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The Crystal Structure of Androsterone*

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Androsterone (5α-androstane-3α-ol-17-one, $C_{19}H_{30}O_2$) is a steroid hormone crystallizing in space group $P2_1$ with $a=9{\cdot}56$, $b=7{\cdot}90$, $c=11{\cdot}78$ Å, and $\beta=111{\cdot}36°$. Intensity data were collected with a General Electric XRD-5 diffractometer. The structure was solved by machine vector-coincidence techniques, which are discussed in some detail. Refinement was carried out with full-matrix least squares to a final R value of 4·0 %.

Molecules related by the 2_1 rotation are weakly hydrogen bonded, the hydroxyl of each one being attached to the carbonyl of the next in spiral fashion along the screw axis. The structure shows considerable strain; C–C–C bond angles vary from 99·2° to 120·8°, the greatest distortion being seen in and adjacent to the D ring.

Introduction

Androsterone was the first steroid with male sex hormone activity to be discovered. Its isolation in 1931 by Butenandt, and other aspects of early research in this area, are reviewed by Fieser & Fieser (1959, pp. 503 ff.). Androsterone is actually a metabolic product derived from testosterone, by which it is far surpassed in androgenic activity. The androsterone molecule is of structural interest, however, in that it comes closest among the naturally occurring steroid hormones to representing the completely saturated fundamental steroid nucleus. The conventional structural formula assigned to androsterone is shown in Fig. 1.

X-ray diffraction methods have been important in steroid chemistry since the work of Bernal in 1932 helped to rule out a suggested structure for cholesterol (Klyne, 1957). The first X-ray study of androsterone was made by Bernal & Crowfoot (1936) who determined the space group and unit-cell dimensions of a number of sex hormones. They were also able to deduce correctly the location of the molecules within the unit cell, from consideration of optic axes and the intense reflections. The first complete X-ray structure determination of a steroid was reported by Carlisle & Crowfoot (1945) for cholesteryl iodide. A number of crystal structures of steroids and related compounds have been reported since that time, including: calciferol 4-iodo-5-nitrobenzoate (Crowfoot & Dunitz, 1948), lanostenyl iodoacetate (Fridrichsons & Mathieson, 1953), 7α-bromocholesteryl chloride (Bürki & Nowacki, 1956), and bromomiroesterol (Taylor, Hodgkin & Rollett, 1960). Most recently, Norton, Kartha & Lu (1963, 1964) have reported the structures of two female sex-hormone derivatives, 4-bromoestrone and 4-bromoestradiol. To date, however, androsterone is the only steroid for which the crystal structure has been determined without introduction of a bromine or iodine atom. It therefore represents the only case for which accurate bond lengths and angles are available.

Experimental

A highly purified sample of crystalline androsterone was presented to us by the research division of the Schering Corporation. A more or less isometric crystal was obtained by recrystallization from an evaporating solution in diethyl ether. Its dimensions were approximately 0·19 by 0·21 by 0·13 mm. Unit-cell parameters were measured both by precession photography (assumed mean Cu $K\alpha$ wavelength of 1·5418 Å) and with a General Electric XRD-5 diffractometer (assumed Cu $K\alpha_1$ wavelength of 1·54051 Å), and found to be $a=9{\cdot}56\pm0{\cdot}02$, $b=7{\cdot}90\pm0{\cdot}03$, $c=11{\cdot}78\pm0{\cdot}02$ Å, $\beta=111{\cdot}36°\pm0{\cdot}03°$. The indicated errors are estimated standard deviations obtained by comparing the two sets of results. The crystal density measured by flotation in aqueous potassium iodide solution is 1·164 g.cm^{-3}; the density calculated for two $C_{19}H_{30}O_2$ molecules per unit cell is 1·163 g.cm^{-3}. Systematic absence of $0k0$ reflections with k odd, the optical activity of the molecule, and the measured density of the crystals

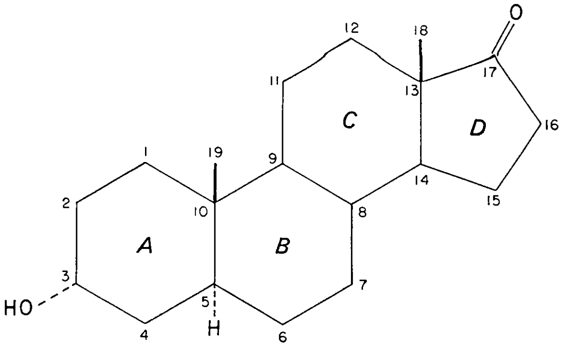

Fig. 1. Conventional structural formula of androsterone.

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* Much of the material in this communication has been abstracted from a Ph.D. thesis submitted by D.F.H. to the University of Washington in 1962.

combine to confirm the space group as $P2_1$, in agreement with the findings of Bernal & Crowfoot (1936).

Intensity data were collected on the diffractometer with Cu $K\alpha$ radiation and a 2θ-scanning technique, with background corrections calculated from the mean of the backgrounds measured on both sides of each peak. A total of 1964 independent reflections were examined, accounting for all reflections within the range of the instrument ($2\theta \le 161°$). Of these, 358 or 18% showed no visible deflection on the recorder chart and were consequently coded as unobserved. The usual Lorentz and polarization corrections were applied to the data, but not an absorption correction.

Determination of the structure

One of the principal reasons for selecting androsterone for crystallographic study was that it presented a fairly challenging problem in structure determination. It is non-centrosymmetric and the asymmetric unit contains 21 atoms of approximately equal scattering power. It was hoped that in attempting to solve such a structure by machine vector-coincidence methods we would gain further appreciation of the practical capabilities and limitations of the method for rapid and semi-automatic solution of complex crystal structure. Successful application of machine vector-coincidence to several problems of somewhat similar difficulty have previously been reported from this laboratory. The last two, harunganin (Alden, Stout, Kraut & High, 1964) and myoinositol (Rabinowitz & Kraut, 1964), were centric structures without heavy atoms, containing respectively 34 and 24 light atoms.

Since a reasonable amount of experience has now been accumulated in applying the method, it may be in order to summarize our techniques and conclusions. Similar procedures have been described recently by Hamilton (1965) and by Simpson, Dobrott, & Lipscomb (1965). The superposition functions we calculated are of the type

$$S(\mathbf{u}) = \mathrm{MIN}\, n \begin{bmatrix} P[\mathbf{u}-G_1(\mathbf{x}_1)], & P[\mathbf{u}-G_2(\mathbf{x}_1)], & \ldots, & P[\mathbf{u}-G_r(\mathbf{x}_1)], \\ P[\mathbf{u}-G_1(\mathbf{x}_2)], & P[\mathbf{u}-G_2(\mathbf{x}_2)], & \ldots, & P[\mathbf{u}-G_r(\mathbf{x}_2)], \\ \ldots & & & \\ P[\mathbf{u}-G_1(\mathbf{x}_s)], & P[\mathbf{u}-G_2(\mathbf{x}_s)], & \ldots, & P[\mathbf{u}-G_r(\mathbf{x}_s)] \end{bmatrix}$$

In this notation it is implied that the space group contains r symmetry elements $G_1 \ldots G_r$, including the identity, and that trial coordinates for s atoms $\mathbf{x}_1 \ldots \mathbf{x}_s$, are known. The MIN n function is constructed by summing, once for each point $\mathbf{u}$ on some selected grid, the smallest n of the $r\,.\,s$ Patterson points $P[\mathbf{u}-G_j(\mathbf{x}_i)]$. It is clear that if there is, in fact, an atom at $\mathbf{x}_i$, then from the general property that the Patterson function tends to give peaks at interatomic vectors, it is to be expected that for all j the $P[\mathbf{u}-G_j(\mathbf{x}_i)]$ will tend to be large at precisely those values of $\mathbf{u}$ where there are other atoms. One can easily show that $S(\mathbf{u})$ has at least the symmetry of the space group $G_1 \ldots G_r$. It may be noted in passing that the MIN n function provides a useful compromise between the more commonly applied minimum function and sum function. We have found it practical to take n approximately equal to $r\,.\,s/3$. Similar superposition functions can also be used to find the initial constellation of s trial atoms, usually just a pair unless a larger geometrical grouping (such as a benzene ring) is present in a known orientation. Since these functions were not applied to androsterone, however, they will not be discussed further in this communication.

Once the initial atom or two have been found, the coordinates of known atoms are used as input to the next round of calculations and additional atoms are sought in the output map. We have found that an efficient practical procedure for solving crystal structures of the complexity being considered here, whether centric or acentric, and whether or not they contain heavy atoms, is to arrive at the approximate coordinates of most of the atoms (say perhaps two-thirds) by successive applications of machine vector coincidence, and then to locate the rest of the atoms on electron-density maps. Our reason for preferring this particular recipe is simply that vector coincidence turns out in practice to be more powerful for locating new atoms when only a few of them are already known, while electron-density calculations appear to be more powerful after the coordinates of most of the atoms have already been established. Superposition functions exhibit an important property which makes them especially useful in the early stages of structure analysis: If incorrect atom coordinates are introduced at any stage, not only does the corresponding peak in the output fail to appear, but the entire map tends to be obliterated. Electron density maps, on the other hand, generally show anything that has been put into the structure-factor calculation, whether it is actually present in the structure or not.

The first step toward solving the structure of androsterone was, as usual, the calculation of a sharpened, origin-removed Patterson map; intervals of the grid were $a/40$, $b/40$, and $c/50$. Visual inspection revealed a set of peaks which were consistent with the existence of a pair of atoms with approximate coordinates (0·22, 0·66, 0·30) and (0·22, 0·33, 0·44). These later turned out to be atoms C(14) and C(11). A superposition map based on these two sites contained very obvious pleated sheets of six-membered rings. Unfortunately, the ring systems were indefinitely extended in the y direction. Ten of the stronger peaks, forming a double-ring system later identified as the B and C rings, were taken as atom sites for the next round of superposition calculations. Seven new peaks now accounted for the A ring, the angular methyl carbon atoms C(18) and C(19) and the hydroxyl oxygen atom O(20). Atoms C(17) and O(21) appeared in the next cycle, but the last two atoms – C(15) and C(16) of the D ring – failed to show up in a final superposition based on the other 19 atoms. However, all 19 input atoms were returned, confirming that they were probably correct. The two missing atoms were finally revealed in a three-dimensional electron-density synthesis phased on these 19 atoms.

The refinement

Refinement was carried out entirely by the method of full-matrix least-squares, using the program ORXLS written by Busing & Levy (1959). The program was run on an IBM 709 computer by means of the 704-compatibility program IBIOC2. A weighting scheme similar to that of Hughes (1941) was applied. All measurable reflections were included in the summations. As the program was set up at that time, reflections which were too weak to measure were assigned a minimum observable F_o but were included in the summations only whenever F_c exceeded this value. The residual minimized was $\Sigma w(F_o - k|F_c|)^2$. The overall scale factor k was refined at each cycle.

Atomic scattering factors for carbon and oxygen were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and for hydrogen from McWeeny (1951). Refinement followed the usual sequence; the R index was reduced from 36% to 9·7% after several cycles, the last two of which included anisotropic temperature factors. A difference map calculated at this point revealed 28 of the 30 hydrogen atoms, with peak heights ranging from 0·2 to 0·6 e.Å^{-3}. These hydrogen atoms (plus the remaining two, H(44) and H(51), which were placed in sterically reasonable locations) were introduced with an isotropic temperature factor of 4 Å^2. The R value dropped to 7·5%; it was reduced to 5·6% by several additional cycles of refinement of all parameters.

