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The Structure of Desoxycholic Acid *p*-Bromoanilide

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The crystal and molecular structure of the *p*-bromoanilide derivative of desoxycholic acid has been determined from three-dimensional X-ray diffraction data. The molecule crystallizes in the space group $P2_12_12_1$, with four molecules in the unit cell. The cell constants are $a=11{\cdot}942$ (8), $b=30{\cdot}62$ (2), $c=7{\cdot}585$ (4) Å. Acentric direct-method phasing techniques successfully avoided pseudosymmetry difficulties generated from phases based on the bromine atom. A cage-like dimeric structure, with a polar interior cavity and a nonpolar exterior surface, characterizes the molecular association found in the crystal. With the aid of the anomalous scattering properties of the bromine atom, the absolute configuration of the ten chiral centers is determined.

Introduction

The bile acids have received little attention in the area of X-ray crystallography. Although the physiological and chemical properties of this steroid system have been extensively studied, little is known concerning the crystal structures of these biologically important compounds. Many possible hydrogen bonding schemes can be formulated involving the various potential hydrogen bonding sites in these molecules (Fieser & Fieser, 1959).

Desoxycholic acid plays a very important role in many biological systems. It is found, combined with glycine or taurine, as a minor component in bile fluids of most mammals. It is generally believed that these compounds are involved as emulsifying agents useful in the solubilization of fats. However, the mechanism of this process is not clearly understood, since it is uncertain if these compounds act alone or in conjunction with enzymes.

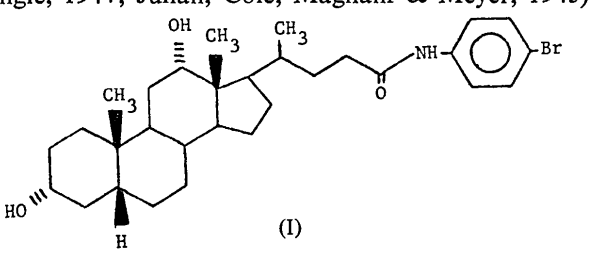
Desoxycholic acid is unique among bile acids in its ability to form molecular inclusion compounds, termed choleic acids. Other bile acids retain solvent molecules such as water or alcohol in the crystal lattice, but do not form complexes with the wide variety of substrates that comprise the choleic acids. A recent X-ray study of the cholic acid–ethanol complex (Johnson & Schaefer, 1971) has revealed a complex hydrogen-bonding scheme involving three molecules of cholic acid and five hydrogen bonds.

The choleic acids commonly show remarkable stability. Indeed, these complexes often remain intact even when the crystal lattice is destroyed. In certain instances, the guest molecule can only be removed by chemically altering the desoxycholic acid molecule, or by adding a suitable substrate that can displace the original guest molecule.

The structure of the interaction between the desoxycholic acid molecule and various substrate molecules in the solid choleic acids still remains to be investigated. In an attempt to gain some preliminary information on choleic acids, the molecular structure of the *p*-bromoanilide derivative of desoxycholic acid has been determined. This derivative is similar to the naturally occurring form of this bile acid, and shows a very simple type of solid-state molecular association compared with cholic acid.

Experimental

The *p*-bromoanilide derivative of desoxycholic acid, 3α,12α-dihydroxycholanic acid (I), was prepared by methods outlined in the literature (Ruzicka, Plattner & Engle, 1944; Julian, Cole, Magnani & Meyer, 1945).



(I)

After recrystallization from ethyl acetate, optically clear, water white crystals of (I) were obtained. The empirical formula, $C_{30}H_{44}O_3BrN$, was confirmed by mass spectrometry ($M.W._{calc}=546$, $M.W._{obs}=546$).

Oscillation and Weissenberg photographs established the crystal system as orthorhombic. The observed systematic absences, $h00$ when $h=2n+1$, $0k0$ when $k=2n+1$ and $00l$ when $l=2n+1$, define the space group $P2_12_12_1$ (D_4^2).

A suitable crystal, measuring $0{\cdot}28\times0{\cdot}20\times0{\cdot}04$ mm, was selected and mounted about the longest dimension (the crystallographic c axis). Unit-cell dimensions $a=11{\cdot}942$ (8), $b=30{\cdot}618$ (20), $c=7{\cdot}585$ (4) Å were determined by least-squares refinement of the angular parameters, defining 7 reciprocal lattice points (from diverse regions of reciprocal space) and manually centered on a Picker FACS-I, computer-controlled diffractometer. Crystal mosaicity was checked with ω scans of each reciprocal lattice point used in the calculation of cell constants. The maximum observed half-height peak width was 0·29°.

