

The Molecular and Crystal Structure of 16 β ,17 β -Dibromoandrostane

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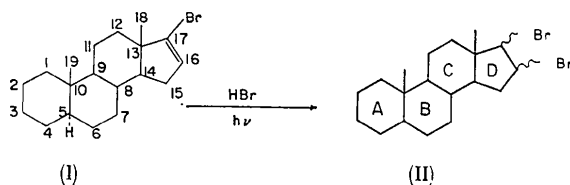
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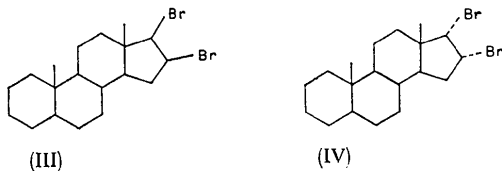
The crystal and molecular structures of 16 β ,17 β -dibromoandrostane, C₁₉H₃₀Br₂, have been determined by three-dimensional X-ray crystallographic techniques. Crystals of 16 β ,17 β -dibromoandrostane belong to space group $P2_1(C_2^2)$ and have two molecules per unit cell with $a = 11.528$ (2), $b = 11.128$ (4), $c = 7.645$ (4) Å, $\beta = 110.61^\circ$ (3). The calculated density with two molecules per unit cell is 1.514 g.cm⁻³. Three-dimensional data were collected at 22°C on a Picker automatic diffractometer (Cu K α radiation) out to maximum $\sin \theta/\lambda = 0.56$, with an average decay of 50% of the observed intensity. The bromine coordinates were obtained from a Patterson function, and a three-dimensional Fourier synthesis gave preliminary carbon coordinates. Block-diagonal least-squares refinement gave a final R of 8.5%. Bond lengths and angles are consistent with currently accepted values for carbon-carbon systems.

Introduction

Recent interest in the stereochemistry of steroids has included conformational studies, especially on ring D (Brutcher & Leopold, 1966; Altona, Geise & Romers, 1968). As a part of this program in these laboratories, the addition product of hydrogen bromide and 17-bromo-5 α -androst-16-ene (I) was synthesized (Stockham, 1970):



The product, dibromoandrostane (II), was isolated in 86% yield. The dipole moment of (II), measured in benzene at 30°C, was found to be 3.46 D, the high value indicating the expected *cis* configuration for the two bromine atoms. Nuclear magnetic resonance spectra and optical rotatory dispersion curves suggested, but not unequivocally, that (II) is 16 β ,17 β -dibromoandrostane (III).



The expected product, on the other hand, of the reaction of (I) with HBr is the 16 α ,17 α derivative (IV). For this reason, and because the n.m.r. data were also not conclusive regarding which of the conformations of ring D was present, a single-crystal investigation of (II) was carried out.

Experimental

Suitable crystals were grown from ethyl acetate-methanol solution in the cold. The crystal used measured 0.35 × 0.15 × 0.20 mm with the longest dimension being the c direction. Preliminary precession photographs $h0l$, $h1l$, $0kl$, $1kl$ gave systematic extinctions of $0k0$ absent when k odd, and the space group is therefore $P2_1(C_2^2)$.

The crystal was transferred to a Picker automatic diffractometer where nine independent 2θ values were obtained with Cu K α radiation at $22 \pm 2^\circ\text{C}$. These values were used in least-squares to obtain cell dimensions of $a = 11.528$ (2), $b = 11.128$ (4), $c = 7.645$ (4) Å, $\beta = 110.61$ (3)°. The calculated density with two molecules per unit cell is 1.514 g.cm⁻³, and the linear absorption coefficient is 61.46 cm⁻¹. Intensity data were collected out to a maximum $\sin \theta/\lambda$ of 0.56, using the moving-crystal moving-counter technique. A Ni filter was used, but no attenuators were needed. The scan rate was 2° min⁻¹, with a 20 second background count, a 2.3° basewidth and a take off angle of 3.0°.

