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The Crystal and Molecular Structure of Suprasteryl II 4-Iodo-5-nitrobenzoate

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The crystal and molecular structure of suprasteryl II 4-iodo-5-nitrobenzoate has been determined by three-dimensional Fourier methods and least-squares refinement. Two acceleration schemes were used. The crystals are monoclinic, with space group $C2$, and cell dimensions

$$a=39{\cdot}14,\ b=10{\cdot}34,\ c=8{\cdot}21\ \text{Å},\ \beta=94°\ 51'.$$

The structure contains a three-membered ring. The hydroxyl oxygen atom is in the axial orientation and the attached nitrobenzoate group is approximately at right angles to the main molecular plane, producing an L-shaped molecule.

Introduction

Suprasterol II is one of at least ten isomers ultimately produced by the ultraviolet irradiation of ergosterol, and with suprasterol I is obtained directly as a photochemical transformation product of calciferol, an antirachitic vitamin. The suprasterols are themselves photochemically stable and physiologically inactive. Considerable early chemical work (Windaus, Gaede, Köser & Stein, 1930; Setz, 1933; Müller, 1935; Ahrens, Fernholz & Stoll, 1933) had established that suprasterol II does not possess the normal steroid skeleton, but conflicting chemical evidence did not permit the assignment of a structure to which any weight could be attached. A two-dimensional X-ray analysis of suprasteryl II 4-iodo-5-nitrobenzoate (Curzon, 1951) was unsuccessful in determining the molecular structure. However, simultaneously with a preliminary report on the results of the present investigation (Saunderson & Hodgkin, 1961), Dauben & Baumann (1961) were able to put forward a full structure for suprasterol II deduced from more recent chemical evidence. The two results are in full agreement.

Experimental

The 4-iodo-5-nitrobenzoate of suprasterol II was prepared by Dr Rita Cornforth from a sample of the methyl dinitrobenzoic ester donated by Prof. Windaus. Crystals for photography were recrystallized from hot benzene solution and occur as yellow plates, often twinned, with (100) the dominating face.

Crystal data

$C_{35}H_{46}O_4NI$; $M=671$.
D_m (by flotation in aqueous potassium iodide solution), $1{\cdot}33$ g.cm^{-3}; D_x, $1{\cdot}35$ g.cm^{-3}.
Monoclinic, $a=39{\cdot}14\pm0{\cdot}10$, $b=10{\cdot}34\pm0{\cdot}03$, $c=8{\cdot}21\pm0{\cdot}02$ Å, $\beta=94°\,51'$.
Space group $C2$ with $Z=4$.
$\mu=88$ cm^{-1} (Cu $K\alpha$).

Equi-inclination multiple-film Weissenberg photographs were taken with unfiltered copper radiation about the b and c axes for values of k from zero to eight and l from zero to four. Although fairly large crystals with dimensions up to $0{\cdot}2\times0{\cdot}4\times0{\cdot}6$ mm were used, exposure times of up to 256 hours were required to record even limited data. The crystals deteriorated in the X-ray beam, giving diffuse reflexions after several hundred hours exposure, and it was therefore necessary to use several specimens for data collection. Reflexions extended noticeably farther in reciprocal space along the b^* axis than in other directions, but generally faded out at θ values of about 60°. Intensities were measured by visual comparison with a standard scale and the appropriate Lorentz and polarization corrections were applied. The various layers of F^2 values were placed on a common arbitrary scale by applying layer scale factors derived by a least-squares procedure (Rollett & Sparks, 1960) from ratios of the F^2 values for reflexions observed on both b- and c-axis photographs. The absolute scale was established later by correlation with the calculated structure factors.

Structure determination

A three-dimensional Patterson synthesis was computed with F^2 values modified by the function $(1/\hat{f})^2 \exp(4 \sin^2 \theta)$, where $\hat{f}$ was the unitary scattering factor for iodine. The x and z coordinates of the iodine atom were deduced from the Harker section at $V=0$, the y coordinate was arbitrarily set as zero, and the positions of six light atoms comprising a benzene ring, to which the iodine atom was attached, were then obtained. Vectors representing a carboxyl group attached to the benzene ring could also be distinguished, but less clearly.