The calculated crystal density, corresponding to four molecules in the unit cell, is 1·31 g.cm^{-3} and is in good agreement with the observed density of 1·30 g.cm^{-3}, determined by flotation in aqueous NaI.

Intensity data were collected on a Picker FACS-I, four-circle diffractometer, using Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) and a graphite monochromator. The θ–2θ scanning technique was characterized by a scan rate of 2·0° min^{-1}, covering an interval of 2·0°. Ten-sec background measurements were obtained at the limits of the scan interval, and attenuators were employed whenever the counting rate exceeded approximately 10^4 cps. Two reflections were periodically collected to serve as standards, and subsequent analysis of these reflections indicated that no crystal decomposition occurred during the time required to collect 2453 independent data. These intensity data were reduced to F_o^2 and $\sigma(F_o^2)$ values as previously described (Corfield, Doedens & Ibers, 1967). Lorentz and polarization corrections were applied. Extinction and absorption corrections were neglected.

Structure solution

The bromine atom was readily located by inspection of the Harker sections $UV\frac{1}{2}$, $U\frac{1}{2}W$, and $\frac{1}{2}VW$ of an unsharpened Patterson synthesis. By this procedure, the bromine atom was found at approximately 0·13, 0·25, 0·00. A Fourier map based on the bromine atom showed fourfold pseudosymmetry with mirror planes at $z=0,\frac{1}{2}$ and $y=\frac{1}{4},\frac{3}{4}$. Under these conditions, structure solution degenerates to an essentially trial-and-error procedure, because one must select the correct structure from the various superimposed mirror image structures. This is by no means an impossible task, but it can be expensive and time consuming, especially if an incorrect start is made. Initially, the trial-and-error method was tried. This method consisted of first selecting atoms from peaks near the bromine atom which best fit a model of the phenyl ring. After five cycles of structure-factor calculation and electron density synthesis, a 20-atom model had been constructed. However, this approach was abandoned because of very poor agreement between F_o and F_c values and the fact that the model could not be extended to include any additional atoms that made chemical sense. The most likely cause for the failure of this approach was the ambiguity in the choice of a starting point due to spurious maxima around the bromine atom, which were later ascribed to thermal motion and inaccurate placement of the bromine atom.

At this point it was decided to attempt a solution of this structure using acentric direct-method procedures. This approach had been successfully applied in the solution of a heavy-atom derivative of batrachotoxinin (Karle & Karle, 1969), where phases based on the heavy atom resulted in fourfold ambiguity for the remainder of the structure. In that particular instance, the tangent formula was used to refine phases based on a known structural fragment.

One important difference between the method used in the solution of batrachotoxinin and the present example is that no partial structure was assumed in order to obtain an initial approximate phase set. The success of this approach, in this work, has deonstrated that direct methods might be useful in those cases where pseudosymmetry lessens the usefulness of the conventional heavy-atom method of structure determination.

The origin- and enantiomorph-defining reflections (Hauptman & Karle, 1956) were automatically selected by the computer program *CONVERGE* (Germain, Main & Woolfson, 1970). These four reflections, plus three structure invariants whose phases were determined by $\sum_1$ relationships (Hauptman & Karle, 1953), were used as input for the program *FASTAN* (Germain, Main & Woolfson, 1970). These seven reflections are listed in Table 1, where E is the normalized structure-factor magnitude and $\varphi(hkl)$ is the phase angle.

FASTAN extended this basic phase set, using the weighted tangent formula:

Table 1. *Phase assignments for desoxycholic acid p-bromoanilide*

	h	k	l	E	$\phi(hkl)$
	2	25	0	3·28	0
Origin	0	27	1	3·11	$\pi/2$
	3	10	0	2·92	$\pi/2$
Enantiomorph	1	0	6	2·47	0
	4	10	0	3·56	0
$\sum_1$*	4	0	2	2·24	π
	0	0	2	2·11	0

* $\sum_1$ relationships accepted if the associated probability $\geq 0{\cdot}90$.