Determination of the structure

The crystal of the dibromide steroid decayed very rapidly with X-ray exposure, as shown in Fig. 1. The decay appeared to be anisotropic, but a linear decay rate as signified by the solid line was used to scale the data. The units along the abscissa are separations of 50 reflections between each set of standard measurements ($i=1$ is after a total of 53 reflections, $i=2$ is after a total of 106 reflections, etc.). The equation used for correcting the data is

$$I_{\text{corr}} = I_{\text{obs}} + I_{\text{obs}} \left(1.20 \times \frac{\text{reflection number}}{\text{total number of reflections}} \right);$$

where I_{corr} is the corrected intensity and I_{obs} is the uncorrected intensity, after subtraction of backgrounds.

This correction dropped the average decay from 50 to 15%, and, as will be shown later, was sufficient to solve the structure. The method is similar to that suggested by Ibers (1969) for $\text{IrCl}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$. Of the 1419 independent reflections collected, 63 had intensities

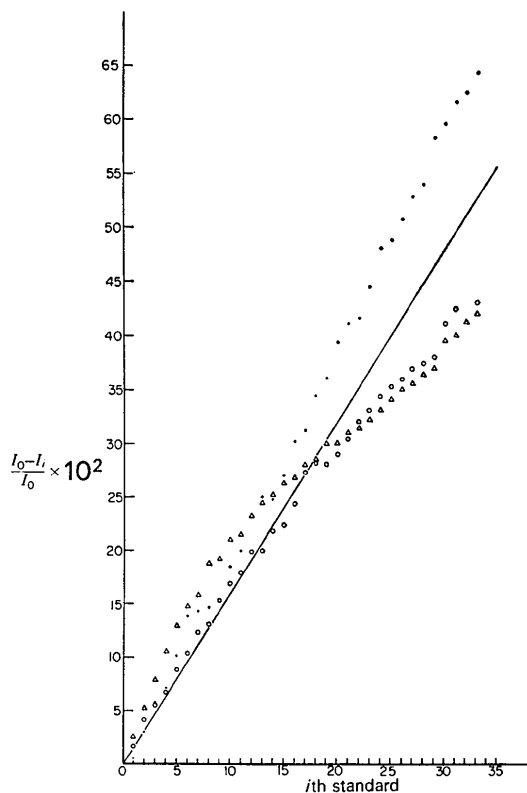


Fig. 1. Rate of decay during data collection.

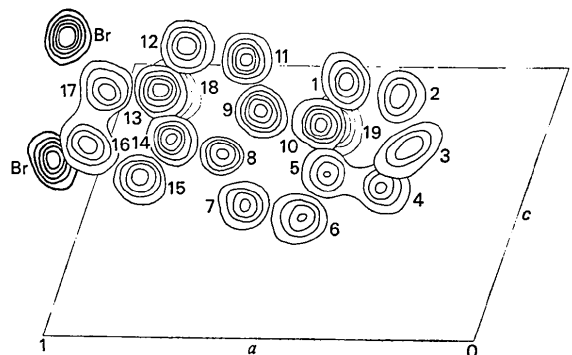


Fig. 2. Final Fourier map in projection down [010].

less than 2.33σ (I) and were considered unobserved. The usual Lorentz and polarization corrections were applied, after which an absolute scale factor and overall temperature factor were calculated from Wilson statistics.

The Br-Br vectors were easily distinguishable in a three-dimensional Patterson function. The y coordinate of Br(17) was chosen as the arbitrary one, and held constant at $\frac{1}{4}$ during the structure refinement. The coordinates of the two Br atoms were used to phase a three-dimensional electron density function in which all 19 carbon atoms were easily recognized. The 21 atomic positions and the isotropic temperature factor were refined by least-squares with a block-diagonal approximation. The function minimized was $\sum \omega [|F_o| - (1/k) |F_c|]^2$ where k is the scale factor for the observed structure factors. Weights were assigned as being inversely proportional to the standard errors of the observed structure amplitudes, where $\sigma = (F_o^2 + \sigma(I))^{1/2} - F_o$. Scattering factors were taken from *International*