Before a final round of refinement was undertaken, the counter data were reprocessed, and 24% of the reflections were now coded as too weak to observe on the basis of counting statistics, the minimum observable intensity being taken as $2{\cdot}3\sigma$, where σ is the standard deviation of F estimated from counting statistics. The statistical R, $\Sigma\sigma(F)/\Sigma F$, was 0·028; this figure represents an approximate limit to which R could be refined if the only errors in $F_o - |F_c|$ were due to counting statistics. Four of the remaining 1496 reflections were apparently suffering from appreciable secondary extinction and were flagged so as to be omitted from subsequent refinement calculations.

Because of machine-size limitations, the final round of refinement calculations was carried out by adjusting parameters separately in three groups: all positional and thermal parameters of C(1), C(2), C(9), C(10), C(11), C(12), C(13), C(17), C(18), C(19) and O(21) comprised group 1; all parameters for the other ten C and O atoms comprised group 2; and all parameters for hydrogen atoms comprised group 3. Nine refinement cycles were run, adjusting parameters by groups in the sequence 1,2,3,3,3,1,2,1,2. The final R value was 4·0% calculated over 1492 observed and unextinguished reflections with equal weights. The average ratio of the last shift in each parameter to the estimated standard deviation of the parameter was 5·5%; the maximum ratio was 28%.

Two final difference maps were calculated as a check on the refinement. The first was computed using non-hydrogen atoms alone and showed 29 of the 30 hydrogen atoms as peaks ranging from 0·2 to 0·6 e.Å^{-3}. H(44) was still somewhat dubious as a peak of only 0·15 e.Å^{-3}. All hydrogen-atom peaks were close to but not necessarily centered at the least-squares coordinates. Fig. 2 is a composite of sections through the hydrogen atoms in this difference map.

The second difference-Fourier synthesis was based on all atoms, including hydrogen atoms with their final refined parameters. It showed no distinct peaks, and its range of electron density was −0·18 to 0·15 e.Å^{-3}.

The final values of the atomic parameters are listed with their estimated standard deviations in Tables 1, 2 and 3. The standard deviations are those output by ORXLS; no correction has been applied for the fact that the parameters were varied in groups. Observed reflection amplitudes and structure factors calculated from these parameters are listed in Table 4.

Results and discussion

The structure of a single molecule of androsterone is illustrated in Fig. 3; the arrangement of molecules is shown in Fig. 4. Molecules related by the twofold screw axes are weakly hydrogen bonded to one another, the hydroxyl group of one donating a proton to form a hydrogen bond with the carbonyl oxygen atom of the next. The hydrogen bond length, O(20)–O(21′), is 3·04 Å, unusually long, and the proton involved is fairly far off the O–O axis, the angle O(21′)–O(20)–H(51) being 12·3°.

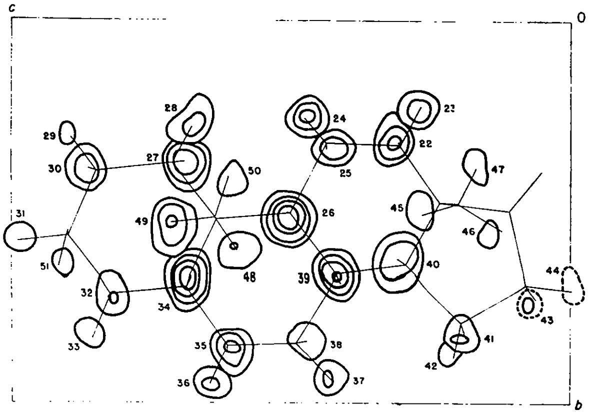

Fig. 2. Composite of sections of difference map showing hydrogen atoms. Contours are at intervals of 0·1 e.Å^{-3}, beginning at 0·2; dotted contours are at 0·15. The figure was prepared from a difference synthesis calculated at intervals of 1/40 along x; contours were drawn from a section neighboring each atom. The view is a clinographic projection along **a** onto the **b**, **c** plane. The line drawing shows the least-squares positions of the atoms.

Covalent bond lengths and angles are given in Tables 5 and 6, and for convenient reference, the C–C and C–O bond lengths are shown schematically in Fig. 5. The C–C bonds range in length from 1·491 Å for C(3)–C(4) to 1·551 Å for C(9)–C(10). The mean C–C bond length among 22 bonds is 1·530 Å, with an r.m.s. deviation of 0·017 Å. The mean e.s.d. for the individual bonds is only 0·006 Å, however. Thus the observed spread is about three times as great as expected if in fact all the bonds were of the same length. Similar analysis of the 29 C–H bond lengths yields an average length of 0·99 Å with an r.m.s. deviation of 0·07 Å and a mean e.s.d. of 0·05 Å. Bond angles, as expected, vary much more widely than bond lengths, the observed r.m.s. deviation amounting to about twelve times the mean of individual e.s.d.'s. The smallest C–C–C angle is 99·2° at C(14)–C(13)–C(17), and the largest is 120·8° at C(8)–C(14)–C(15).

Appreciable distortion of the molecule is evident in Fig. 4. Especially obvious is the splaying of the angular methyl groups. Although one might have expected

Table 1. *Positional parameters of non-hydrogen atoms, and their estimated standard deviations*

Atom	$10^4x/a$	$10^4y/b$	$10^4z/c$
C(1)	3802 (4)	3831 (4)	7108 (3)
C(2)	4102 (5)	4032 (5)	8470 (3)
C(3)	4857 (4)	5694 (5)	8973 (3)
C(4)	4025 (4)	7154 (4)	8229 (3)
C(5)	3731 (3)	6943 (4)	6867 (2)
C(6)	3005 (4)	8500 (4)	6111 (3)
C(7)	2903 (4)	8327 (4)	4815 (3)
C(8)	2123 (2)	6695 (3)	4205 (2)
C(9)	2838 (2)	5136 (3)	4998 (2)
C(10)	2873 (2)	5293 (3)	6321 (2)
C(11)	2134 (4)	3481 (4)	4366 (2)
C(12)	2166 (4)	3297 (4)	3069 (3)
C(13)	1434 (3)	4816 (4)	2313 (2)
C(14)	2190 (3)	6459 (3)	2946 (2)
C(15)	1586 (4)	7822 (5)	1964 (3)
C(16)	1548 (4)	6899 (6)	805 (3)
C(17)	1658 (3)	5024 (5)	1110 (3)
C(18)	−287 (3)	4852 (6)	1991 (3)
C(19)	1272 (3)	5268 (5)	6347 (3)
O(20)	6369 (3)	5607 (4)	8980 (2)
O(21)	1937 (3)	3943 (5)	523 (2)

Table 3. *Parameters of hydrogen atoms, and their estimated standard deviations*

Atom	$10^3x/a$	$10^3y/b$	$10^3z/c$	Isotropic temperature factor
H(22)	323 (4)	323 (5)	309 (3)	2·5 (0·7) Å^2
H(23)	168 (4)	227 (6)	267 (4)	3·1 (0·8)
H(24)	258 (3)	259 (4)	476 (3)	1·6 (0·6)
H(25)	107 (4)	340 (5)	436 (3)	2·4 (0·7)
H(26)	390 (3)	510 (4)	506 (3)	1·3 (0·5)
H(27)	483 (4)	376 (5)	689 (3)	2·2 (0·7)
H(28)	324 (4)	282 (5)	679 (3)	2·0 (0·6)
H(29)	490 (5)	312 (6)	897 (4)	4·0 (1·0)
H(30)	318 (4)	393 (5)	865 (3)	2·7 (0·7)
H(31)	498 (5)	588 (6)	989 (4)	3·6 (0·8)
H(32)	296 (5)	720 (6)	831 (4)	3·9 (0·9)
H(33)	455 (5)	829 (7)	854 (4)	5·0 (1·1)
H(34)	468 (4)	677 (6)	680 (4)	2·7 (0·7)
H(35)	194 (4)	868 (5)	615 (3)	2·7 (0·7)
H(36)	353 (4)	949 (6)	651 (4)	3·1 (0·8)
H(37)	237 (5)	937 (6)	427 (4)	3·9 (0·9)
H(38)	378 (4)	831 (5)	473 (3)	2·7 (0·7)
H(39)	108 (3)	682 (4)	412 (2)	0·6 (0·5)
H(40)	326 (4)	631 (5)	310 (4)	2·7 (0·7)
H(41)	54 (4)	822 (5)	191 (3)	2·4 (0·7)
H(42)	222 (5)	878 (7)	213 (4)	4·3 (0·9)
H(43)	251 (5)	721 (6)	64 (4)	4·2 (0·9)
H(44)	50 (7)	700 (12)	−2 (6)	9·1 (1·8)
H(45)	−60 (4)	514 (6)	265 (4)	3·8 (0·8)
H(46)	−88 (6)	556 (10)	124 (5)	7·5 (1·5)
H(47)	−65 (4)	392 (6)	168 (4)	3·8 (0·9)
H(48)	72 (6)	610 (8)	585 (6)	6·5 (1·4)
H(49)	129 (4)	543 (6)	713 (3)	2·9 (0·7)
H(50)	83 (7)	418 (9)	612 (6)	7·5 (1·6)
H(51)	668 (7)	652 (9)	917 (6)	8·1 (1·7)

Table 2. *Thermal parameters of non-hydrogen atoms, and their estimated standard deviations*

β as given here is defined by: $T=\exp[-10^{-4}(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