$$\tan \varphi_{\mathbf{h}} = \frac{\sum_{\mathbf{k}} w_{\mathbf{k}} w_{\mathbf{h}-\mathbf{k}} |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \sin(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})}{\sum_{\mathbf{k}} w_{\mathbf{k}} w_{\mathbf{h}-\mathbf{k}} |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \cos(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})} = \frac{N_{\mathbf{h}}}{D_{\mathbf{h}}},$$

where $w_{\mathbf{h}} = \tanh \frac{\alpha_{\mathbf{h}}}{2}$ and $\alpha_{\mathbf{h}} = |E_{\mathbf{h}}| (N_{\mathbf{h}}^2 + D_{\mathbf{h}}^2)^{1/2}$, and produced a set of 301 phased, normalized structure factors with $E > 1{\cdot}50$. A measure of the correctness of a phase set computed by *FASTAN* is given by the consistency index C. Values of $C > 1{\cdot}0$ generally lead to crystallographically meaningful E maps. The value of C for this phase set was 1·41. A good description of the calculation method has been presented by the authors of this computer package (Germain *et al.*, 1970). The resulting E map, based on 301 data, revealed all 35 nonhydrogen atoms. The clearest portion of the structure (other than the bromine atom) was the ten-atom fragment constituting the *B* and *C* rings. There was little difficulty in locating the remaining 24 atoms. Only the atoms in the side chain and C(17) had peak heights near the level of background.

It is interesting to compare the coordinates of the bromine atom that were determined from the unsharpened Patterson synthesis and those that were determined independently by direct methods. The coordinates are listed in Table 2.

Table 2. *Bromine atom coordinates of desoxycholic acid p-bromoanilide*

x	*y*	*z*	Method
0·130	0·250	0·000	Unsharpened Patterson synthesis
0·150	0·260	0·060	Direct methods
0·151	0·266	0·003	Refined coordinates

The approximate coordinates derived from the Patterson synthesis were sufficiently inaccurate to give considerable false detail in the original electron density maps.

Structure refinement

1995 unique data with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. Five cycles of full-matrix least-squares refinement, based on F, employing anisotropic thermal parameters for bromine (for the final two cycles) and isotropic parameters for the remaining atoms, resulted in a conventional R value of 0·112. Each reflection was assigned a statistically determined weight: $4F_o^2/\sigma^2(F_o^2)$ (Corfield *et al.*, 1967). A difference electron density map was calculated, and regions of electron density were observed around the majority of the atomic sites. This can be attributed to the lack of correction for anisotropic motion for the model and the missing hydrogen atoms. The maximum peak height of approximately 0·9 e.Å^{-3} was near the bromine atoms.

The model was considered complete, and additional refinement using a fully anisotropic treatment was not undertaken, owing principally to the expense involved for the rather limited additional information that would have been obtained. The atomic scattering factors used for all atoms were those tabulated by Hanson (Hanson, Herman, Lea & Skillman, 1964).

The absolute configuration of the molecule was determined by one cycle of refinement of the positional and thermal parameters of the bromine atom and the overall scale factor where the effects of anomalous dispersion were included in F_c (Ibers & Hamilton, 1964). The values of $\Delta f'$ and $\Delta f''$ for bromine were those from the *International Tables for X-ray Crystallography* (1962). The resulting R values (R_2) for the two enantiomorphous structures were 0·147 and 0·150. The difference between the two models (0·003) for 1995 data and one degree of freedom was tested by Hamilton's R-ratio method (Hamilton, 1965). The hypothesis that the absolute configuration resulting in the larger R value was correct could be rejected at the 0·005 level. The Figures show the correct absolute configuration for the molecule. Statistical tests, such as described above, can be invalidated by systematic errors present in the data. The lack of an absorption correction constitutes one source of systematic error in the present case.

A final structure factor calculation using all 2453 data resulted in $R_1 = 0{\cdot}132$ and $R_2 = 0{\cdot}149$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

Results and discussion

The final atomic coordinates and temperature factors are presented in Table 3. Fig. 1 is a stereoscopic view of the molecule, and Fig. 2 depicts a perspective view of a unit cell showing the molecular packing. Figs. 3 and 4 summarize the observed distances and angles. The observed average bond distance (Csp^3–sp^3, 1·54 Å) and tetrahedral bond angle (111°) are in good agreement with the commonly accepted values found in alkanes (Sutton, 1965). However, the individual variations in bond lengths and angles, over presumably chemically equivalent functions, are not necessarily significant.