Table 1. Final positional parameters and anisotropic temperature factors, with their *e.s.d.*'s (all $\times 10^4$)

The form of the temperature factors is $\exp[-(h^2b_{11} \dots 2hkb_{12} \dots)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(β_{16})	1188 (2)	1655 (2)	6400 (3)	148 (20)	148 (2)	411 (5)	68 (4)	270 (5)	-103 (6)
Br(β_{17})	1910 (1)	$\frac{1}{4}$	941 (2)	92 (1)	148 (2)	326 (4)	30 (3)	62 (3)	51 (5)
C(1)	5049 (12)	4824 (17)	9399 (18)	59 (11)	149 (18)	214 (31)	13 (25)	120 (32)	-41 (40)
C(2)	3691 (12)	4987 (18)	8926 (22)	65 (11)	135 (17)	262 (34)	43 (24)	37 (31)	40 (41)
C(3)	3018 (26)	5646 (20)	7079 (26)	302 (35)	112 (19)	241 (37)	168 (46)	61 (55)	23 (44)
C(4)	3379 (15)	4954 (20)	5523 (22)	109 (16)	164 (22)	206 (31)	87 (32)	106 (35)	60 (44)
C(5)	4739 (14)	4802 (16)	5984 (18)	108 (14)	125 (16)	141 (26)	48 (25)	79 (31)	73 (34)
C(6)	5025 (13)	4174 (20)	4407 (19)	69 (12)	206 (24)	174 (29)	81 (29)	46 (31)	-1 (45)
C(7)	6411 (13)	4211 (20)	4794 (18)	78 (13)	218 (25)	134 (25)	41 (29)	99 (28)	151 (41)
C(8)	7139 (12)	3601 (13)	6670 (15)	102 (12)	82 (12)	109 (20)	7 (20)	95 (25)	-34 (27)
C(9)	6778 (11)	4161 (11)	8272 (15)	95 (12)	71 (10)	104 (20)	3 (19)	126 (25)	28 (24)
C(10)	5305 (11)	4133 (11)	7854 (16)	78 (10)	66 (10)	123 (21)	-3 (17)	61 (22)	37 (24)
C(11)	7554 (11)	3614 (15)	209 (15)	56 (10)	125 (15)	135 (21)	27 (19)	52 (23)	25 (30)
C(12)	8973 (11)	3649 (14)	558 (16)	63 (11)	121 (15)	138 (23)	-7 (20)	38 (25)	-38 (31)
C(13)	9286 (13)	3052 (12)	9045 (18)	96 (12)	76 (11)	153 (26)	-21 (19)	69 (28)	13 (27)
C(14)	8587 (11)	3709 (13)	7169 (16)	77 (11)	86 (12)	145 (22)	4 (18)	105 (25)	8 (27)
C(15)	9049 (13)	3243 (19)	5775 (19)	95 (14)	170 (20)	167 (25)	75 (29)	123 (30)	20 (40)
C(16)	503 (17)	3143 (13)	6941 (20)	190 (21)	75 (12)	225 (31)	-71 (27)	203 (41)	24 (33)
C(17)	535 (14)	3317 (14)	9029 (19)	121 (16)	79 (13)	198 (27)	8 (24)	39 (33)	24 (32)
C(18)	9010 (13)	1706 (16)	9010 (22)	98 (14)	72 (11)	265 (35)	10 (23)	106 (34)	26 (36)
C(19)	4883 (11)	2820 (13)	7780 (22)	58 (10)	94 (14)	360 (39)	-32 (18)	147 (32)	93 (36)