B_i are the thermal parameters reduced to orthogonal axes, in Å^2.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_1	B_2	B_3
C(1)	218 (5)	118 (4)	74 (2)	18 (4)	51 (3)	13 (3)	7·0 (0·2)	3·6 (0·1)	2·7 (0·1)
C(2)	277 (7)	206 (7)	73 (3)	16 (6)	58 (4)	13 (4)	9·0 (0·3)	5·2 (0·2)	3·2 (0·2)
C(3)	233 (6)	212 (7)	72 (2)	41 (5)	39 (3)	−21 (3)	8·5 (0·2)	5·0 (0·2)	3·0 (0·2)
C(4)	176 (4)	174 (6)	88 (3)	28 (4)	46 (3)	−30 (3)	6·4 (0·2)	4·9 (0·1)	2·8 (0·2)
C(5)	112 (3)	117 (4)	79 (2)	11 (3)	31 (2)	−19 (2)	4·4 (0·2)	3·5 (0·1)	2·4 (0·1)
C(6)	171 (4)	97 (4)	109 (3)	11 (3)	41 (3)	−17 (3)	6·1 (0·2)	5·1 (0·1)	2·2 (0·1)
C(7)	167 (4)	102 (4)	101 (3)	−10 (3)	38 (3)	11 (3)	5·8 (0·2)	4·8 (0·1)	2·4 (0·1)
C(8)	93 (2)	107 (4)	81 (2)	5 (3)	30 (2)	13 (2)	4·1 (0·1)	3·0 (0·1)	2·5 (0·1)
C(9)	105 (3)	107 (4)	72 (2)	4 (3)	37 (2)	5 (2)	3·6 (0·1)	3·0 (0·1)	2·6 (0·1)
C(10)	111 (3)	118 (4)	75 (2)	4 (3)	41 (2)	−2 (2)	3·8 (0·1)	3·2 (0·2)	2·8 (0·1)
C(11)	221 (6)	118 (4)	71 (2)	−20 (4)	48 (3)	2 (3)	7·2 (0·2)	3·3 (0·1)	2·8 (0·1)
C(12)	209 (5)	140 (5)	81 (3)	−2 (4)	44 (3)	−13 (3)	6·8 (0·2)	4·2 (0·1)	3·2 (0·1)
C(13)	116 (3)	177 (5)	73 (2)	−13 (3)	37 (2)	4 (3)	4·6 (0·1)	3·7 (0·1)	3·2 (0·2)
C(14)	100 (3)	138 (4)	85 (2)	−5 (3)	35 (2)	17 (2)	4·5 (0·1)	3·3 (0·1)	2·8 (0·1)
C(15)	193 (5)	201 (7)	96 (3)	11 (5)	45 (3)	45 (4)	6·5 (0·2)	6·2 (0·2)	3·2 (0·2)
C(16)	209 (5)	273 (8)	93 (3)	15 (6)	61 (3)	46 (4)	7·7 (0·2)	6·5 (0·2)	3·5 (0·2)
C(17)	117 (3)	264 (7)	75 (2)	9 (4)	36 (2)	12 (4)	6·7 (0·2)	3·7 (0·1)	3·5 (0·2)
C(18)	118 (3)	305 (9)	100 (3)	−59 (5)	40 (3)	−38 (4)	8·4 (0·2)	4·6 (0·2)	3·1 (0·1)
C(19)	146 (4)	213 (6)	117 (3)	−34 (4)	79 (3)	−14 (4)	6·6 (0·1)	5·0 (0·2)	3·0 (0·2)
O(20)	195 (4)	255 (6)	116 (3)	60 (4)	−1 (2)	−24 (3)	10·6 (0·2)	5·3 (0·2)	4·2 (0·1)
O(21)	214 (4)	327 (7)	90 (2)	31 (5)	74 (2)	−7 (3)	8·6 (0·2)	6·5 (0·1)	3·4 (0·2)

Table 4. *Observed and calculated structure factors*

Within each group of constant h and k, the columns contain from left to right: l, $10F_o$, $10|F_c|$ and the phase angle in millicycles. An asterisk indicates the estimated minimum observable $10F_o$ for reflections considered too weak to be measured. A letter E indicates a reflection omitted from the final stages of refinement because of apparent high secondary extinction.

0,0,L			
1	122	121	500
2	120	120	500
3	117	118	500
4	209	215	500
5	220	213	500
6	18*	13	500
7	48	50	500
8	69	70	500
9	23	30	500
10	106	106	000
11	17*	3	500
12	23	16	500
13	15*	4	500
14	13	11	000

0,1,L			
1	104	105	485
2	104	107	967
3	153	150	378
4	122	115	389
5	241	244	791
6	98	92	670
7	39	39	682
8	27	29	771
9	53	52	270
10	67	67	683
11	16*	15	198
12	23	20	266
13	12*	10	348

0,2,L			
0	238	246	857
1	174	188	150
2	66	61	999
3	101	99	357
4	159	167	659
5	113	111	673
6	85	81	626
7	120	119	517
8	175	179	031
9	56	54	179
10	46	45	273
11	31	30	225
12	33	31	339
13	21	21	604

0,3,L			
1	56	57	453
2	330	340	701
3	430	423	356
4	132	129	315
5	81	84	445
6	112	113	469
7	102	106	898
8	104	111	082
9	28	30	767
10	17*	16	672
11	35	33	678
12	28	27	425
13	23	24	748

0,4,L			
0	90	93	325
1	104	104	815
2	118	112	335
3	149	136	549
4	54	51	748
5	76	76	871
6	61	59	013
7	160	161	561
8	107	103	137
9	47	48	093
10	32	33	180
11	32	36	155
12	28	28	852

0,5,L			
1	103	106	569
2	87	84	683
3	17	18	682
4	39	41	479
5	22	26	698
6	74	79	241
7	77	77	194
8	39	40	988
9	20	20	286
10	37	36	854
11	20	20	508
12	8*	6	606

0,6,L			
0	239	250	121
1	176	180	519
2	51	51	166
3	39	36	142
4	77	84	815
5	36	41	689
6	17*	5	263
7	17*	13	472
8	16*	7	438
9	30	30	745
10	30	28	021
11	29	30	413

0,7,L			
1	145	147	644
2	41	42	957
3	49	48	912
4	46	50	397
5	53	53	004
6	16*	17	199
7	15*	4	258
8	13*	12	641
9	38	36	250
10	18	18	830

0,8,L			
0	16*	1	420
1	16*	14	392
2	16*	14	575
3	25	23	318
4	30	30	934
5	14*	13	947
6	13*	10	135
7	12*	4	605
8	22	21	076

0,9,L			
1	44	41	280
2	46	42	825
3	30	34	523
4	45	43	961
5	11*	12	617
6	36	37	510

0,10,L			
0	13	12	374
1	36	34	883
2	24	23	380

1,0,L			
-14	10*	2	500
-13	13*	12	500
-12	16*	21	500
-11	17*	10	500
-10	40	45	000
-9	68	66	500
-8	111	112	500
-7	63	61	500
-6	279	265	500
-5	699	724	000
-4	217	209	000
-3	271	267	000
-2	295	301	000
-1	178	176	000
0	87	78	500
1	230	237	500
2	335	342	500
3	178	175	500
4	63	58	000
5	141	136	500
6	31	29	000
7	87	88	500
8	30	28	000
9	96	96	000
10	76	75	500
11	19*	9	500
12	16*	14	500
13	12*	11	500

1,1,L			
-14	15	16	710
-13	24	24	458
-12	15	17	240
-11	17*	46	237
-10	66	69	061
-9	23	25	978
-8	48	46	935
-7	60	58	550
-6	120	114	751
-5	231	220	114
-4	43	44	420
-3	174	171	561
-2	423	460	300
-1	562E	689	331
0	605E	769	818
1	296	309	740
2	318	329	790
3	205	208	725
4	82	82	638
5	56	53	143
6	80	80	129
7	54	57	454
8	40	41	342
9	88	93	390
10	41	44	985
11	19	16	024
12	28	24	012
13	11*	15	966

1,2,L			
-14	24	25	330
-13	34	32	107
-12	21	24	465
-11	17*	14	382
-10	46	47	873
-9	92	89	762
-8	85	87	295
-7	105	102	638
-6	49	48	859
-5	130	134	882
-4	92	93	068
-3	81	80	367
-2	53	56	992
-1	178	179	575
0	101	107	942
1	178	179	778
2	407	416	517
3	58	55	987
4	24	21	691
5	100	104	127
6	104	101	117
7	156	156	224
8	38	34	719
9	17*	21	747
10	43	43	512
11	15*	16	614
12	13*	3	716
13	9*	17	434

1,3,L			
-13	22	21	344
-12	32	31	363
-11	22	21	373
-10	22	19	337
-9	34	32	309
-8	292	296	821
-7	138	146	151
-6	64	68	995
-5	76	71	768
-4	125	119	657
-3	143	131	269
-2	50	49	294
-1	139	136	399
0	195	205	449
1	393	398	450
2	224	229	763
3	275	267	131
4	93	93	120
5	80	83	825
6	112	114	734
7	231	236	311
8	131	131	767
9	17*	5	200
10	23	20	899
11	25	23	835
12	13	11	936

1,4,L			
-13	28	28	107
-12	23	21	546
-11	18	22	054
-10	25	22	939
-9	44	47	808
-8	64	61	795
-7	139	143	321
-6	15*	16	657
-5	34	37	430
-4	58	58	525
-3	111	102	596
-2	44	40	797
-1	33	31	770
0	116	118	938
1	116	116	838
2	279	274	616
3	99	97	200
4	47	45	147
5	70	70	183
6	168	171	246
7	72	72	935
8	29	32	932
9	19*	10	801
10	32	30	780
11	25	22	686
12	9*	7	493

1,5,L			
-12	40	42	632
-11	14*	17	083
-10	15	20	658
-9	59	58	820
-8	51	48	725
-7	34	38	299
-6	79	87	024
-5	49	52	189
-4	44	44	346
-3	33	34	630
-2	80	83	552
-1	90	90	288
0	117	120	717
1	47	49	194
2	32	35	059
3	48	48	006
4	64	65	233
5	29	26	164
6	19*	16	809
7	17*	7	256
8	30	32	478
9	17*	6	648
10	40	36	631
11	29	29	086

1,6,L			
-11	26	27	763
-10	31	29	970
-9	15*	8	378
-8	16*	0	030
-7	35	38	929
-6	106	111	550
-5	81	87	136
-4	55	58	512
-3	80	82	305
-2	137	138	304
-1	145	152	858
0	106	115	858
1	87	90	254
2	16*	13	613
3	37	41	654
4	17*	3	711
5	57	63	596
6	38	44	996
7	16	12	372
8	26	30	279
9	46	39	008
10	41	40	683

1,7,L			
-10	10	12	890
-9	27	25	596
-8	14*	10	276
-7	23	23	552
-6	46	44	084
-5	54	59	269
-4	58	60	617
-3	24	25	708
-2	43	42	951
-1	80	82	473
0	117	116	912
1	37	36	377
2	47	50	090
3	34	42	175
4	17*	18	904
5	16*	17	496
6	15*	11	373
7	24	21	661
8	38	34	018
9	37	37	542

1,8,L			
-9	35	38	853
-8	16	16	235
-7	12*	8	697
-6	30	30	238
-5	19	17	456
-4	15*	16	694
-3	28	29	486
-2	23	22	137
-1	16*	11	884
0	20	21	073
1	16*	25	998
2	16*	19	558
3	15*	13	043
4	22	23	576
5	14*	13	281
6	12*	10	742
7	11*	8	559
8	25	24	761

1,9,L			
-6	17	19	832
-5	11*	15	215
-4	19	18	652
-3	13*	11	125
-2	13*	14	821
-1	13*	11	240
0	24	24	883
1	36	36	553
2	19	19	800
3	40	40	183
4	27	26	572
5	31	30	266

1,10,L			
-2	16	17	934
-1	8*	8	541
0	8*	9	552
1	20	20	058

2,0,L			
-14	11*	3	500
-13	14*	9	500
-12	13*	10	500
-11	33	37	000
-10	17*	2	000
-9	23	25	500
-8	111	109	000
-7	135	127	000
-6	43	41	000
-5	177	174	000
-4	47	47	500
-3	209	206	500
-2	179	174	500
-1	770E	1116	000
0	526E	666	500
1	140	129	500
2	265	266	500
3	92	85	500
4	44	45	500
5	47	44	000
6	35	36	000
7	44	44	500
8	48	47	500
9	83	88	000
10	22	25	500
11	29	31	000
12	18	21	000

2,1,L			
-14	14	13	054
-13	13	14	966
-12	21	19	137
-11	45	45	047
-10	31	31	832
-9	29	30	629
-8	90	84	723
-7	87	99	239
-6	343	333	311
-5	83	75	745
-4	139	136	550
-3	305	305	694
-2	205	208	787
-1	292	297	860
0	264	260	759
1	134	139	042
2	154	161	624
3	75	74	265
4	199	194	248
5	86	87	287
6	67	70	331
7	30	28	203
8	29	29	057
9	80	82	789
10	16*	33	146
11	14*	6	951
12	12*	10	523