The relative configurations at C(3), C(12) and C(17), described as $3\alpha{:}12\alpha{:}17\beta$, can be seen in Fig. 1

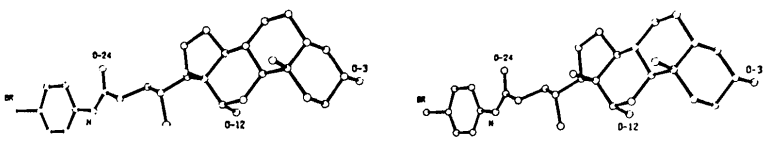


Fig. 1. Stereoscopic view of desoxycholic acid *p*-bromoanilide.

Table 3. *Atomic coordinates and thermal parameters of desoxycholic acid p-bromoanilide*

x, *y*, and *z* are expressed as fractional cell coordinates. E.s.d.'s are in parentheses. Isotropic temperature factors in Å².

	x	*y*	*z*	*B*
Br	0·1508 (2)	0·2664 (1)	0·0033 (4)	*
O(3)	0·7020 (9)	0·1139 (3)	0·4319 (17)	4·7 (3)
O(12)	0·2475 (9)	0·0346 (4)	0·6326 (18)	4·8 (3)
O(24)	0·2845 (10)	0·4037 (4)	0·2067 (19)	5·3 (3)
N	0·3063 (10)	0·3777 (4)	−0·0702 (18)	3·5 (2)
C(1)	0·4458 (15)	0·1675 (5)	0·6189 (25)	4·6 (3)
C(2)	0·5416 (14)	0·1367 (5)	0·6196 (25)	4·1 (3)
C(3)	0·6114 (13)	0·1444 (5)	0·4470 (24)	4·1 (3)
C(4)	0·5397 (14)	0·1378 (5)	0·2828 (24)	4·1 (3)
C(5)	0·4363 (14)	0·1698 (5)	0·2874 (23)	3·7 (3)
C(6)	0·3641 (14)	0·1645 (5)	0·1175 (26)	4·6 (4)
C(7)	0·2989 (12)	0·1204 (4)	0·1203 (22)	3·9 (3)
C(8)	0·2291 (11)	0·1163 (4)	0·2844 (20)	2·9 (3)
C(9)	0·2975 (13)	0·1210 (5)	0·4533 (23)	3·3 (3)
C(10)	0·3653 (12)	0·1667 (4)	0·4553 (21)	3·7 (3)
C(11)	0·2305 (14)	0·1124 (5)	0·6156 (25)	3·9 (3)
C(12)	0·1701 (12)	0·0700 (4)	0·6197 (20)	3·2 (3)
C(13)	0·0952 (11)	0·0646 (4)	0·4609 (19)	2·6 (2)
C(14)	0·1705 (12)	0·0707 (5)	0·2902 (21)	3·3 (3)
C(15)	0·0949 (12)	0·0594 (4)	0·1390 (22)	3·5 (3)
C(16)	0·0217 (12)	0·0219 (4)	0·2119 (22)	3·2 (3)
C(17)	0·0446 (11)	0·0186 (4)	0·4119 (20)	2·6 (3)
C(18)	−0·0010 (11)	0·0989 (4)	0·4669 (23)	3·8 (3)
C(19)	0·2817 (12)	0·2036 (4)	0·4578 (23)	4·1 (3)
C(20)	0·0570 (11)	0·5035 (4)	−0·0181 (22)	3·1 (3)
C(21)	−0·0229 (15)	−0·0016 (6)	0·7195 (28)	4·3 (4)
C(22)	0·0986 (11)	0·4606 (4)	0·0543 (21)	3·3 (3)
C(23)	0·2101 (14)	0·4472 (5)	−0·0281 (27)	4·6 (3)
C(24)	0·2679 (13)	0·4083 (5)	0·0431 (25)	3·9 (3)
C(25)	0·3790 (10)	0·3426 (4)	−0·0425 (19)	2·9 (2)
C(26)	0·4055 (15)	0·3173 (6)	−0·1809 (26)	4·6 (4)
C(27)	−0·0122 (15)	0·2137 (6)	0·1727 (26)	4·5 (4)
C(28)	0·0350 (14)	0·2225 (5)	0·0213 (28)	5·0 (4)
C(29)	0·0165 (16)	0·1989 (6)	−0·1408 (27)	5·5 (4)
C(30)	0·4329 (18)	0·3332 (6)	0·1267 (30)	6·0 (5)

* Bromine anisotropic temperature factor coefficients:

$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
96 (2)	12 (0)	499 (8)	−8 (5)	−48 (4)	26 (1).