The phases from a set of structure factors calculated on the basis of these ten atomic positions were then used in computing a three-dimensional electron-den-

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sity distribution, ϱ_1. Because the iodine positions were related by mirror planes normal to the b axis, spurious mirror-plane symmetry would have been introduced into an electron-density distribution phased only on the heavy atom. The inclusion of nine additional atoms in the structure factor calculation might be expected to have destroyed the spurious symmetry, but actually had very little effect. On the first map there were about eighty peaks of approximately one electron per Å^3 in height, plus ten much higher peaks corresponding to the atom sites already selected. Most of the low peaks occurred in mirror image pairs; it was possible to select one peak from each of seventeen of these pairs using only the criteria of reasonable interatomic distances and angles. Five more atom sites were chosen from peaks lying on the pseudo-mirror plane at $y=\frac{1}{2}$.

A second structure factor calculation based on the thirty-two atomic positions then known, gave phases for a new electron density map, ϱ_2. This showed much less doubling of peaks than was evident on ϱ_1. Table 1 lists the peak heights in ϱ_1 and ϱ_2 of all atom sites together with the heights of their mirror images. Five more atom sites were selected and small adjustments were made to the coordinates already picked. The agreement between observed and calculated structure factors improved greatly at this stage; the R value dropped from 0·405 to 0·244. These structure factors were used to obtain a difference map, from which positions for the last four atoms were determined.

Table 1. *Peak heights of atoms and their mirror images on ϱ_1 and ϱ_2*

	ϱ_1		ϱ_2	
Atom	P	M	P	M
I	72·5	—	58·7	—
N	2·7	2·7	4·6	0·8
O(1)	8·7	1·4	6·3	1·2
O(2)	8·0	1·6	6·2	0·3
O(3)	2·8	2·0	5·5	—
O(4)	2·0	0·6	4·9	—
C(1)	3·0	3·0	4·6	0·6
C(2)	2·0	1·7	4·4	—
C(3)	1·8	1·8	2·5	0·2
C(4)	1·8	1·8	3·8	—
C(5)	2·1	2·0	4·5	—
C(6)	1·8	1·5	3·7	—
C(7)	1·9	1·8	3·9	—
C(8)	2·4	2·4	4·5	—
C(9)	3·9	*	3·7	*
C(10)	2·6	2·2	4·7	0·1
C(11)	2·3	*	2·6	*
C(12)	1·7	*	2·8	*
C(13)	2·0	2·4	4·3	0·2
C(14)	2·2	1·3	4·3	—
C(15)	2·1	1·8	3·9	—
C(16)	1·0	0·9	1·4	0·5
C(17)	1·6	1·6	1·8	1·0
C(18)	2·0	1·9	3·7	0·1
C(19)	0·9	0·6	1·1	0·9
C(20)	2·3	1·6	4·4	0·1
C(21)	2·0	*	2·5	*
C(22)	2·6	*	3·4	*
C(23)	1·2	1·6	1·5	0·6
C(24)	2·3	2·4	2·0	1·6
C(25)	1·6	1·4	1·4	0·8
C(26)	2·9	*	1·4	*
C(27)	0·7	0·9	1·0	0·5
C(28)	1·1	1·1	1·0	0·6
C(29)	5·5	5·0	4·8	0·9
C(30)	6·0	1·0	5·7	—
C(31)	5·0	2·1	4·9	0·7
C(32)	4·7	—	4·3	0·5
C(33)	7·5	3·6	6·8	2·6
C(34)	4·6	—	3·9	—
C(35)	5·1	2·5	4·6	1·8

* On mirror plane.