2,2,L			
-14	21	26	727
-13	26	25	247
-12	28	25	575
-11	16*	15	826
-10	67	62	975
-9	123	126	995
-8	114	112	580
-7	32	29	670
-6	75	74	555
-5	85	90	982
-4	12*	11	965
-3	83	86	583
-2	101	100	349
-1	286	287	619
0	189	191	145
1	252	252	091
2	216	219	310
3	53	52	188
4	41	40	188
5	33	31	483
6	17	19	585
7	97	100	924
8	62	59	462
9	48	49	433
10	16*	1	411
11	14*	7	074
12	11*	10	971

2,3,L			
-14	33	34	241
-13	45	43	839
-12	19	21	171
-11	38	37	947
-10	24	27	992
-9	118	118	708
-8	57	58	311
-7	51	51	056
-6	29	28	619
-5	89	92	465
-4	95	90	389
-3	114	108	408
-2	115	117	415
-1	101	104	285
0	107	108	941
1	347	345	777
2	422	411	290
3	76	76	819
4	65	65	445
5	67	63	473
6	83	89	921
7	75	82	951
8	56	58	804
9	17*	13	218
10	15*	6	638
11	13*	9	450
12	9*	6	398

2,4,L			
-13	42	42	899
-12	35	29	263
-11	21	16	222
-10	34	28	068
-9	30	30	261
-8	159	162	519
-7	26	29	076
-6	52	50	647
-5	22	23	867
-4	98	101	679
-3	44	43	773
-2	85	84	932
-1	47	43	558
0	102	99	895
1	242	244	248
2	119	119	392
3	107	105	124
4	71	70	076
5	50	48	974
6	114	118	672
7	61	58	078
8	17*	14	695
9	16*	14	479
10	14*	9	576
11	11*	9	647

2,5,L			
-12	11*	8	058
-11	14*	7	142
-10	19	19	919
-9	27	24	420
-8	43	42	753
-7	18*	17	683
-6	88	95	232
-5	29	30	314
-4	64	62	441
-3	18	14	976
-2	77	76	034
-1	25	21	211
0	40	39	933
1	26	29	635
2	15*	20	891
3	30	29	505
4	37	33	399
5	26	27	303
6	17*	19	301
7	29	33	755
8	25	26	811
9	38	36	886
10	27	28	294
11	16	13	804

2,6,L			
-11	20	16	991
-10	13*	3	717
-9	25	25	570
-8	28	26	401
-7	78	83	371
-6	30	27	645
-5	69	73	921
-4	52	51	141
-3	44	42	068
-2	97	101	630
-1	160	161	076
0	157	158	531
1	60	62	993
2	27	30	696
3	28	28	593
4	17*	14	524
5	22	23	899
6	38	36	181
7	20	16	964
8	42	40	744
9	29	26	099
10	45	44	448

2,7,L			
-10	11	11	702
-9	14	16	183
-8	14*	7	687
-7	15*	14	545
-6	53	51	477
-5	81	82	893
-4	46	47	439
-3	25	24	013
-2	104	107	142
-1	23	22	897
0	80	82	651
1	56	58	126
2	19*	23	841
3	14*	16	380
4	18*	6	345
5	15	11	713
6	25	26	608
7	23	22	575
8	35	32	273
9	24	24	857

2,8,L			
-9	23	21	084
-8	19	18	430
-7	23	20	304
-6	21	21	697
-5	26	28	998
-4	15*	7	329
-3	16*	10	838
-2	23	24	221
-1	16*	19	766
0	17*	12	594
1	17*	13	550
2	25	20	510
3	16*	7	902
4	14*	5	077
5	13*	8	764
6	12*	8	065
7	21	20	044

2,9,L			
-6	15	14	161
-5	22	21	520
-4	23	19	010
-3	13*	8	480
-2	32	29	760
-1	13*	5	471
0	53	53	271
1	41	42	788
2	44	39	415
3	51	52	937
4	13*	15	451
5	18	17	534

3,0,L			
-14	12*	2	500
-13	21	22	000
-12	17	16	000
-11	17*	5	000
-10	32	33	000
-9	16*	3	500
-8	35	32	500
-7	216	206	500
-6	405	397	000
-5	53	51	500
-4	25	26	000
-3	51	49	500
-2	44	45	000
-1	595	650	500
0	165	169	500
1	124	119	000
2	77	74	500
3	72	71	500
4	24	20	000
5	14*	1	500
6	30	28	000
7	95	94	000
8	90	95	000
9	87	86	500
10	15*	15	000
11	13*	3	000
12	9*	6	500

3,1,L			
-14	20	19	513
-13	26	20	856
-12	26	21	145
-11	16	14	057
-10	22	20	486
-9	42	40	514
-8	110	110	562
-7	76	74	558
-6	143	137	094
-5	191	187	700
-4	100	97	672
-3	150	149	795
-2	9*	10	571
-1	259	263	902
0	75	72	223
1	143	143	283
2	157	158	311
3	92	91	270
4	98	100	199
5	66	64	100
6	67	66	749
7	39	40	765
8	41	44	559
9	56	56	012
10	30	29	268
11	12*	1	548
12	11	10	783

3,2,L			
-14	44	42	996
-13	24	23	706
-12	15	18	773
-11	42	46	827
-10	69	71	852
-9	81	81	385
-8	94	90	615
-7	15	19	164
-6	44	46	602
-5	67	72	136
-4	67	68	154
-3	93	101	403
-2	114	114	296
-1	155	149	196
0	43	41	947
1	126	118	402
2	94	93	847
3	63	67	562
4	14*	6	621
5	28	26	907
6	53	55	126
7	48	49	645
8	25	29	605
9	16*	11	482
10	14*	15	856
11	12*	13	959
12	7*	6	991

3,3,L			
-14	9*	8	612
-13	17	14	603
-12	15*	13	458
-11	16*	9	663
-10	21	23	472
-9	131	134	815
-8	100	101	261
-7	92	93	428
-6	87	84	459
-5	40	42	317
-4	37	40	261
-3	49	50	865
-2	55	56	862
-1	96	100	363
0	175	169	445
1	104	105	884
2	157	158	105
3	91	90	813
4	45	45	876
5	73	74	865
6	101	106	286
7	129	128	758
8	17*	10	197
9	16*	7	190
10	26	25	339
11	10*	15	310

3,4,L			
-13	35	35	484
-12	13*	13	305
-11	20	20	608
-10	25	22	684
-9	59	57	671
-8	84	82	291
-7	34	31	791
-6	54	57	609
-5	72	72	852
-4	80	83	990
-3	33	33	099
-2	120	128	191
-1	90	84	128
0	46	43	231
1	146	135	629
2	114	112	122
3	35	35	849
4	16*	6	574
5	34	34	412
6	74	77	896
7	17*	24	720
8	49	50	495
9	14*	12	589
10	12*	8	585
11	8*	5	498

3,5,L			
-13	36	36	687
-12	12*	14	121
-11	14*	8	954
-10	21	20	924
-9	27	23	539
-8	53	52	313
-7	74	75	118
-6	59	59	290
-5	18	13	981
-4	18	17	652
-3	56	56	770
-2	22	25	139
-1	72	72	684
0	35	38	143
1	31	33	558
2	45	44	542
3	15*	12	202
4	23	25	084
5	17*	18	948
6	33	32	843
7	20	22	533
8	15*	15	885
9	26	24	590
10	28	29	136

3,6,L			
-12	13	10	703
-11	12*	5	357
-10	24	23	297
-9	15*	5	599
-8	30	26	970
-7	82	80	569
-6	114	115	058
-5	25	21	499
-4	36	31	142
-3	34	32	371
-2	107	107	881
-1	63	65	664
0	51	52	281
1	17*	9	271
2	34	33	677
3	24	21	606
4	25	19	972
5	16*	22	983
6	16*	9	187
7	25	25	299
8	20	18	122
9	50	48	561

3,7,L			
-10	11*	3	657
-9	14	13	477
-8	25	23	683
-7	40	41	097
-6	48	49	195
-5	50	50	664
-4	25	25	090
-3	50	54	995
-2	60	62	551
-1	60	61	901
0	50	46	271
1	17*	5	347
2	39	39	513
3	20	18	784
4	19	21	534
5	21	19	385
6	13*	3	964
7	37	34	065
8	34	34	595

3,8,L			
-9	18	17	354
-8	12*	13	675
-7	28	28	227
-6	16	12	617
-5	23	21	740
-4	15*	6	465
-3	15*	10	022
-2	16*	7	484
-1	16*	5	438
0	16	17	750
1	15*	15	392
2	25	22	977
3	14*	12	536
4	18	15	190
5	15	14	842
6	9*	6	634

3,9,L			
-6	9*	4	396
-5	10*	5	086
-4	11*	6	666
-3	13	11	622
-2	18	18	181
-1	12*	7	990
0	39	36	589
1	19	19	938
2	38	37	181
3	31	31	603
4	23	23	254

4,0,L			
-15	15	15	000
-14	12*	9	000
-13	13*	13	000
-12	17	12	500
-11	31	34	500
-10	17*	7	500
-9	56	55	000
-8	23	17	500
-7	46	43	000
-6	108	107	500
-5	91	90	500
-4	47	46	000
-3	148	141	500
-2	306	302	000
-1	445	450	500
0	105	98	500
1	68	69	000
2	60	58	000
3	73	73	000
4	78	79	000
5	73	76	000
6	53	58	000
7	17*	12	500
8	17*	7	000
9	47	46	500
10	23	21	000
11	11*	3	000

4,1,L			
-15	7*	6	178
-14	15	15	812
-13	24	24	722
-12	16*	14	629
-11	27	30	533
-10	60	62	572
-9	47	46	622
-8	22	23	036
-7	128	125	292
-6	133	134	801
-5	80	81	776
-4	38	42	925
-3	99	95	914
-2	162	162	918
-1	288	288	297
0	269	270	232
1	56	55	459
2	41	40	083
3	35	34	828
4	50	49	846
5	17	19	496
6	24	23	750
7	17*	10	838
8	60	64	806
9	47	46	295
10	15	18	316
11	10*	14	614

4,2,L			
-14	11*	12	239
-13	27	23	656
-12	16*	11	849
-11	17*	7	293
-10	59	60	089
-9	91	96	556
-8	40	40	402
-7	78	79	325
-6	89	85	186
-5	77	79	128
-4	107	107	142
-3	72	73	343
-2	57	62	564
-1	35	34	351
0	43	44	696
1	48	46	905
2	75	76	789
3	47	45	601
4	15*	8	139
5	16*	9	899
6	85	87	927
7	40	38	371
8	47	49	435
9	15*	5	826
10	13	12	882
11	15	14	009

4,3,L			
-14	52	50	785
-13	13*	2	583
-12	15*	4	708
-11	16*	7	464
-10	54	53	662
-9	130	130	312
-8	22	23	758
-7	28	30	722
-6	57	57	241
-5	50	49	078
-4	14	10	833
-3	30	29	439
-2	40	41	788
-1	48	46	088
0	209	204	849
1	265	266	260
2	157	158	760
3	68	70	747
4	16*	9	299
5	52	54	067
6	50	51	834
7	35	36	509
8	47	45	368
9	25	22	363
10	18	16	307

