, and to the staffs of the computing laboratories of Imperial College and the University of London for facilities. One of us (E.H.) held a research bursary provided by Associated Lead Manufacturers Ltd., during which this work was done.

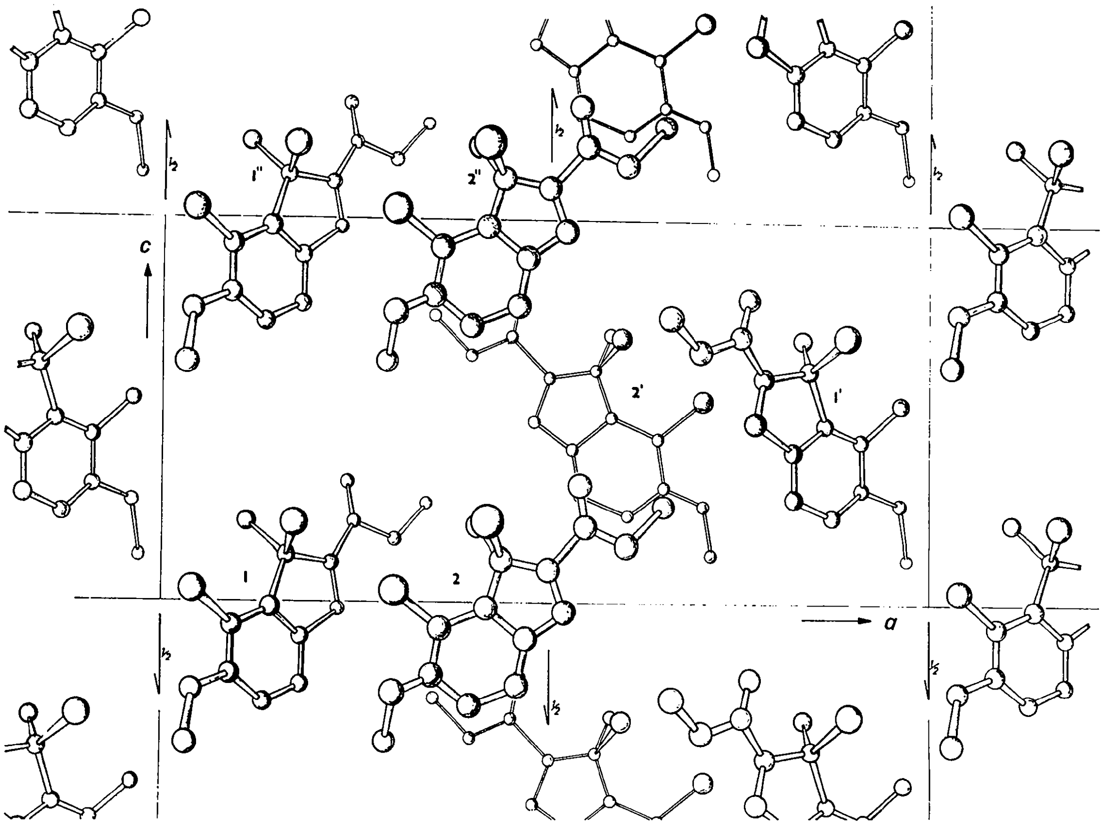


Fig. 10. (010) projection of layer A of the structure.

Table 9. *The shorter intermolecular contacts* (Å)

In the notation used 'N(1)–C(2) $2/0\bar{1}0$' implies that the distance quoted is from N(1) in equivalent position 1 to C(2) in equivalent position 2 and translated one unit cell in the $-y$ direction. The figures in parentheses refer to molecules illustrated in Fig. 10.

Cl(34)–C(13)	1/000	3·604	(1–2)
Cl(34)–O(12)	1/000	3·614	(1–2)
Cl(36)–Cl(15)	1/000	3·505	(1–2)
Cl(35)–C(8)	3/000	3·552	(2–1″)
O(11)–C(8)	1/001	3·373	(1–1″)
O(31)–C(28)	1/001	3·413	(2–2″)
Cl(15)–C(38)	1/001	3·599	(1–2″)
C(33)–N(1)	2/110	3·157	(2–1′)
Cl(34)–N(21)	2/110	3·381	(2–2′)
Cl(14)–N(21)	2/110	3·544	(1–2′)
Cl(14)–O(32)	2/110	3·536	(1–2′)
Cl(14)–C(30)	$3/0\bar{1}0$	3·574	
O(12)–C(38)	$3/0\bar{1}0$	3·485	
C(10)–O(37)	$3/0\bar{1}0$	3·303	
O(12)–O(37)	$3/0\bar{1}0$	3·209	
O(31)–C(18)	4/001	3·385	
C(26)–Cl(14)	$3/00\bar{1}$	3·574	
O(37)–C(10)	$3/00\bar{1}$	3·303	
N(1)—C(33)	$2/1\bar{1}\bar{1}$	3·167	
Cl(35)–Cl(16)	4/010	3·481	
C(22)–Cl(16)	4/010	3·460	
N(21)–Cl(16)	4/010	3·478	
C(28)–O(31)	$1/00\bar{1}$	3·413	
Cl(14)–O(17)	2/010	3·318	
C(18)–O(31)	$4/\bar{1}1\bar{1}$	3·385	

Equivalent positions in $Pna2_1$

(1)	x	y	z
(2)	$-x$	$-y$	$\frac{1}{2}+z$
(3)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}+z$
(4)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z

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