Refinement

The refinement of this structure presented considerable difficulty; the main factors giving rise to this difficulty are considered to be (1) an insufficient number of observed reflexions and (2) systematic errors in the observed data due to absorption. It seems worth while to report this experience in slightly more detail than the accuracy of the results justifies, if only to indicate unprofitable lines of attack to other investigators of similar problems.

Least-squares refinement of the structure commenced as soon as all the light atoms, apart from hydrogen, had been located. Because the vibration of the iodine atom had appeared to be markedly anisotropic on the difference map, approximate anisotropic thermal parameters were assigned to the iodine atom for the first least-squares cycle. The other forty atoms were given individual isotropic temperature factors. However, the structure-factor-and-least-squares (SFLS) program available (Rollett, 1961) did not provide for the simultaneous refinement of anisotropic and isotropic temperature factors, so that for each light atom as well as for the iodine atom, 3 × 3 and 6 × 6 matrices were developed for the positional and thermal parameter shifts respectively. The weighting scheme used for the first three cycles of refinement was of the form

$$\begin{aligned} \omega^{\frac{1}{2}} &= 1 \text{ if } F_o \le F^* \\ &= F^*/F_o \text{ if } F_o > F^* \end{aligned}$$

with $F^* = 120$e. The average indicated coordinate shift from the third least-squares cycle was 0·023 Å, the maximum was 0·09 Å, and the R value was 0·163. After the third cycle of least-squares calculations, the value of F^* used in the weighting scheme was decreased to 72e.

An acceleration scheme attributed to A. R. Curtis and described by Sparks (1961) was used for the next three cycles in order to hasten convergence. The shifts applied after each cycle were a linear combination of the calculated shifts for that cycle, Y_i, and the applied shifts of the previous cycle, Z_{i-1}; $Z_i = aY_i + bZ_{i-1}$ with $a=1·0$ and $b=0·25$. Unfortunately the magnitude of the average indicated coordinate shift did not decrease during three cycles of refinement using this acceleration scheme, although the R value dropped to 0·127 and $\Sigma\omega\Delta^2$ also decreased. The magnitudes of about two dozen indicated coordinate shifts were substantially larger than their associated standard deviations, so that it was considered unwise to stop refinement attempts at this stage. At the same time it was hoped that further refinement might lead to improved bond lengths in the structure; some of these deviated by as much as 0·30 Å from accepted values, particularly in the region near the iodine atom.

Positions for the hydrogen atoms were calculated, assuming a C–H bond length of 1·09 Å, and assuming that methyl-group hydrogen atoms would adopt the staggered conformation. These calculated positions were compatible with the appearance of a difference synthesis computed at this stage. Introduction of the hydrogen-atom positions, with individual isotropic temperature factors, into the SFLS calculations had very little effect on either the least-squares shifts or the structure factor agreement.