4,4,L			
-13	11*	35	297
-12	16	16	383
-11	15*	18	545
-10	16	16	246
-9	77	76	539
-8	76	75	931
-7	33	31	963
-6	49	46	048
-5	42	46	084
-4	63	63	103
-3	50	53	157
-2	48	47	402
-1	44	42	668
0	97	99	382
1	15*	14	939
2	91	91	917
3	43	42	574
4	17*	10	792
5	88	88	671
6	50	50	168
7	16*	16	414
8	22	23	448
9	12*	6	467
10	9*	6	660

4,5,L			
-13	21	19	176
-12	18	17	229
-11	15*	16	209
-10	32	34	318
-9	16*	7	404
-8	23	30	879
-7	66	67	235
-6	16	15	615
-5	30	32	751
-4	33	32	729
-3	21	28	879
-2	56	58	691
-1	18	17	420
0	28	27	493
1	26	25	845
2	24	22	415
3	32	32	976
4	17*	18	037
5	26	26	217
6	24	24	730
7	24	24	685
8	13*	11	813
9	37	37	258

4,6,L			
-12	8*	6	375
-11	11*	3	544
-10	13*	11	729
-9	15*	6	958
-8	43	43	376
-7	57	55	951
-6	56	54	893
-5	40	37	203
-4	19	19	050
-3	100	104	666
-2	81	82	180
-1	124	125	506
0	69	68	875
1	32	31	861
2	17*	11	404
3	26	22	209
4	16*	15	246
5	39	35	269
6	14*	8	929
7	33	30	730
8	13	18	238

4,7,L			
-10	10*	12	096
-9	12*	6	706
-8	14*	12	000
-7	43	38	477
-6	68	72	891
-5	33	36	288
-4	17*	13	134
-3	29	29	241
-2	39	43	759
-1	76	77	574
0	47	47	168
1	21	21	703
2	16*	16	313
3	15*	9	451
4	19	16	908
5	13*	7	300
6	11*	4	824
7	24	23	371

4,8,L			
-9	17	16	509
-8	10*	5	253
-7	24	22	718
-6	23	21	976
-5	16	13	440
-4	14*	6	111
-3	15*	9	439
-2	15*	12	657
-1	13*	13	623
0	15*	4	814
1	14*	7	095
2	18	16	963
3	12*	10	160
4	11*	4	410
5	10	7	546

4,9,L			
-6	14	14	457
-5	9*	7	030
-4	17	15	587
-3	11*	8	770
-2	11*	7	739
-1	40	39	315
0	40	40	860
1	10*	40	345
2	42	40	866

5,0,L			
-15	7*	4	000
-14	14	10	000
-13	20	18	500
-12	32	31	500
-11	28	30	500
-10	17*	11	500
-9	16*	0	000
-8	138	136	500
-7	249	254	000
-6	119	122	500
-5	39	39	500
-4	107	99	000
-3	64	64	500
-2	418	432	500
-1	48	49	000
0	136	128	000
1	205	200	000
2	130	123	000
3	50	49	000
4	18	19	500
5	17*	5	500
6	20*	20	000
7	30	27	000
8	140	135	500
9	16*	12	000
10	12*	7	000

5,1,L			
-15	30	32	553
-14	15	13	716
-13	23	17	714
-12	23	25	418
-11	25	27	397
-10	17*	14	754
-9	23	29	354
-8	38	42	782
-7	138	141	963
-6	39	40	346
-5	83	87	205
-4	106	103	174
-3	122	115	269
-2	184	162	816
-1	115	110	256
0	50	48	261
1	39	40	781
2	38	41	668
3	63	64	773
4	16*	11	393
5	17*	25	350
6	17*	21	673
7	32	35	565
8	40	38	051
9	12*	13	328
10	10*	5	692

5,2,L			
-14	28	27	614
-13	14*	6	507
-12	16	10	307
-11	28	32	532
-10	89	91	383
-9	22	24	067
-8	60	60	171
-7	71	69	125
-6	46	46	224
-5	29	30	503
-4	36	36	784
-3	105	101	674
-2	45	44	702
-1	87	87	754
0	102	103	550
1	176	177	932
2	57	58	083
3	40	42	337
4	21	21	148
5	15*	10	155
6	51	50	561
7	16*	14	602
8	17	17	592
9	12*	5	854
10	16	15	065

5,3,L			
-14	24	23	454
-13	14	15	597
-12	17	15	560
-11	16*	26	343
-10	76	78	909
-9	79	80	220
-8	30	32	540
-7	16*	16	695
-6	60	61	211
-5	60	60	869
-4	15	11	920
-3	40	42	744
-2	74	76	797
-1	44	49	406
0	107	110	077
1	100	103	950
2	81	80	662
3	18*	27	528
4	17*	7	267
5	127	127	334
6	70	71	684
7	28	27	337
8	14*	7	035
9	12	12	114

5,4,L			
-13	11*	2	655
-12	13	14	726
-11	30	28	662
-10	30	32	853
-9	91	95	112
-8	29	28	873
-7	22	24	265
-6	16	17	990
-5	20	21	184
-4	15	18	294
-3	25	21	636
-2	42	40	586
-1	36	36	432
0	156	156	680
1	133	134	076
2	16*	17	950
3	60	64	463
4	53	49	400
5	40	37	931
6	27	27	712
7	18	19	469
8	12*	5	659
9	9*	4	191

5,5,L			
-13	15	15	028
-12	10*	8	220

Table 4 (*cont.*)