Table 2. Observed and calculated structure factors

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	
-12	1	0	9.6	8.8	-6	5	-1	7.4	7.4	-11	-1	0	4.4	5.5	-2	10	-2	8.5	9.4	0	6	-4	17.4	12.1	2	1	-1	44.1	42.5	1	4	-1	34.6	35.4	
-11	1	-1	12.2	11.3	-6	5	-2	12.3	13.1	-10	-1	1	4.4	5.5	-2	10	-2	8.5	9.4	0	6	-4	17.4	12.1	2	1	-2	51.3	43.5	1	4	-2	58.0	54.9	
-11	2	-1	9.0	8.5	-6	5	-2	12.3	13.1	-10	-1	1	4.4	5.5	-2	10	-2	8.5	9.4	0	6	-4	17.4	12.1	2	1	-1	27.9	20.8	1	4	-1	27.3	24.4	
-11	1	1	11.5	11.3	-6	5	-4	2.1	2.8	-10	-3	0	4.7	5.1	-2	11	-1	3.5	4.1	0	6	-1	31.1	32.6	2	1	-4	26.8	23.1	3	4	-4	24.8	23.0	
-11	0	0	6.4	6.2	-6	6	-4	11.7	11.3	-9	-4	0	2.7	2.9	-2	12	-2	1.2	0.9	0	6	0	15.4	16.8	2	1	-5	5.0	4.0	3	4	-5	5.3	5.7	
-10	0	-1	10.1	10.5	-6	6	-3	6.7	6.7	-9	-3	1	0.2	0.2	-2	12	-2	1.2	0.9	0	7	-1	24.9	32.8	2	1	-7	14.4	13.1	3	4	-7	14.5	14.1	
-10	0	2	5.9	5.2	-6	6	-2	16.2	17.7	-9	-2	0	9.4	9.8	-2	10	-2	5.5	4.7	0	7	-2	5.5	4.7	2	1	-7	19.5	19.7	1	4	-7	11.1	11.1	
-10	0	-1	18.1	18.5	-6	6	-1	8.3	8.6	-9	-1	0	7.6	8.0	-1	11	-1	3.2	2.9	0	7	-3	35.2	38.1	2	1	-8	2.3	1.4	3	4	-8	2.9	1.8	
-10	1	0	18.8	18.4	-6	7	-1	4.2	5.1	-9	-1	1	14.0	15.1	-1	11	-2	5.8	6.8	0	7	-4	14.4	15.0	2	2	-8	4.5	4.3	3	3	-8	6.2	6.1	
-10	1	-1	5.7	5.9	-6	7	-2	6.2	5.8	-9	-2	0	8.2	8.6	-1	11	-1	3.4	3.2	0	7	-5	3.5	3.4	2	2	-7	4.6	3.9	3	3	-7	9.0	8.4	
-10	1	2	8.2	8.1	-6	7	-3	5.5	5.8	-9	-3	0	7.9	8.0	-1	10	-0	10.5	11.5	0	7	-6	7.0	6.9	2	2	-6	10.4	9.8	3	3	-6	14.0	14.2	
-10	2	-2	8.7	7.8	-6	7	-4	5.7	6.2	-9	-4	0	6.7	5.2	-1	10	-1	1.6	0.7	0	8	-8	3.9	4.6	2	2	-5	22.3	20.6	3	3	-5	30.0	28.5	
-10	2	1	15.8	14.8	-6	7	-3	7.1	7.3	-9	-5	0	8.5	8.4	-1	10	-2	8.9	7.9	0	8	-5	6.4	7.4	2	2	-4	26.4	24.7	3	3	-4	30.0	28.5	
-10	3	-1	8.1	8.6	-6	8	-2	7.8	8.4	-9	-5	1	4.3	3.9	-1	10	-3	5.5	6.5	0	8	-4	6.3	5.7	2	2	-3	10.5	11.3	3	3	-3	17.3	18.6	
-10	3	0	10.4	10.5	-6	8	-1	6.4	6.7	-9	-6	0	3.8	4.0	-1	9	-4	3.1	3.8	0	8	-1	18.3	17.6	3	3	-2	51.3	46.1	2	2	-2	52.1	49.6	