Anisotropic thermal parameters are of the form:
$\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

and agree with the configurations reported for desoxycholic acid (Mattox, Turner, McKenzie, Engle & Kendall, 1948). The absolute configuration at C(20), determined indirectly by Cornforth (Cornforth, Youhotsky & Popjak, 1954), was confirmed in the present investigation. The configurations at the ten asymmetric centers are thus described as (3*R*), (5*S*), (8*S*), (9*S*), (10*S*), (12*S*), (13*R*), (14*R*), (17*R*), and (20*R*).

Desoxycholic acid forms molecular complexes with acids, alcohols, hydrocarbons and a wide variety of other molecules. For example, xylene forms a 1:2 molecular complex with desoxycholic acid. This complex is quite stable and, at atmospheric pressure, the xylene is only completely released when the crystal lattice is destroyed at the melting point of the complex, some 40° above the boiling point of xylene. A knowledge of the molecular packing and hydrogen bonding in the *p*-bromoanilide derivative of desoxycholic acid affords preliminary information that may be useful in understanding the molecular complexes of desoxycholic acid.

Fig. 2 reveals that the ring portion of the molecule has the hydroxyl at C(12) and the angular methyls C(18) and C(19) on opposite sides of the mean molecular plane. The C(3) hydroxyl group and the O(24) carbonyl form a hydrogen bond (contact distance 2·96 Å) in a fashion to effectively produce a dimeric structure, with a polar interior cavity and nonpolar exterior surface.

It is interesting to note the lack of any hydrogen bonding involving O(12). This free hydroxyl group could conceivably be used in binding to a larger biological function, such as an enzyme. This situation, if confirmed for choleic acids, could explain the usefulness of this bile acid as an emulsifying agent in biological systems.

While it remains to be seen what the structures of choleic acids are, the present model is consistent with a 1:2 xylene–desoxycholic acid molecular complex. This choleic acid crystallizes in the space group $P2_12_12_1$, $a=13{\cdot}514$, $b=26{\cdot}516$, $c=7{\cdot}272$ Å, with four desoxycholic acid molecules and two xylene molecules per cell. Consideration of models based on a hydrogen bonding scheme and cage structure shown for desoxycholic acid *p*-bromoanilide reveals that a xylene molecule could be located within the cage. Our attempts to solve the disordered xylene choleic acid have failed, but new approaches are being pursued.

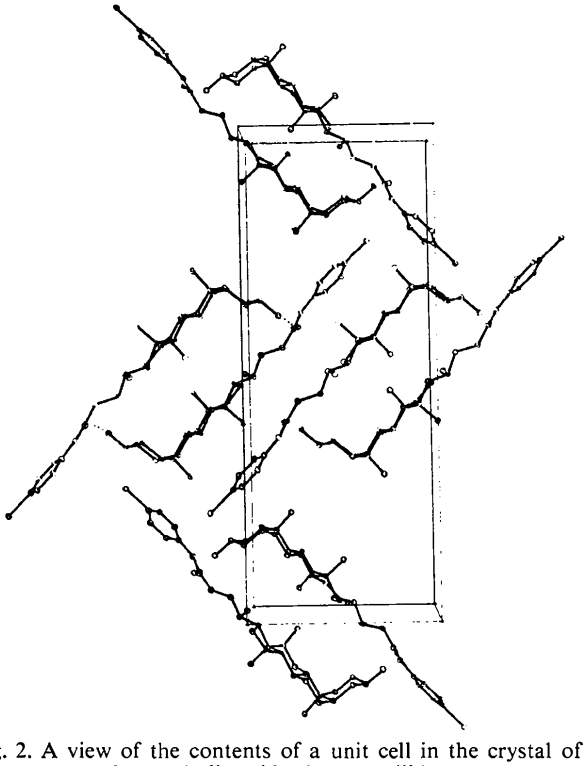


Fig. 2. A view of the contents of a unit cell in the crystal of desoxycholic acid *p*-bromoanilide.

A listing of h, k, l, F_o, and F_c for the 2453 data collected is available from the dissertation of one of us (L.L.R.).