5,5,L			
-11	13•	8	187
-10	15•	9	846
-9	45	42	297
-8	46	48	044
-7	42	44	620
-6	47	47	685
-5	40	38	732
-4	56	56	700
-3	36	35	444
-2	65	67	785
-1	57	59	150
0	45	45	197
1	23	21	200
2	14•	9	200
3	17•	12	827
4	17•	8	768
5	16•	13	586
6	22	20	511
7	12•	5	457
8	16	13	494
5,6,L			
-12	7•	4	132
-11	11•	4	083
-10	21	16	994
-9	35	34	021
-8	62	61	654
-7	101	102	091
-6	72	70	473
-5	26	29	597
-4	18	16	560
-3	66	67	851
-2	60	58	575
-1	62	61	176
0	17•	6	485
1	17•	13	236
2	17•	13	256
3	22	18	169
4	29	27	362
5	13	16	774
6	12•	9	678
7	20	23	071
5,7,L			
-10	9•	1	265
-9	11•	8	569
-8	29	30	101
-7	23	21	158
-6	67	65	579
-5	30	28	070
-4	24	23	842
-3	69	70	571
-2	43	43	924
-1	59	60	245
0	17	18	244
1	15•	10	471
2	15•	12	574
3	15	16	782
4	12•	6	499
5	13	13	132
6	19	25	042
5,8,L			
-8	9•	8	235
-7	11	10	430
-6	25	25	666
-5	13•	4	514
-4	18	15	061
-3	12•	13	824
-2	14•	7	181
-1	13	11	128
0	13•	10	397
1	26	21	008
2	12•	11	395
3	10•	9	407
4	9	6	540
5,9,L			
-5	16	17	805
-4	8•	5	457
-3	14	14	168
-2	14	14	064
-1	33	33	614
0	28	27	086
6,0,L			
-14	11•	9	500
-13	58	52	500
-12	16•	10	000
-11	17•	6	500
-10	30	31	000
-9	83	82	000
-8	50	52	000
-7	154	155	500
-6	69	71	500
-5	59	53	500
-4	34	33	000
-3	226	216	000
-2	113	108	500
-1	165	165	000
0	81	85	000
1	54	55	000
2	64	68	000
3	128	124	500
4	61	59	500
5	17•	7	500
6	40	38	500
7	15•	5	000
8	14•	6	500
9	27	30	000
6,1,L			
-14	12	11	368
-13	19	19	643
-12	16•	8	802
-11	25	28	306
-10	31	32	050
-9	78	79	118
-8	112	113	248
-7	145	149	769
-6	62	63	247
-5	56	56	118
-4	93	92	845
-3	68	61	837
-2	93	89	476
-1	65	61	293
0	73	72	356
1	26	24	744
2	48	44	640
3	42	42	756
4	17•	17	573
5	17•	10	186
6	22	19	903
7	68	65	840
8	45	46	333
9	10•	4	261
6,2,L			
-14	15	14	487
-13	16	11	380
-12	40	36	221
-11	44	47	216
-10	41	47	562
-9	81	80	068
-8	25	23	468
-7	27	22	795
-6	59	55	734
-5	95	95	626
-4	78	77	889
-3	76	77	889
-2	30	29	479
-1	75	74	130
0	44	45	997
1	17•	20	974
2	17	22	325
3	64	67	513
4	61	59	537
5	44	43	872
6	20	21	358
7	23	24	214
8	13	18	070
9	8•	8	106
6,3,L			
-14	19	19	235
-13	17	15	911
-12	20	18	938
-11	17	12	234
-10	87	87	265
-9	33	33	772
-8	30	31	716
-7	41	40	863
-6	15•	7	981
-5	33	33	929
-4	31	32	914
-3	15	13	547
-2	48	47	915
-1	104	106	876
0	277	274	302
1	149	152	679
2	69	72	535
3	40	39	381
4	33	36	051
5	21	27	892
6	19	17	264
7	13•	4	164
8	11•	4	135
6,4,L			
-13	11	12	738
-12	12•	8	092
-11	23	22	171
-10	31	29	490
-9	78	75	977
-8	24	28	677
-7	17•	6	265
-6	25	27	352
-5	72	76	622
-4	33	32	070
-3	19	14	665
-2	62	62	545
-1	97	98	303
0	28	30	115
1	70	70	872
2	27	25	513
3	26	30	636
4	55	53	680
5	15•	35	142
6	12•	3	499
7	22	22	151
8	14	14	193
6,5,L			
-12	10•	3	400
-11	26	29	394
-10	13•	13	838
-9	41	40	795
-8	44	41	456
-7	86	84	729
-6	22	25	692
-5	26	26	020
-4	54	54	083
-3	22	22	420
-2	43	46	171
-1	25	21	329
0	33	34	352
1	17•	8	641
2	30	32	688
3	23	22	637
4	21	21	059
5	14•	8	226
6	12•	6	068
7	12	10	857
6,6,L			
-11	10•	7	644
-10	12•	7	563
-9	38	36	335
-8	47	47	901
-7	37	33	666
-6	32	28	285
-5	30	27	728
-4	47	43	694
-3	81	84	212
-2	81	83	463
-1	31	32	031
0	16•	17	770
1	16•	8	550
2	46	43	076
3	26	25	611
4	13•	12	243
5	26	24	852
6	35	34	751
6,7,L			
-10	8•	6	950
-9	10•	5	086
-8	47	48	530
-7	74	74	850
-6	44	42	290
-5	21	19	140
-4	14•	16	221
-3	16	12	552
-2	32	32	493
-1	26	28	108
0	21	17	627
1	20	17	033
2	31	27	621
3	24	24	842
4	19	21	096
6,8,L			
-7	20	19	016
-6	19	20	264
-5	11•	8	036
-4	11•	9	261
-3	12•	4	046
-2	14	15	597
-1	24	23	296
0	11•	10	730
1	15	16	777
2	12	12	145
7,0,L			
-14	11•	11	000
-13	13•	3	500
-12	15•	9	000
-11	16•	16	000
-10	31	33	500
-9	37	35	500
-8	154	158	000
-7	131	131	500
-6	59	58	000
-5	70	70	000
-4	54	54	000
-3	94	88	500
-2	44	38	000
-1	22	17	000
0	15•	12	000
1	55	55	500
2	17•	8	500
3	67	67	500
4	17•	9	500
5	43	44	000
6	39	39	000
7	73	71	500
8	37	39	000
7,1,L			
-14	20	20	176
-13	46	45	263
-12	15•	15	852
-11	34	36	158
-10	53	51	214
-9	63	63	783
-8	96	92	899
-7	70	71	649
-6	29	27	236
-5	84	85	259
-4	55	50	426
-3	53	55	597
-2	66	62	375
-1	56	54	717
0	23	22	259
1	47	44	732
2	118	119	808
3	17•	10	307
4	17•	20	094
5	16•	15	187
6	33	34	355
7	24	24	174
8	14	15	376
7,2,L			
-14	27	29	092
-13	20	16	339
-12	14•	13	585
-11	34	35	427
-10	39	40	790
-9	60	61	955
-8	60	62	899
-7	72	72	606
-6	16	14	217
-5	26	26	725
-4	39	42	933
-3	79	81	071
-2	57	58	543
-1	107	111	477
0	89	87	906
1	41	41	456
2	31	28	232
3	17•	9	268
4	24	18	322
5	25	17	252
6	22	20	014
7	11•	14	909
8	7•	5	005
7,3,L			
-13	10•	5	394
-12	13•	5	865
-11	24	25	995
-10	18	26	201
-9	44	43	732
-8	17•	10	498
-7	34	33	907
-6	66	67	833
-5	110	107	284
-4	30	29	686
-3	60	58	528
-2	94	96	432
-1	38	38	144
0	37	35	829
1	39	39	659
2	24	26	928
3	32	28	032
4	42	45	278
5	14•	18	723
6	28	28	296
7	13	15	766
7,4,L			
-13	23	23	741
-12	12	9	699
-11	13	14	946
-10	25	24	061
-9	20	21	751
-8	18	11	512
-7	37	41	563
-6	50	49	266
-5	48	47	429
-4	17•	14	780
-3	26	24	151
-2	37	34	488
-1	99	97	715
0	106	108	041
1	55	53	680
2	27	21	320
3	32	33	301
4	19	19	169
5	13•	7	162
6	11•	6	227
7,5,L			
-12	22	23	725
-11	20	21	662
-10	13	13	326
-9	44	44	973
-8	51	48	600
-7	35	32	876
-6	30	30	152
-5	48	49	310
-4	37	37	289
-3	35	37	638
-2	24	24	306
-1	24	25	922
0	27	22	286
1	16•	19	965
2	28	31	790
3	14•	11	206
4	14	11	951
5	11•	12	372
6	19	20	367
7,6,L			
-11	11	10	188
-10	10•	10	870
-9	36	38	718
-8	72	70	110
-7	83	83	479
-6	14•	16	378
-5	21	18	565
-4	17	18	933
-3	18	13	462
-2	32	34	035
-1	15•	4	511
0	16	16	029
1	40	37	808
2	27	26	092
3	31	30	401
4	19	18	701
7,7,L			
-9	24	26	037
-8	13	14	227
-7	39	39	534
-6	12•	31	098
-5	13•	7	566
-4	21	28	599
-3	13•	11	867
-2	23	24	232
-1	25	27	886
0	12•	2	644
1	11•	4	352
2	22	22	914
3	27	23	399
7,8,L			
-6	26	25	264
-5	9•	5	757
-4	16	17	723
-3	10	9	204
-2	12	10	959
-1	13	12	482
0	24	24	981
8,0,L			
-14	8•	8	500
-13	52	50	000
-12	15	11	500
-11	26	26	000
-10	36	33	000
-9	59	63	000
-8	77	75	500
-7	45	46	500
-6	17•	1	000
-5	15•	8	500
-4	34	30	000
-3	19•	5	000
-2	28	21	000
-1	55	54	500
0	18	19	000
1	53	52	000
2	88	86	500
3	20	23	000
4	15•	8	500
5	30	28	500
6	11•	4	000
7	8	10	000
8,1,L			
-14	8•	7	610
-13	18	18	043
-12	33	27	764
-11	28	28	917
-10	38	36	142
-9	26	21	373
-8	99	103	690
-7	68	67	345
-6	17•	4	740
-5	44	42	304
-4	32	28	701
-3	56	55	597
-2	18	18	848
-1	51	51	837
0	34	34	917
1	17•	21	254
2	17•	15	838
3	48	48	309
4	32	31	259
5	13•	13	160
6	25	25	895
8,2,L			
-13	21	20	991
-12	11	10	653
-11	24	26	780
-10	33	36	992
-9	16•	14	648
-8	39	41	968
-7	45	47	568
-6	60	65	477
-5	43	43	966
-4	17•	12	668
-3	19	23	267
-2	37	35	262
-1	17•	4	699
0	45	42	185
1	22	23	283
2	16•	3	491
3	16•	9	449
4	19	19	748
5	12•	4	748
6	10•	7	939
8,3,L			
-13	9•	7	234
-12	13	15	817
-11	27	29	299
-10	13•	14	648
-9	31	28	815
-8	16•	7	664
-7	48	46	472
-6	17•	12	413
-5	55	51	313
-4	21	21	544
-3	35	38	846
-2	72	72	894
-1	106	107	278
0	101	98	732
1	46	48	295
2	16•	9	183
3	15•	5	187
4	13•	7	815
5	11•	13	241
6	8•	4	479
8,4,L			
-12	10•	5	383
-11	23	20	346
-10	14	12	854
-9	26	27	562
-8	36	38	182
-7	47	49	429
-6	58	60	591
-5	60	55	026
-4	53	52	767
-3	16	15	916
-2	41	37	204
-1	27	30	161
0	21	25	913
1	32	33	445
2	15•	11	202
3	13•	3	734
4	14	13	376
5	9•	6	737
8,5,L			
-11	12	13	955
-10	11•	11	952
-9	21	26	368
-8	36	36	693
-7	28	28	313
-6	22	22	046
-5	48	50	238
-4	16•	5	705
-3	22	18	001
-2	13	12	509
-1	20	19	948
0	21	21	927
1	16	22	487
2	23	22	642
3	11•	4	328
4	8•	10	434
8,6,L			
-10	25	25	395
-9	25	24	941
-8	30	30	538
-7	12•	9	423
-6	12•	11	817
-5	21	17	832
-4	27	30	141
-3	14•	8	236
-2	28	28	962
-1	17	17	657
0	12	12	374
1	23	22	072
2	43	43	545
3	19	18	146
8,7,L			
-7	36	37	283
-6	21	20	913
-5	13	11	411
-4	11•	8	052
-3	11•	5	582
-2	10•	2	054
-1	9•	11	932
0	20	18	113
9,0,L			
-13	20	25	000
-12	13	14	500
-11	14•	20	500
-10	34	36	500
-9	39	39	000
-8	56	54	500
-7	19	20	000
-6	16•	18	500
-5	17•	19	000
-4	37	30	500
-3	53	48	000
-2	18	16	000
-1	27	26	500
0	43	43	500
1	14	12	500
2	15•	30	500
3	27	26	000
4	12•	8	000
5	11•	20	000
9,1,L			
-13	32	30	748
-12	12•	6	712
-11	14•	7	496
-10	20	24	561
-9	42	41	834
-8	50	51	520
-7	30	30	274
-6	17•	10	980
-5	19	17	373
-4	17•	1	559
-3	27	32	840
-2	16•	23	847
-1	31	32	217
0	14•	13	306
1	29	29	955
2	46	44	340
3	13•	15	885
4	12•	11	851
5	10	10	498
9,2,L			
-13	22	23	895
-12	24	25	539
-11	13•	13	858
-10	16	13	963
-9	15•	14	789
-8	33	34	538
-7	40	42	327
-6	20	19	544
-5	46	48	074
-4	31	32	161
-3	16	12	202
-2	41	43	426
-1	35	33	857
0	38	33	428
1	15•	13	904
2	14•	21	733
3	13•	5	014
4	11•	6	483
5	8•	7	886
9,3,L			
-12	10•	8	640
-11	14	14	695
-10	15	17	448
-9	19	20	340
-8	15•	13	740
-7	38	37	809
-6	71	73	249
-5	32	32	790
-4	16•	6	314
-3	17	16	463
-2	23	22	231
-1	51	54	780
0	13•	9	340
1	30	33	222
2	12•	10	895
3	12•	5	567
4	9•	7	862
9,4,L			
-11	11	12	275
-10	16	16	517
-9	12•	10	661
-8	14•	6	738
-7	16	14	134
-6	13•	18	365
-5	43	45	951
-4	15•	8	153
-3	22	22	206
-2	34	35	769
-1	30	33	147
0	46	48	552
1	13•	4	128
2	12•	1	718
3	9•	11	056
9,5,L			
-10	26	25	158
-9	25	25	600
-8	21	23	002
-7	28	30	235
-6	16	16	259
-5	13	12	135
-4	13	16	673
-3	11•	13	754
-2	20	18	735
-1	13•	6	431
0	11•	9	828
1	22	19	595
2	17	18	192
9,6,L			
-8	36	36	467
-7	20	19	933
-6	10•	8	715
-5	24	24	097
-4	12	12	777
-3	15	15	997
-2	13	16	352
-1	13	13	479
0	23	26	729
10,0,L			
-12	16	16	500
-11	12•	10	500
-10	18	19	000
-9	72	73	500
-8	28	26	000
-7	25	25	000
-6	19	19	500
-5	23	17	000
-4	19	18	000
-3	14•	8	500
-2	24	24	500
-1	25	22	500
0	27	26	000
1	49	48	500
2	53	58	000
3	13	14	000
10,1,L			
-12	9•	3	773
-11	11•	9	805
-10	34	32	333
-9	28	30	626
-8	33	34	261
-7	21	21	932
-6	16•	12	152
-5	16•	5	876
-4	16•	9	236
-3	15	11	867
-2	13•	15	943
-1	12•	10	890
0	14•	11	268
1	13•	15	300
2	11•	17	337
3	17	18	756
10,2,L			
-12	8•	8	570
-11	15	12	304
-10	17	18	392
-9	13•	0	597
-8	13•	14	191
-7	30	29	390
-6	31	30	975
-5	20	17	259
-4	13•	8	456
-3	15•	2	828
-2	29	27	862
-1	31	28	438
0	18	14	551
1	27	24	851
2	13	10	029
3	12	11	003
10,3,L			
-11	11	11	760
-10	15	11	112
-9	12•	10	071
-8	18	15	528
-7	17	24	254
-6	15	12	899
-5	14	14	721
-4	22	18	156
-3	45	44	869
-2	43	44	363
-1	48	47	730
0	35	35	197
1	11•	11	134
2	9•	5	737
10,4,L			
-10	8•	6	783
-9	16	18	119
-8	16	17	255
-7	30	30	696
-6	39	40	049
-5	16	15	693
-4	13•	5	695
-3	13•	7	236
-2	20	21	195
-1	32	32	622
0	22	22	481
1	14	16	027
10,5,L			
-8	15	16	231
-7	9•	7	766
-6	13	11	196
-5	23	24	754
-4	10•	5	501
-3	9•	11	653
-2	13	13	700
-1	15	14	903
11,0,L			
-11	34	32	500
-10	19	19	000
-9	11•	12	500
-8	44	44	000
-7	13•	3	000
-6	14	13	500
-5	13•	1	000
-4	11•	5	500
-3	12•	2	000
-2	15	12	000
-1	28	27	500
0	12	10	500
1	21	22	000
11,1,L			
-10	17	16	987
-9	39	40	305
-8	14	13	979
-7	12•	12	997
-6	15	11	669
-5	13•	8	883
-4	16	12	084
-3	11•	7	862
-2	12•	7	508
-1	12	11	410
0	18	23	915
1	40	43	349
11,2,L			
-10	11	12	096
-9	24	24	523
-8	28	27	171
-7	28	28	903
-6	12•	5	269
-5	11•	12	408
-4	19	18	776
-3	20	22	568
-2	28	26	942
-1	22	20	456
0	10	7	898
11,3,L			
-9	11	9	254
-8	36	36	861
-7	42	42	291
-6	45	43	755
-5	11•	7	035
-4	21	20	315
-3	11•	6	307
-2	42	44	764
-1	19	20	238
11,4,L			
-7	16	19	152
-6	18	18	744
-5	21	23	431
-4	9•	5	187
-3	28	28	741
12,0,L			
-8	7•	8	000
-7	10	10	000
-6	12	14	500
-5	9•	9	500
-4	9•	0	000
-3	8•	2	500
12,1,L			
-7	13	11	666
-6	8•	8	650
-5	15	18	855
-4	20	21	325
-3	8	9	210
12,2,L			
-6	25	28	483
-5	18	16	552