-10	4	-2	8.2	7.9	-6	8	-3	7.1	7.3	-9	-6	1	8.5	7.5	8.8	-1	9	-5	4.7	6.0	0	8	-2	12.8	13.5	2	2	-1	42.9	42.7	3	3	-1	31.4	31.4
-10	4	-1	10.7	10.9	-6	9	-2	6.0	6.2	-9	-7	2	6.3	6.2	-1	9	-4	7.5	6.9	0	8	-1	22.0	22.0	2	3	-1	71.0	67.1	3	3	-2	71.0	70.6	
-10	4	0	10.4	10.5	-6	9	-1	6.7	6.7	-9	-7	1	12.8	14.0	-1	9	-3	3.1	3.8	0	8	-1	18.3	17.6	3	3	-2	51.3	46.1	2	2	-1	52.1	49.6	
-10	6	-1	9.8	9.5	-5	11	-1	5.2	4.9	-9	-8	0	3.1	3.0	-1	9	-2	8.9	9.5	0	9	-3	13.6	14.5	2	3	-3	55.3	51.2	3	3	-2	55.3	51.2	
-9	7	-1	4.7	4.3	-5	10	-1	8.4	8.9	-9	-6	-2	12.5	14.5	-1	9	-1	14.0	15.8	0	9	-2	20.3	21.6	2	3	-4	13.6	13.3	3	3	-3	23.6	23.4	
-9	6	-1	4.4	4.6	-5	10	-2	8.4	8.4	-9	-6	-3	14.7	16.4	-1	8	-0	12.0	13.8	0	9	-3	11.1	12.1	2	3	-5	11.6	11.6	3	2	-4	36.0	25.9	
-9	6	2	6.5	6.5	-5	9	-3	4.4	4.6	-9	-6	-4	3.4	2.1	-1	8	-1	7.0	7.6	0	9	-4	2.7	2.8	2	3	-6	28.0	21.7	3	3	-5	31.1	26.4	
-9	5	-2	9.4	9.7	-5	9	-2	3.4	2.5	-9	-6	-9	12.5	14.5	-1	8	-1	8.2	7.3	0	9	-5	1.9	3.3	2	3	-7	6.9	6.9	3	2	-6	25.1	22.5	
-9	5	-1	10.6	9.4	-5	9	-1	7.0	8.8	-9	-6	-0	6.0	6.0	-1	8	-2	11.5	13.4	0	10	-4	4.9	5.6	3	3	-8	3.8	3.3	3	2	-7	10.6	10.9	
-9	4	-1	6.4	6.5	-5	8	-1	6.0	7.1	-9	-6	-1	3.0	2.8	-1	8	-3	9.8	10.4	0	10	-4	2.7	4.1	3	3	-9	4.1	3.0	2	2	-8	3.0	2.9	
-9	4	-2	11.9	12.3	-5	8	-1	12.3	12.7	-9	-5	-5	6.8	5.7	-1	8	-4	4.6	4.7	0	10	-2	3.6	2.4	2	4	-10	16.2	17.8	3	1	-8	1.3	1.2	
-9	4	0	7.2	6.2	-5	8	-2	5.1	6.8	-9	-5	-4	5.1	6.7	-1	8	-5	3.9	2.6	0	10	-1	5.3	8.8	2	4	-5	18.7	19.7	3	1	-7	8.9	9.2	
-9	3	-2	8.7	8.3	-5	8	-3	3.8	3.8	-9	-5	-3	3.8	3.8	-1	7	-4	6.2	6.4	0	10	-1	14.9	17.6	2	4	-6	32.4	34.6	3	1	-6	9.8	10.6	
-9	3	-1	6.7	7.2	-5	8	-4	3.0	3.4	-9	-5	-2	12.7	13.4	-1	7	-5	11.6	13.0	0	11	-1	2.0	0.6	2	4	-3	53.6	40.3	3	1	-5	29.9	27.2	
-9	3	0	16.1	15.8	-5	7	-4	3.0	3.4	-9	-5	-1	18.8	19.8	-1	7	-4	7.2	7.6	0	11	-2	9.3	10.1	2	4	-2	34.8	34.1	3	1	-4	13.1	13.2	
-9	2	-2	10.2	9.5	-5	7	-5	3.9	4.9	-9	-5	-3	18.8	11.7	-1	7	-3	3.4	2.9	0	12	-3	11.0	11.7	2	4	-1	32.4	34.6	3	1	-3	49.8	49.8	