Accordingly, an acceleration scheme described by Hodgson & Rollett (1963) was tried. Seven cycles of anisotropic least-squares calculations were carried out, and after each cycle a specified relaxation factor was applied to the indicated shifts. The factors used were 0·35, 0·60, 1·4, 2·0, 0·9, 0·38, and 0·45, in that order, and were calculated assuming the maximum and minimum latent roots of the matrix $\mathbf{D}^{-1}\mathbf{A}$[*] to be 2·90 and 0·47 respectively. The weighting scheme used for these seven cycles was $\omega=1/[1+\{(F_o-b)/a\}^2]$ with $a=30$e and $b=90$e. The hydrogen atoms were included in the structure-factor calculations but were not refined. Under these conditions convergence was achieved, the largest positional shift from the last cycle being 0·0078 Å. The average shift was 0·0021 Å, and the *R* value was 0·116. Unfortunately, however, serious deviations from accepted values were still observed among the bond lengths and angles. The most probable source of serious error in the intensity measurements arises from wide variation in the transmission factor over the sampled volume of reciprocal space; the linear absorption coefficient for this compound for Cu $K\alpha$ radiation is 87·8 cm^{-1} and the crystals used were quite thin plates. In order to determine how seriously the least-squares results were being affected by these systematic errors, a rather unconventional weighting scheme, $\omega=1/[1+\{(F_o-b)/a\}^2]$ with $b=-20$e and $a=40$e, was used for one cycle of refinement. This scheme had the effect of weighting reflexions with low F_o values extremely heavily, and since these reflexions tended to occur at high $\sin\theta$ values where absorption is expected to be less significant, it was hoped that the bad effects of uncorrected absorption errors would be minimized. Further justification for the use of this weighting scheme was provided by a structure factor agreement analysis. The analysis showed that the reliability of $|F_o|$ values, as expressed by $1/(\bar{\Delta})^2$ for small ranges of $|F_o|$, was greatest for low values of $|F_o|$ and decreased rapidly as $|F_o|$ increased. Starting parameters used for this refinement cycle were the same positions, vibrations and scale factor as were used to start the seven-cycle accelerated refinement. The shifts were relatively large; the average coordinate shift was 0·014 Å and the maximum was 0·066 Å. The new bond distances and angles showed a slight over-all improvement with respect to the set obtained at the end of the acceleration experiments in the sense that fewer deviated by 2σ (or more) from accepted values. It seemed likely that some further improvement might have resulted had refinement been continued with this weighting scheme and the Hodgson–Rollett acceleration scheme. However, the two descriptions of the molecule were very similar, and since the data seemed incapable of yielding very accurate results, the latest set of parameters was accepted as final, on the ground that it gave the most chemically satisfying model.

Table 2 lists the final preferred positions together with isotropic temperature factors obtained by averaging the equivalent anisotropic vibration coefficients. For the iodine atom only, the coefficients, B_{ij}, in the temperature factor expression

$$T=2^{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{23}kl+B_{13}hl+B_{12}hk)}$$

are as follows: $B_{11}=0{\cdot}00210$, $B_{22}=0{\cdot}01371$, $B_{33}=0{\cdot}03201$, $B_{23}=-0{\cdot}00066$, $B_{13}=-0{\cdot}00231$, $B_{12}=-0{\cdot}00311$. A complete list of structure factors, calculated for both observed and unobserved reflexions, is given in Saunderson (1963), and an agreement analysis of observed and calculated structure factors is given in Table 3. Scattering factor values were taken from Thomas & Umeda (1957) for iodine, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, Freeman (1959) for oxygen and nitrogen, and McWeeny (1951) for hydrogen. The iodine *f*-curve was corrected for anomalous dispersion using the values of $\Delta f'$ and $\Delta f''$ listed by Dauben & Templeton (1955).

Table 2. *Atomic parameters*

Atom	*x*	*y*	*z*	*B*
I	0·03896	−0·00045	0·21085	6·3
N	0·04196	0·27289	0·46647	8·9
O(1)	0·04908	0·62365	−0·10934	4·6
O(2)	0·03900	0·70032	0·16706	4·5
O(3)	0·03948	0·16045	0·50665	11·1
O(4)	0·03767	0·35168	0·55226	22·9
C(1)	0·06290	0·68819	−0·43260	4·5
C(2)	0·04074	0·77044	−0·33351	5·2
C(3)	0·05156	0·76454	−0·15684	6·2
C(4)	0·08845	0·80715	−0·10468	5·5
C(5)	0·11265	0·74920	−0·22591	4·8
C(6)	0·14657	0·74218	−0·19613	4·4
C(7)	0·15967	0·66958	−0·34732	5·2
C(8)	0·16315	0·60449	−0·17232	6·3
C(9)	0·14070	0·50388	−0·14495	7·0
C(10)	0·10032	0·69575	−0·37125	4·8
C(11)	0·13876	0·47575	0·04739	5·0

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[*] $\mathbf{D}^{-1}$ represents the inverse of the left-hand side of the normal-equation matrix actually used, with 3 × 3 and 6 × 6 blocks, and $\mathbf{A}$ represents the corresponding full left-hand side matrix.