the bonds C(10)–C(19) and C(13)–C(18) to be parallel, in fact they diverge by 14·4°. Since the methyl groups are separated by 4·80 Å, or about 0·80 Å more than the normal separation of two such groups in van der Waals contact, it is unlikely that this effect is the result of repulsion between the methyl groups themselves. Apparently it is a consequence of the general deformation of the whole molecule caused by attaching ring *D* to ring *C*. (An extensive analysis of the inter-planar angles in androsterone was carried out by Norton & Ohrt (1964), using the atomic coordinates from this investigation.)

The strain in the *D* ring has interesting effects on the stereochemistry of the keto group. It is instructive to compare the bond lengths and angles found in androsterone with those found in acetone by Swalen & Costain (1959), using microwave spectroscopy:

	Acetone	Androsterone
C=O	1·215 Å (assumed)	1·189 ± 0·006 Å
C–C	1·515 ± 0·005 Å	1·517 ± 0·005 and 1·520 ± 0·008 Å
C–CO–C	116° 14′ ± 1°	107·8° ± 0·4°

The C–CO–C angle in androsterone is much smaller than one would expect at an atom with sp^2 (planar-trigonal) hybridization; indeed, it is smaller than an sp^3 (tetrahedral) angle. It is reasonable to surmise, then, that the σ orbital hybridization at C(17) is not exactly sp^2. There is evidence for a general dependence of bond

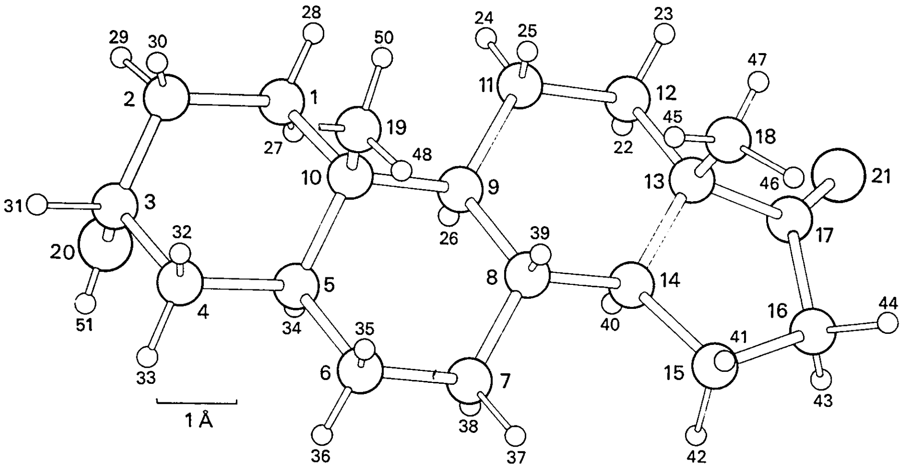

Fig. 3. The androsterone molecule, viewed in an orthographic projection along vector 2·114**a** – 1·056**b** – 0·137**c**. Atom H(49) was omitted for clarity.

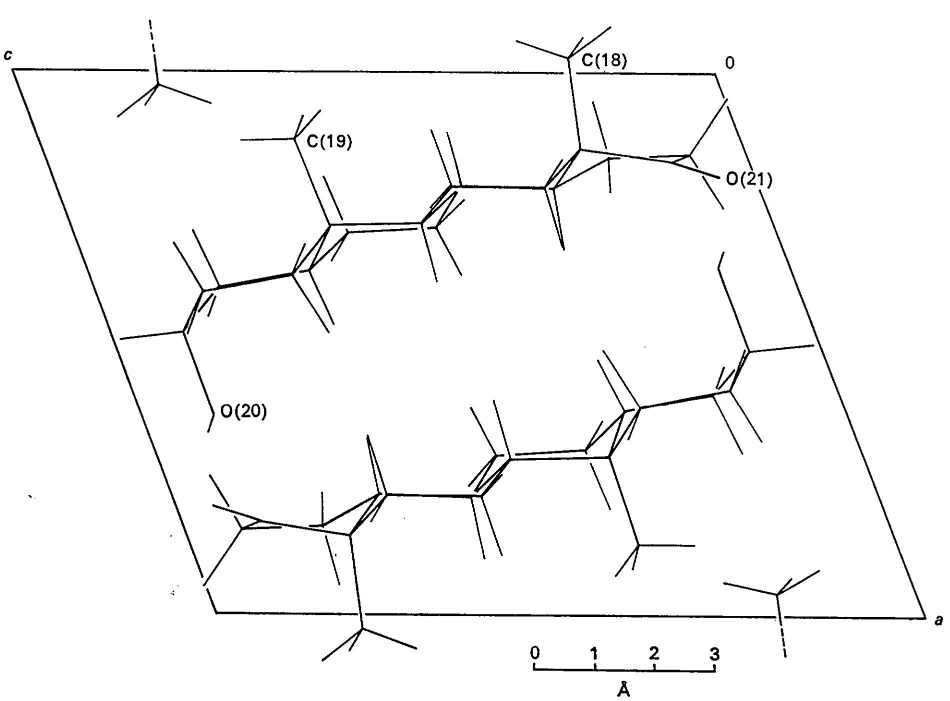

Fig. 4. The unit cell, viewed in an orthographic projection along **b**.

length on orbital hybridization; Dewar (1962) shows that bond length decreases linearly with increasing *s* character of the bond. Decreasing the C–CO–C angle would presumably cause the orbitals forming the C–C bonds to assume somewhat more *p* character (closer to sp^3) and hence the C=O bond would assume somewhat more *s* character and be shortened. The C(17)–O(21) bond is indeed shorter than the carbonyl bond assumed by Swalen & Costain, and is shorter than the normal C=O bond length of about 1·23 Å for an unconjugated system (*International Tables for*

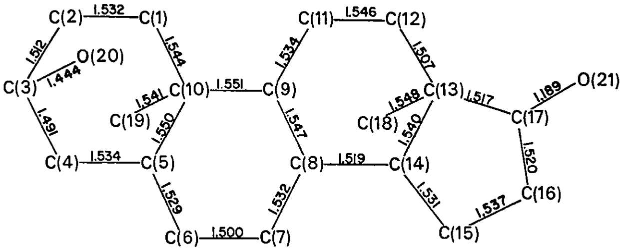

Fig. 5. Schematic representation of the androsterone molecule, showing bond lengths in the molecular skeleton.

Table 5. *Bond lengths and their estimated standard deviations*

C(1)—C(2)	1·532 (0·005) Å	C(1)—H(27)	1·10 (0·04) Å
C(1)—C(10)	1·544 (0·005)	C(1)—H(28)	0·96 (0·04)
C(2)—C(3)	1·512 (0·007)	C(2)—H(29)	1·06 (0·04)
C(3)—C(4)	1·491 (0·006)	C(2)—H(30)	0·98 (0·04)
C(3)—O(20)	1·444 (0·006)	C(3)—H(31)	1·05 (0·05)
C(4)—C(5)	1·534 (0·005)	C(4)—H(32)	1·06 (0·05)
C(5)—C(6)	1·529 (0·005)	C(4)—H(33)	1·03 (0·05)
C(5)—C(10)	1·550 (0·006)	C(5)—H(34)	0·94 (0·04)
C(6)—C(7)	1·500 (0·006)	C(6)—H(35)	1·05 (0·04)
C(7)—C(8)	1·532 (0·006)	C(6)—H(36)	0·95 (0·04)
C(8)—C(9)	1·547 (0·005)	C(7)—H(37)	1·06 (0·04)
C(8)—C(14)	1·519 (0·005)	C(7)—H(38)	0·88 (0·04)
C(9)—C(10)	1·551 (0·005)	C(8)—H(39)	0·97 (0·03)
C(9)—C(11)	1·534 (0·006)	C(9)—H(26)	0·99 (0·03)
C(10)-C(19)	1·541 (0·005)	C(11)-H(24)	0·87 (0·03)
C(11)-C(12)	1·546 (0·005)	C(11)-H(25)	1·02 (0·04)
C(12)-C(13)	1·507 (0·006)	C(12)-H(22)	1·01 (0·04)
C(13)-C(14)	1·540 (0·006)	C(12)-H(23)	0·97 (0·04)
C(13)-C(17)	1·517 (0·005)	C(14)-H(40)	0·98 (0·04)
C(13)-C(18)	1·548 (0·005)	C(15)-H(41)	1·03 (0·04)
C(14)-C(15)	1·531 (0·005)	C(15)-H(42)	0·94 (0·05)
C(15)-C(16)	1·537 (0·006)	C(16)-H(43)	1·04 (0·05)
C(16)-C(17)	1·520 (0·008)	C(16)-H(44)	1·11 (0·06)
C(17)-O(21)	1·189 (0·006)	C(18)-H(45)	0·96 (0·05)
		C(18)-H(46)	1·03 (0·06)
		C(18)-H(47)	0·84 (0·05)
		C(19)-H(48)	0·91 (0·06)
		C(19)-H(49)	0·93 (0·04)
		C(19)-H(50)	0·96 (0·07)
		O(20)-H(51)	0·78 (0·07)

X-ray Crystallography, 1962, p.276). Similarly, Schleyer & Nicholas (1961) found that the frequency of the carbonyl stretching band in unconjugated ketones increases with diminishing C–CO–C angle, implying a decrease in bond length. By the same argument, we would expect the increased *p* character of the C–C bonds to cause them to be lengthened. The difference between these bonds in androsterone and in acetone is not significant, but the effect could be masked by changes in the hybridization at C(13) and C(17). C(13) especially shows departure from tetrahedral conformation; the angle C(14)–C(13)–C(17) is only 99·2°. The conclusion that C(17) does not have exactly sp^2 hybridization is consistent with the observation that O(21) lies 0·05 Å out of the plane through C(13), C(17), and C(16). However, the effect is slight; if a plane is fitted to all four atoms the largest atom-to-plane distance is 0·016 Å.