The authors wish to acknowledge the generous financial assistance of the University of Arizona Computer Center. This work represents a portion of

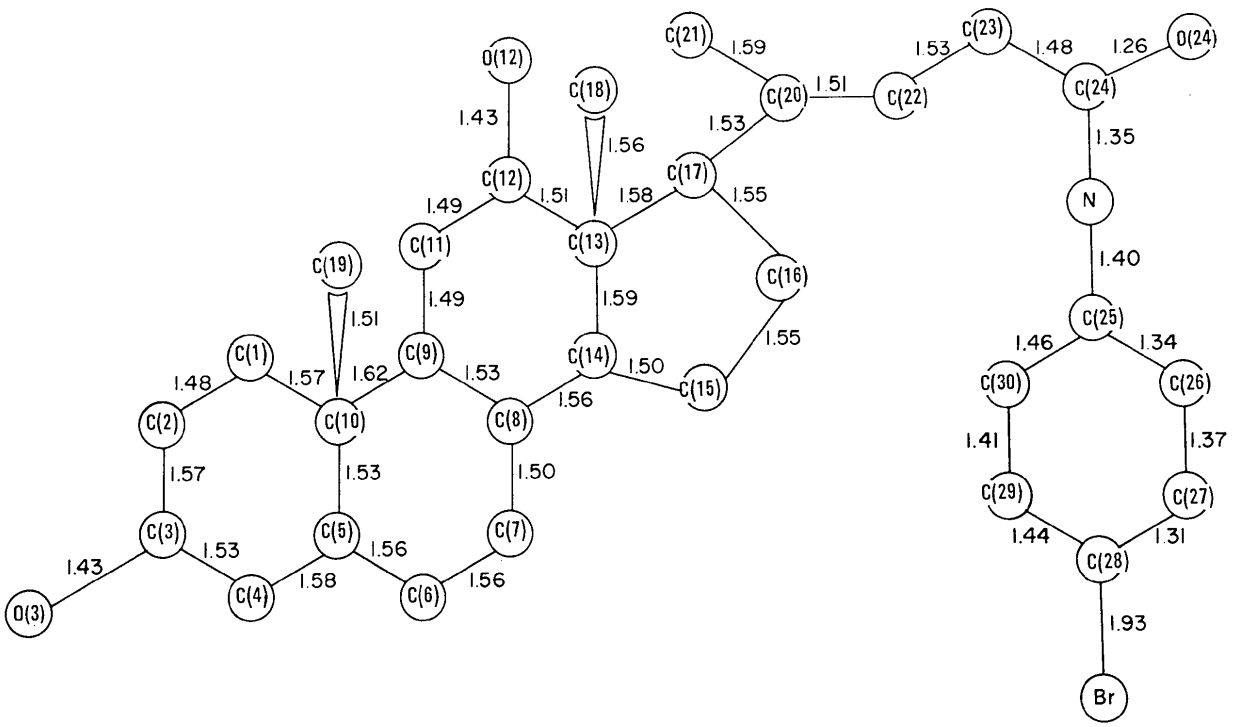


Fig. 3. Schematic drawing of desoxycholic acid *p*-bromoanilide, showing bond distances.