-9	2	-1	12.0	13.5	-5	7	-2	15.0	16.7	-9	-4	-2	22.2	23.4	-1	7	-2	10.3	11.0	0	12	-2	0.8	1.0	2	5	0	30.2	29.8	3	1	-2	41.7	42.9	
-9	2	0	12.7	11.2	-5	7	-1	11.5	13.2	-9	-4	-3	16.2	15.5	-1	7	-1	44.9	47.1	0	12	-1	1.5	2.0	2	5	-1	66.5	66.3	3	1	-1	68.7	64.7	
-9	1	-2	7.0	7.8	-5	6	-2	7.4	8.9	-9	-4	-1	10.8	11.6	-1	6	-1	18.0	17.7	0	12	-1	1.0	1.5	2	5	-2	15.9	16.7	3	1	-2	68.9	68.9	
-9	1	-1	9.9	2.9	-5	6	-1	14.5	15.8	-9	-4	-0	12.5	13.8	-1	6	-2	9.8	9.8	0	12	0	4.5	3.8	2	5	-3	23.3	18.8	3	0	-1	71.8	75.4	
-9	0	-1	20.6	20.9	-5	6	-2	10.6	11.5	-9	-4	-6	5.5	5.9	-1	6	-3	29.6	32.7	0	12	-1	2.2	1.7	2	5	-4	27.5	25.9	3	0	-2	16.6	17.3	
-9	0	0	11.9	11.9	-5	6	-1	15.5	16.5	-9	-4	-5	6.5	6.5	-1	6	-4	6.5	6.5	0	12	-1	2.2	1.7	2	5	-5	14.7	14.7	3	0	-1	62.1	58.4	
-9	0	0	4.4	1.4	-5	6	-0	11.2	11.8	-9	-3	-5	3.2	3.9	-1	6	-5	4.6	4.1	0	11	-4	5.4	5.8	2	5	-6	14.2	14.2	3	0	-1	8.5	8.5	
-9	0	-1	6.4	7.4	-5	6	-5	8.5	10.0	-9	-3	-4	8.3	8.5	-1	6	-6	4.5	4.8	0	11	-3	5.1	5.0	2	5	-7	1.6	1.2	3	0	-5	22.3	22.9	
-9	0	1	12.3	9.5	-5	5	-5	11.1	12.6	-9	-3	-3	26.5	29.5	-1	5	-7	4.0	3.9	0	11	-2	4.8	4.5	2	6	-7	1.2	1.3	3	0	-6	12.7	12.1	
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-9	0	-1	8.0	6.6	-5	5	-3	18.2	19.2	-9	-3	-1	35.8	39.4	-1	5	-9	16.4	16.3	0	11	0	8.1	8.0	2	6	-9	3.9	4.0	3	0	-8	4.6	4.8	
-9	0	0	8.1	8.9	-5	5	-2	30.8	33.7	-9	-3	0	32.9	38.6	-1	5	-4	3.0	4.2	0	10	-1	6.8	7.5	2	6	-4	35.6	36.5	3	0	-8	1.8	3.0	
-9	0	1	16.5	16.5	-5	4	-2	18.8	21.1	-9	-3	1	32.9	38.6	-1	5	-3	3.0	4.2	0	10	-2	6.8	7.5	2	6	-3	35.6	36.5	3	0	-9	1.2	1.3	
-9	0	-1	26.0	24.8	-5	4	-1	23.6	23.7	-9	-2	-2	28.4	27.3	-1	5	-2	19.4	21.2	0	10	-3	6.7	7.5	2	6	-2	24.1	24.3	3	0	-8	3.0	3.1	
-9	0	0	9.6	3.3	-5	4	-2	7.4	9.8	-9	-2	-3	14.4	14.3	-1	5	-1	79.8	82.4	0	10	-4	0.0	0.8	2	6	-1	4.4	4.9	3	0	-9	4.9	4.1	
-9	0	1	18.5	18.5	-5	4	-1	18.8	18.8	-9	-2	-2	14.4	14.3	-1	5	-1	79.8	82.4	0	10	-4	0.0	0.8	2	6	-1	4.4	4.9	3	0	-9	4.9	4.1	
-9	1	-2	7.0	6.3	-5	3	-2	12.6	13.2	-9	-2	-4	41.2	44.7	-1	4	-																		