The last three columns of Table 2 show the thermal parameters reduced to principal axes, with standard deviations derived from the standard deviations for the β_{ij}. The principal-axis directions are not given; for all the strongly anisotropic atoms the largest component is approximately normal to a plane through the ring system. It is therefore unlikely that rigid body libration of the whole molecule would be sufficient to have

Table 6. *Bond angles and their estimated standard deviations*

C(2)—C(1)—C(10)	113·5 (0·3)°	C(2)—C(1)-H(27)	114 (2)°	C(9)—C(11)-H(24)	113 (2)°
C(1)—C(2)—C(3)	112·4 (0·3)	C(2)—C(1)-H(28)	111 (2)	C(9)—C(11)-H(25)	108 (2)
C(2)—C(3)—C(4)	111·5 (0·3)	C(10)-C(1)-H(27)	105 (2)	C(12)-C(11)-H(24)	106 (2)
C(2)—C(3)—O(20)	107·1 (0·4)	C(10)-C(1)-H(28)	106 (2)	C(12)-C(11)-H(25)	112 (2)
C(4)—C(3)—O(20)	111·0 (0·3)	H(27)-C(1)-H(28)	107 (3)	H(24)-C(11)-H(25)	104 (3)
C(3)—C(4)—C(5)	112·7 (0·3)	C(1)—C(2)-H(29)	109 (3)	C(11)-C(12)-H(22)	111 (2)
C(4)—C(5)—C(6)	113·1 (0·3)	C(1)—C(2)-H(30)	112 (2)	C(11)-C(12)-H(23)	112 (3)
C(4)—C(5)—C(10)	113·2 (0·3)	C(3)—C(2)-H(29)	103 (2)	C(13)-C(12)-H(22)	108 (2)
C(6)—C(5)—C(10)	112·1 (0·3)	C(3)—C(2)-H(30)	109 (2)	C(13)-C(12)-H(23)	110 (2)
C(5)—C(6)—C(7)	111·5 (0·3)	H(29)-C(2)-H(30)	110 (4)	H(22)-C(12)-H(23)	106 (4)
C(6)—C(7)—C(8)	113·2 (0·3)	C(2)—C(3)-H(31)	113 (3)	C(8)—C(14)-H(40)	104 (2)
C(7)—C(8)—C(9)	110·8 (0·3)	C(4)—C(3)-H(31)	109 (2)	C(13)-C(14)-H(40)	105 (2)
C(7)—C(8)—C(14)	112·0 (0·3)	O(20)-C(3)-H(31)	105 (3)	C(15)-C(14)-H(40)	108 (2)
C(9)—C(8)—C(14)	109·0 (0·3)	C(3)—C(4)-H(32)	108 (3)	C(14)-C(15)-H(41)	111 (2)
C(8)—C(9)—C(10)	112·7 (0·2)	C(3)—C(4)-H(33)	112 (3)	C(14)-C(15)-H(42)	112 (3)
C(8)—C(9)—C(11)	111·5 (0·3)	C(5)—C(4)-H(32)	106 (2)	C(16)-C(15)-H(41)	113 (2)
C(10)-C(9)—C(11)	113·6 (0·2)	C(5)—C(4)-H(33)	111 (3)	C(16)-C(15)-H(42)	112 (3)
C(1)—C(10)-C(5)	106·2 (0·3)	H(32)-C(4)-H(33)	107 (4)	H(41)-C(15)-H(42)	107 (4)
C(1)—C(10)-C(9)	109·9 (0·3)	C(4)—C(5)-H(34)	107 (2)	C(15)-C(16)-H(43)	108 (3)
C(1)—C(10)-C(19)	109·7 (0·3)	C(6)—C(5)-H(34)	108 (3)	C(15)-C(16)-H(44)	117 (5)
C(5)—C(10)-C(9)	107·4 (0·2)	C(10)-C(5)-H(34)	103 (3)	C(17)-C(16)-H(43)	107 (3)
C(5)—C(10)-C(19)	112·4 (0·3)	C(5)—C(6)-H(35)	109 (2)	C(17)-C(16)-H(44)	104 (5)
C(9)—C(10)-C(19)	111·1 (0·2)	C(5)—C(6)-H(36)	109 (2)	H(43)-C(16)-H(44)	113 (5)
C(9)—C(11)-C(12)	113·4 (0·3)	C(7)—C(6)-H(35)	111 (2)	C(13)-C(18)-H(45)	115 (2)
C(11)-C(12)-C(13)	109·7 (0·3)	C(7)—C(6)-H(36)	113 (3)	C(13)-C(18)-H(46)	115 (4)
C(12)-C(13)-C(14)	110·5 (0·3)	H(35)-C(6)-H(36)	103 (3)	C(13)-C(18)-H(47)	109 (3)
C(12)-C(13)-C(17)	116·4 (0·3)	C(6)—C(7)-H(37)	113 (3)	H(45)-C(18)-H(46)	109 (5)
C(12)-C(13)-C(18)	112·5 (0·3)	C(6)—C(7)-H(38)	114 (2)	H(45)-C(18)-H(47)	112 (4)
C(14)-C(13)-C(17)	99·2 (0·3)	C(8)—C(7)-H(37)	109 (2)	H(46)-C(18)-H(47)	95 (5)
C(14)-C(13)-C(18)	111·9 (0·3)	C(8)—C(7)-H(38)	105 (3)	C(10)-C(19)-H(48)	109 (4)
C(17)-C(13)-C(18)	105·5 (0·2)	H(37)-C(7)-H(38)	102 (4)	C(10)-C(19)-H(49)	111 (2)
C(8)—C(14)-C(13)	113·4 (0·3)	C(7)—C(8)-H(39)	106 (2)	C(10)-C(19)-H(50)	111 (4)
C(8)—C(14)-C(15)	120·8 (0·3)	C(9)—C(8)-H(39)	111 (2)	H(48)-C(19)-H(49)	110 (5)
C(13)-C(14)-C(15)	104·3 (0·3)	C(14)-C(8)-H(39)	108 (2)	H(48)-C(19)-H(50)	112 (5)
C(14)-C(15)-C(16)	102·6 (0·4)	C(8)—C(9)-H(26)	107 (2)	H(49)-C(19)-H(50)	104 (5)
C(15)-C(16)-C(17)	106·0 (0·3)	C(10)-C(9)-H(26)	106 (2)	C(3)—O(20)-H(51)	104 (5)
C(13)-C(17)-C(16)	107·8 (0·3)	C(11)-C(9)-H(26)	105 (2)		
C(13)-C(17)-O(21)	127·1 (0·4)				
C(16)-C(17)-O(21)	125·1 (0·4)				

an important effect on our calculated bond lengths.

The effect of thermal motion of the individual atoms on the bond lengths was estimated by the method of Busing & Levy (1964). The lower-limit correction, corresponding to correlated parallel motion, averaged 0·001 Å and ranged up to 0·003 Å. The upper-limit correction averaged 0·16 and ranged from 0·10 to 0·19 Å. Since no information is available on the joint distribution of thermal motion for atoms in a structure like androsterone, we have not attempted to apply these corrections to the observed bond lengths. If the thermal motion is largely molecular, as seems reasonable in such a rigid molecule, the lower-limit corrections are probably about right. However, it should be emphasized that the ambiguity introduced by thermal effects makes questionable any deductions requiring precise knowledge of bond lengths. For example, the assumption that O(21) is 'riding' on C(17) would indicate that the corrected bond length is 1·215 Å (instead of 1·189 Å) and would invalidate our argument concerning hydribization in the carbonyl group. On the other hand, a parallel assumption that (C18) and C(19) are 'riding' on C(13) and C(10), respectively, would indicate that the methyl C–C bond lengths are actually 1·566 and 1·560 Å, which seems unlikely.

It is interesting to observe that the *B*'s for the hydrogen atoms appear to be considerably smaller than the *B*'s for the atoms to which they are bonded for all except six of the thirty hydrogen atoms in androsterone. The average *B* for 17 atoms having attached hydrogen atoms is 4·7 Å^2, whereas the average *B* for the 30 hydrogen atoms is only 3·8 Å^2; and this in spite of the fact that one would expect the hydrogen-atom temperature factors to be larger, not smaller. This phenomenon is general and has been discussed by Jensen & Sundaralingam (1964). It is believed to be the consequence of refining with a scattering factor calculated for non-bonded hydrogen atoms. The correct scattering factor for bonded hydrogen atoms ought to allow for a greater concentration of electron density in the immediate vicinity of the proton.

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References

ALDEN, R. A., STOUT, G. H., KRAUT, J. & HIGH, D. F. (1964). *Acta Cryst.* **17**, 109.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BERNAL, J. D. & CROWFOOT, D. (1936). *Z. Kristallogr.* **93**, 464.

BÜRKI, H. & NOWACKI, W. (1956). *Z. Kristallogr.* **108**, 206.

BUSING, W. R. & LEVY, H. A. (1959). *A Crystallographic Least Squares Program for the IBM* 704. Atomic Energy Commission Publication ORNL 59-4-37.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.

CARLISLE, C. H. & CROWFOOT, D. (1945). *Proc. Roy. Soc.* A, **184**, 64.

CROWFOOT, D. & DUNITZ, J. D. (1948). *Nature, Lond.* **162**, 608.

DEWAR, M. J. S. (1962). *Hyperconjugation*, p. 53. New York: Ronald Press.

FIESER, L. F. & FIESER, M. (1959). *Steroids*. New York: Reinhold.

FRIDRICHSONS, J. & MATHIESON, A. MCL. (1953). *J. Chem. Soc.* p. 2159.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 866.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JENSEN, L. H. & SUNDARALINGAM, M. (1964). *Science*, **145**, 1185.

KLYNE, W. (1957). *The Chemistry of the Steroids*. New York: John Wiley.

MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.

NORTON, D. A., KARTHA, G. & LU, C. T. (1963). *Acta Cryst.* **16**, 89.

NORTON, D. A., KARTHA, G. & LU, C. T. (1964). *Acta Cryst.* **17**, 77.

NORTON, D. A. & OHRT, J. M. (1964). *Nature, Lond.* **203**, 754.

RABINOWITZ, I. N. & KRAUT, J. (1964). *Acta Cryst.* **17**, 159.

SCHLEYER, P. VON R. & NICHOLAS, R. D. (1961). *J. Amer. Chem. Soc.* **83**, 182.

SIMPSON, P. G., DOBROTT, R. D. & LIPSCOMB, W. N. (1965). *Acta Cryst.* **18**, 169.

SWALEN, J. D. & COSTAIN, C. C. (1959). *J. Chem. Phys.* **31**, 1562.

TAYLOR, N. E., HODGKIN, D. C. & ROLLETT, J. S. (1960). *J. Chem. Soc.* 3685.