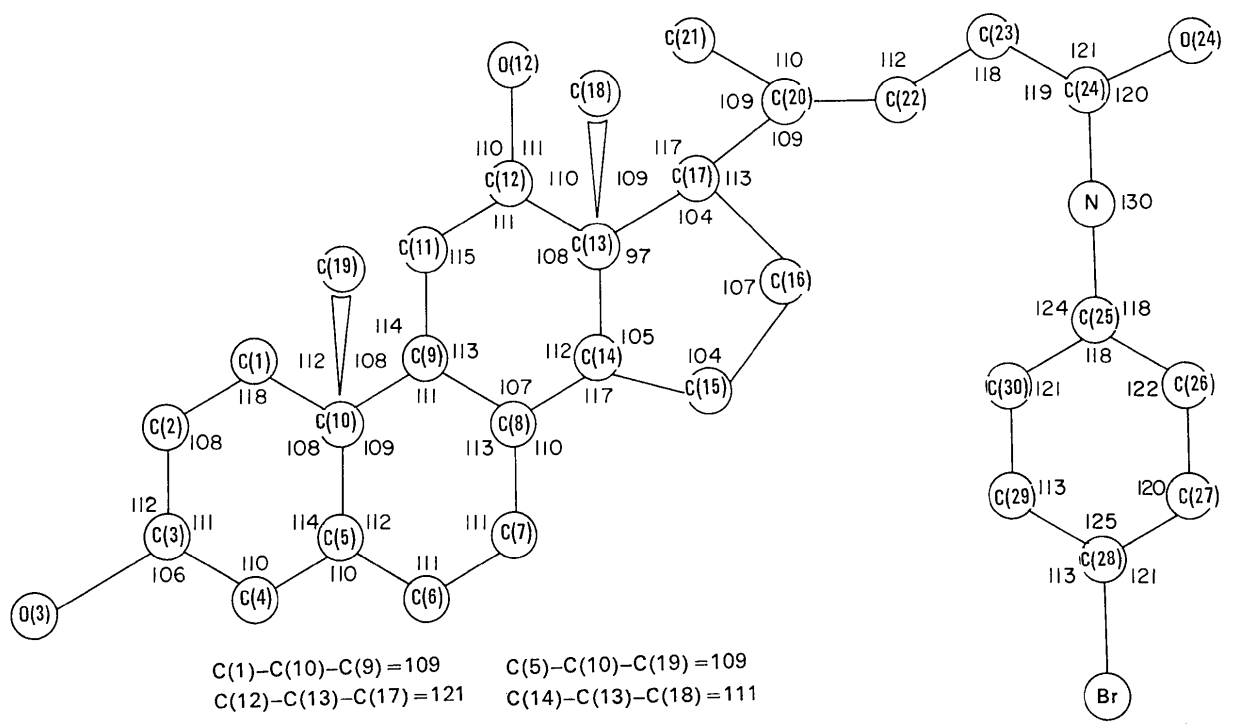


Fig. 4. Schematic drawing of desoxycholic acid *p*-bromoanilide, showing bond angles.

the dissertation of L.L.R. which was presented to the Graduate College of the University of Arizona in partial fulfillment of the requirements for the Ph.D. degree. Programs used in this investigation included Zalkin's *FORDAP* Fourier program, Busing's *ORFFE* and *ORFLS* programs, and Johnson's *ORTEP* plotting program. The necessary computations were performed on a CDC 6400 computer.

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Acta Cryst. (1972). B**28**, 1748

The Crystal Structure of 2-Amino-3-chloropyrazine, $C_4H_2N_2ClNH_2$

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The crystal structure of 2-amino-3-chloropyrazine, $C_4H_2N_2ClNH_2$, has been determined by single-crystal X-ray diffraction techniques. Crystals are orthorhombic, space group *Pbca*, with unit-cell dimensions $a=13{\cdot}880$ (4), $b=10{\cdot}685$ (4), $c=7{\cdot}196$ (4) Å; the cell contains 8 molecules. The observed and calculated densities are 1·60 and 1·612 g.cm^{-3} respectively. 648 unique intensities were obtained photometrically from film exposed to Cu $K\alpha$ radiation in an integrating Weissenberg camera. Phases were obtained by the symbolic addition method, and the structure was refined by least-squares techniques to a conventional R value of 7·7%. Pairs of planar molecules form centrosymmetric dimers through N–H···N hydrogen bonds [3·178 (8) Å]. The crystal consists of stacks of pleated sheets, formed from dimers linked with zigzag chains of other N–H···N bonds [3·275 (7) Å].

Introduction

Pyrazines are important in the synthesis of chemotherapeutic agents. They have not been studied as extensively as have the derivatives of the related diazine, pyrimidine, with which they have a number of important similarities. They possess interesting structural properties, especially when hydrogen bond networks are formed. This paper presents the crystal and molecular structure of 2-amino-3-chloropyrazine.

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Crystal data

2-Amino-3-chloropyrazine: $C_4H_2N_2ClNH_2$
F.W. 129·550
$a=13{\cdot}880$ (4), $b=10{\cdot}685$ (4), $c=7{\cdot}196$ (4) Å
Cu $K\alpha_1=1{\cdot}54051$ Å
White, acicular (c) crystals; $V=1067$ (1) Å^3
$Z=8$; $F(000)=528$
$D_x=1{\cdot}612$, $D_m=1{\cdot}60$ g.cm^{-3} (flotation in $CH_3I/CCl_4/C_6H_6$)
Linear absorption coefficient: $\mu=53$ cm^{-1} (Cu $K\alpha$)
Space group: *Pbca* (No. 61)
Absent spectra: $hk0$ for h odd; $0kl$ for k odd; $h0l$ for l odd.