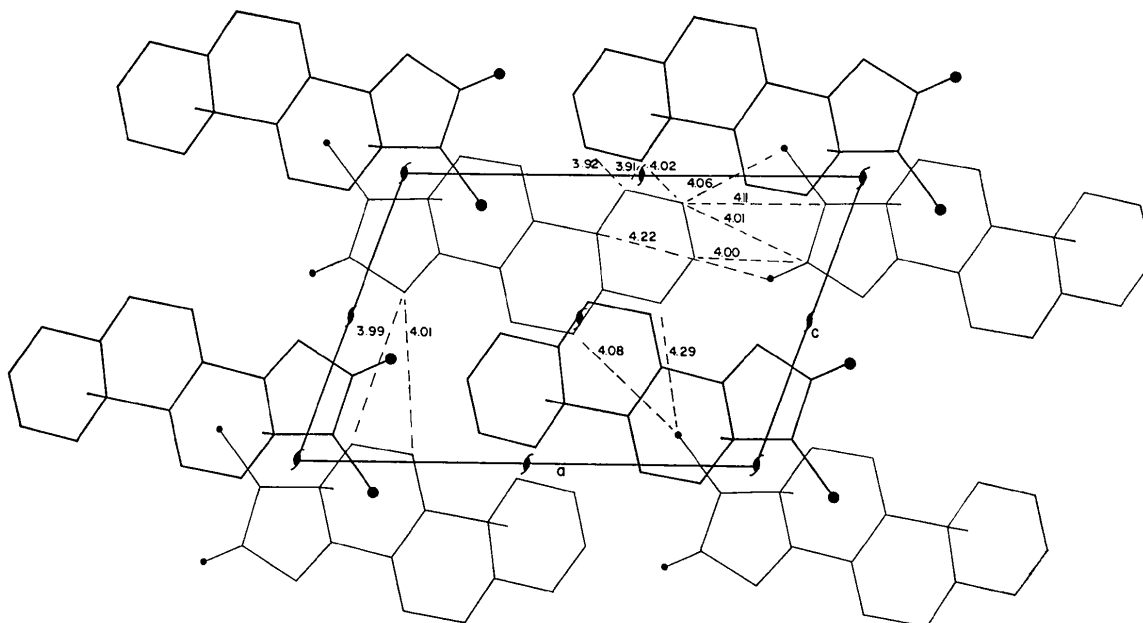


Fig. 6. The structure in projection down the b axis.

Table 4. Best plane calculation for ring D

Four-membered planes

Atom number	$\sum_{i=1}^4 (d^2)$ atoms in plane
13, 14, 15, 16	0.15
14, 15, 16, 17	0.02
15, 16, 17, 13	0.04
16, 17, 13, 14	0.17
17, 13, 14, 15	0.24

Three-membered planes
Atom number
in plane

Atom number in plane	Atom number out of plane (deviation)
13, 14, 15	16 (-1.03), 17 (-1.17)
13, 14, 16	15 (-0.62), 17 (0.64)
13, 14, 17	15 (-1.09), 16 (-1.0)
14, 15, 16	13 (-0.97), 17 (-0.34)
14, 15, 17	13 (-0.78), 16 (0.24)
15, 16, 17	13 (-0.48), 14 (0.31)
16, 17, 13	14 (1.02), 15 (0.54)
17, 13, 15	14 (0.73), 16 (-0.35)
16, 17, 14	13 (-0.67), 15 (-0.23)
15, 16, 13	14 (0.59), 17 (0.33)

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