Table 2 (*cont.*)

Atom	x	y	z	B
C(12)	0·17664	0·45885	0·13759	5·3
C(13)	0·19801	0·56250	0·09292	5·0
C(14)	0·19790	0·58626	−0·09099	5·7
C(15)	0·22685	0·66740	−0·11289	6·5
C(16)	0·25463	0·63643	0·03579	8·0
C(17)	0·23762	0·54052	0·15413	6·8
C(18)	0·18519	0·68865	0·18781	6·6
C(19)	0·12827	0·65122	−0·45611	7·1
C(20)	0·25118	0·54906	0·33331	5·6
C(21)	0·23515	0·48233	0·44018	11·5
C(22)	0·28790	0·51347	0·33904	8·4
C(23)	0·31305	0·59527	0·39706	8·4
C(24)	0·35151	0·56598	0·39386	6·1
C(25)	0·36792	0·58580	0·57003	9·3
C(26)	0·35568	0·46187	0·71791	11·7
C(27)	0·37097	0·75457	0·58568	23·2
C(28)	0·37024	0·61545	0·24185	10·3
C(29)	0·04511	0·60385	0·05420	6·4
C(30)	0·04331	0·46318	0·08326	2·9
C(31)	0·03996	0·44680	0·22521	2·7
C(32)	0·04093	0·29672	0·27664	3·3
C(33)	0·04093	0·17070	0·15938	7·6
C(34)	0·04398	0·24855	0·00979	5·5
C(35)	0·04577	0·36762	−0·04217	4·8
H(1)	0·05936	0·71590	−0·56120	8
H(1)	0·05373	0·58609	−0·42587	8
H(2)	0·04306	0·87044	−0·37761	8
H(2)	0·01419	0·74213	−0·36059	8
H(3)	0·06917	0·70619	−0·22496	8
H(4)	0·09078	0·91009	−0·10271	8
H(4)	0·09649	0·76624	0·01881	8
H(6)	0·15983	0·82877	−0·14687	8
H(7)	0·18519	0·70683	−0·38492	8
H(9)	0·14866	0·41703	−0·20884	8
H(9)	0·11452	0·53159	−0·20520	8
H(11)	0·12590	0·55996	0·11019	8
H(11)	0·12311	0·38869	0·07088	8
H(12)	0·17625	0·45529	0·27401	8
H(12)	0·18790	0·36795	0·09632	8
H(14)	0·20619	0·49268	−0·13758	8
H(15)	0·21889	0·77001	−0·10783	8
H(15)	0·23707	0·64507	−0·23135	8
H(16)	0·26176	0·72649	0·10174	8
H(16)	0·27742	0·58999	−0·01506	8
H(17)	0·24328	0·44166	0·10562	8
H(18)	0·18865	0·67180	0·31808	10
H(18)	0·15791	0·70439	0·14804	10
H(18)	0·20026	0·77201	0·15276	10
H(19)	0·13435	0·73008	−0·56979	8
H(19)	0·12934	0·55592	−0·51472	8
H(20)	0·24994	0·65409	0·36567	9
H(21)	0·23456	0·38830	0·41634	10
H(21)	0·24815	0·51061	0·56314	10
H(21)	0·20842	0·52892	0·43879	10
H(22)	0·29509	0·41277	0·31166	9
H(23)	0·30489	0·69181	0·43258	9
H(24)	0·35181	0·45699	0·37997	9
H(25)	0·39568	0·55578	0·55614	10
H(26)	0·32938	0·48055	0·73655	12
H(26)	0·37277	0·47191	0·82662	12
H(26)	0·35875	0·36638	0·66043	12
H(27)	0·38506	0·79472	0·48510	14
H(27)	0·38240	0·78558	0·70216	14
H(27)	0·34393	0·79511	0·56697	14
H(28)	0·37104	0·72009	0·24011	12
H(28)	0·39618	0·57468	0·24177	12
H(28)	0·35521	0·58136	0·12562	12
H(31)	0·03696	0·54330	0·27561	8
H(34)	0·04507	0·18247	−0·09184	8
H(35)	0·04961	0·38531	−0·17097	8

Table 3. *Agreement analysis*

F_{obs} range	Number of reflexions	$100\Sigma F_o$	$100\Sigma F_c$	$100\Sigma\Delta/n$	R value
0–12 e.	106	104508	112346	368	37·2
12–16	193	270086	272162	342	24·4
16–20	243	437432	418970	352	19·5
20–24	159	350396	331188	380	17·3
24–28	135	350726	353142	382	14·7
28–32	142	427156	416350	344	11·4
32–36	125	424720	408950	434	12·8
36–40	86	327150	327152	478	12·6
40–48	160	704792	684510	460	10·5
48–56	142	737486	723092	548	10·6
56–64	108	650916	616002	694	11·5
64–80	116	834766	802402	694	9·6
80–100	133	1197702	1171048	876	9·7
100–140	94	1091714	1041894	1088	9·4
140–200	41	658716	656914	1538	9·6
200–440	13	340436	355916	1438	5·5

Description of the structure

The numbering scheme is shown in Fig. 1, and Fig. 2 gives a view of the molecule. Average values for different classes of bond distances and angles are given in Table 4. No significance is claimed for individual bond lengths or angles. The benzene ring is planar within 0·04 Å despite the very large deviations from normalcy of the bond distances. The iodine atom appears to be 0·05 Å out of the benzene-ring plane, and the nitro-group is also bent out of the plane, by 9·6°. C(32)–N is *cis* to C(33)–I. The carboxyl group is rotated about 7° out of the benzene-ring plane, and is joined to ring *A* in such a way that the orientation at C(3) is axial, rather than equatorial. An axial orientation of the oxygen atom attached to C(3) is also found in the crystal structure of lumisteryl 4-iodo-5-nitrobenzoate (Hodgkin & Sayre, 1952), but in that structure C(3)–O(1) is *cis* with respect to C(13)–C(18) whereas here it is *trans*.

Table 4. *Bond distances and angles*

Type of bond	l	Av. $\sigma(l)$	Av. dev.
C–C	$1{\cdot}53_2$ Å	0·053 Å	0·078 Å
C–C (in three-membered ring)	$1{\cdot}57_5$	0·042	0·006
C–C (in side-chain)	$1{\cdot}57_5$	0·066	0·118
C–C (in benzene ring)	$1{\cdot}44_1$	0·038	0·129
C=C	$1{\cdot}36_0$	0·054	0·005
C–O	$1{\cdot}44_7$	0·036	0·066
N–O	$1{\cdot}15_7$	0·044	0·058
Individual values			
C=O	$1{\cdot}39_6$	0·040	
N–C	$1{\cdot}57_5$	0·034	
I–C	$1{\cdot}82_3$	0·046	
Type of angle	α	$\sigma(\alpha)$	av. dev.
C–C–C (unstrained single bonds)	111·6°	3·0°	5·2°
C–C–C (in three-membered ring)	60·0	1·9	0·3
C–C=C	119·6	2·8	9·1

The most interesting feature of this structure is the presence of a three-membered ring, comprising C(6), C(7) and C(8). The three-membered ring is *cis*-fused to the five-membered ring and joins the six-membered ring *C* at a spiro-junction. Relatively small movements are required of the atoms in the calciferol structure (Hodgkin, Rimmer, Dunitz & Trueblood, 1963) to take up these new positions. C(19) is only 3·2 Å from C(7) in the calciferol structure, and even this large a separation (required by the presence of the attached hydrogen atoms) is effected only by a twisting of the conjugated double bond system C(19)–C(10)–C(5)–C(6) about the C(5)–C(10) bond by an angle of about 54°. The distance between C(6) and C(8) in calciferol (2·5 Å) is also quite small.

The region C(1), C(10), C(19), C(4), C(5), C(6) is planar within experimental error, as expected with a double bond joining C(5) and C(10). C(7) also lies in this plane. Ring *C* has the chair conformation, and the fusion of rings *C* and *D* is *trans*. The side chain appears in the same configuration as that found in calciferol and lumisterol.

It is interesting to note that the side chain curls at C(24) in each of the three sterols studied in this series (lumisterol, calciferol and suprasterol II), in a direction such that the C(24)–C(25) bond lies almost at right angles to the approximate plane of the C(20)–C(22)–C(23)–C(24) zigzag system. The effect in the case of suprasterol II may easily be seen in Fig. 2. The curl seems to be associated with the adjacent double bond, and tends to give the molecule a somewhat more compact shape than it would have if the side chain were fully extended. The same phenomenon occurs in the structure of prostaglandin F_2 (Abrahamsson, 1963).

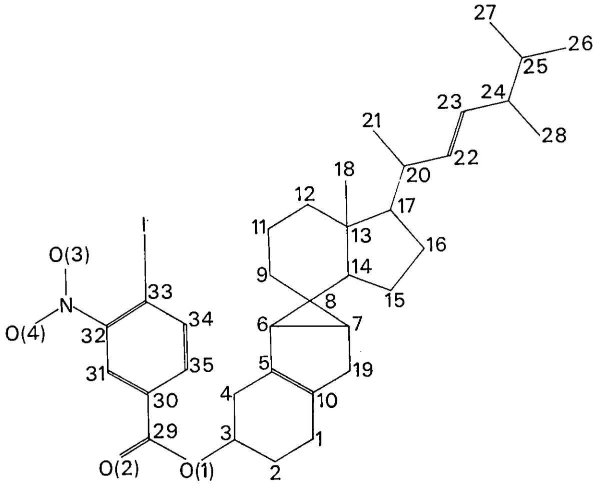

Fig. 1. Numbering scheme for the molecule.

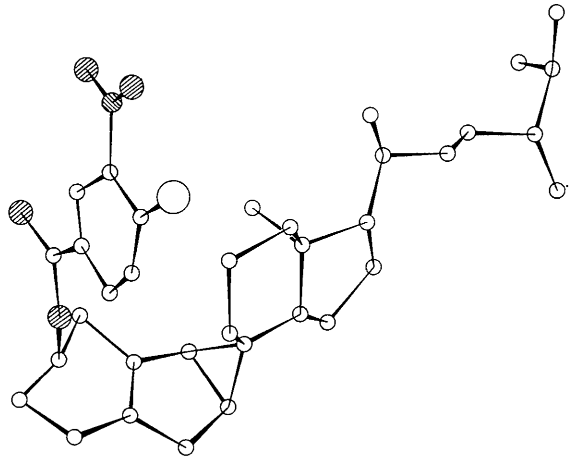

Fig. 2. View of the molecule approximately along the normal to the (210) plane.

○ carbon ▨ nitrogen ▨ oxygen ○ iodine

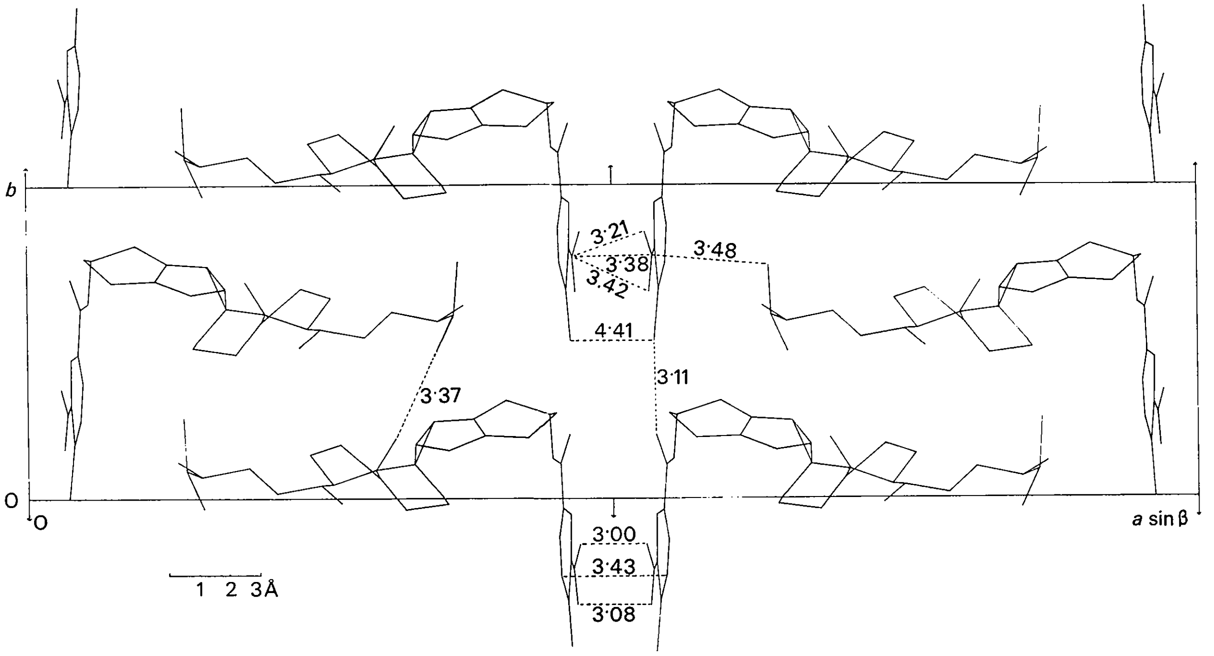

Fig. 3. Projection of the structure down the *c* axis showing the packing arrangement.

The molecular packing arrangement is shown in Fig. 3. No intermolecular hydrogen bonding is observed; instead the shortest intermolecular distances are between the iodine atom and the carbonyl oxygen (3·1 Å) and between each of the nitro-group oxygen atoms and its symmetry-related atom (3·0 Å and 3·1 Å). A number of contact distances less than 3·5 Å also occur between other atoms in the parallel nitrobenzoate groups. The shortest iodine–iodine contact distance is 4·4 Å; this seems short enough to account for the tendency of the crystals to turn yellow-brown in the X-ray beam.

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The Crystal Structure of CuCN . NH_3*

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The compound CuCN . NH_3 is monoclinic, space group $P2_1/c$, with $a=5·814$, $b=7·977$ and $c=8·193$ Å, $\beta=125·8°$ and there are four formula units per unit cell. The structure consists of polymer sheets of composition $(CuCN)_\infty$ with NH_3 molecules, bonded to Cu, protruding from both sides of these sheets. There is ambiguity in the orientation of the cyanide group but the X-ray data appear to favor one arrangement over the other. The bonding about the Cu is particularly unusual, there being five close neighbors including a Cu atom 2·42 Å.

Introduction

A number of years ago, during the course of an attempt to grow single crystals of CuCN†, it was observed that CuCN forms addition compounds with many nitrogen-containing compounds, *e.g.* ammonia, hydrazine, pyridine, aniline and pyrrole. Many of these same reactions are summarized in Gmelin (1961). Because of the unusual structures shown by $KCu(CN)_2$ (Cromer, 1957) and by $KCu_2(CN)_3 . H_2O$ (Cromer & Larson, 1962) it was decided to study the structure of some of these addition compounds. CuCN . NH_3 is the subject of the present paper; a report on CuCN . N_2H_4 will be presented in the near future.

Experimental

Excess powdered CuCN was equilibrated with concentrated aqueous ammonia by shaking for a few minutes in a closed container. The supernatant liquid was de-

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

† Small single crystals of CuCN were eventually grown from water by a special technique (Cromer, Douglass & Staritzky, 1957).