Acta Cryst. (1977). **B33**, 1236–1244

The Crystal Structure of Δ^6-Cholesten-3-one

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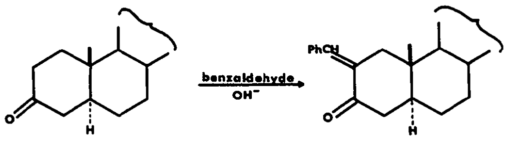
(*Received* 6 *September* 1976; *accepted* 15 *October* 1976)

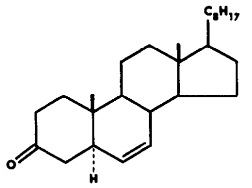
Crystals of Δ^6-cholesten-3-one, $C_{27}H_{44}O$, are monoclinic, space group $P2_1$, $a = 9{\cdot}878\,(1)$, $b = 11{\cdot}502\,(2)$, $c = 21{\cdot}331\,(2)$ Å, $\beta = 92{\cdot}33\,(2)^\circ$, $Z = 4$. Multi-solution direct methods gave a structure which was shifted from its correct position in the cell. The shift vector was determined by averaging coordinates for the initial structure with those of an image structure, which appeared in a difference map based on the initial structure. The trial model was refined to $R = 0{\cdot}091$ for 3251 reflexions measured on a diffractometer. The conformations and geometries of the two independent molecules are almost identical. The chair-form ring *A* is flattened ($\bar{\omega} = 50{\cdot}4^\circ$) as a result of conformational transmission effects originating in the half-chair ring *B*. A comparison of *A*-ring conformations in 3-keto-5α-steroids provides quantitative evidence from solid-state studies that the rate of 2-condensation of these compounds with benzaldehyde is governed by conformational transmission effects, as shown by the chemical study of Barton, McCapra, May & Thudium [*J. Chem. Soc.* (1960), pp. 1297–1311].

Introduction

The relative rates of alkali-catalysed condensations of a series of 3-keto steroids and triterpenoids (I) with benzaldehyde were determined by Barton, Head & May (1957), Barton (1959), and Barton, McCapra, May & Thudium (1960). They found that the condensation product was exclusively the 2-benzylidene ketone (II), there being no tendency for the formation of the 4-derivative, and that the rate-determining step was the elimination of OH^- to form the benzylidene double bond, involving the rehybridization of C(2) from sp^3 to sp^2. Of more fundamental importance was the discovery that the rate of reaction varied according to the presence of ethylenic linkages and/or substituent groups in positions remote from the reaction centre C(2). The work showed that these reactivity differences were due to relatively small conformational changes at the reaction centre produced by larger changes in conformation in the vicinity of the remote substituents. It was found possible (Barton *et al.*, 1960) to express the reaction rate in terms of the rate for a saturated 3-keto skeleton multiplied by a series of group rate factors, each characteristic of the nature and position of substituent group(s). This long-range effect was termed conformational transmission, and has been well explained qualitatively in terms of valence and torsion angle deformations transmitted through the skeleton as a result of unsaturation or substitution (see, for example, Robinson & Whalley, 1963; Bucourt, 1974).



(I) (II)



(III)

Surprisingly, even today the number of published X-ray studies of steroids and triterpenoids which have the same, or similar, substitution patterns to those studied by Barton *et al.* (1960) is small. We now report the analysis of one of these, Δ^6-cholesten-3-one (III), the compound which had the highest relative rate of 2-condensation with benzaldehyde. The analysis was performed to study the stereochemical environment of both C(2) and C(4). We have also been able to compare its conformation, especially in the *A* ring, with other skeletons for which both X-ray results and reaction rates are available.

Experimental

Crystals of Δ^6-cholesten-3-one are colourless plates. The symmetry and space group were determined from

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photographs taken about **a** and **b**. Cell parameters were obtained by least-squares from the 2θ values of 15 reflexions measured on a diffractometer with Cu $K\alpha$ radiation.

Crystal data

Δ^6-Cholesten-3-one, $C_{27}H_{44}O$, $M_r = 384{\cdot}6$, monoclinic, $a = 9{\cdot}878\,(1)$, $b = 11{\cdot}502\,(2)$, $c = 21{\cdot}331\,(2)$ Å, $\beta = 92{\cdot}33\,(2)^\circ$, $U = 2421{\cdot}5\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}055$ g cm^{-3}, $\mu = 3{\cdot}94$ cm^{-1} for Cu $K\alpha$ radiation ($\lambda_{\rm mean} = 1{\cdot}54178$ Å). Space group $P2_1$.

The intensities were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator. The θ–2θ scan mode was employed with a scan range in 2θ of $(2{\cdot}5 + 0{\cdot}383 \tan\theta)^\circ$ for Cu $K\alpha$ radiation. Reflexions in the range $4^\circ < 2\theta < 94^\circ$ were scanned at 1° min^{-1} in 2θ and those in the range $94^\circ < 2\theta < 127{\cdot}2^\circ$ at 0·5° min^{-1}. Three crystals were used for the data collection since it was found that the intensities of six monitor reflexions fell by an average of 15% during the measurement of some 1500 reflexions. For each new crystal some overlapping regions were measured for scaling purposes and the same set of monitors was used throughout. The standard deviation of an intensity was calculated from counting statistics as $\sigma^2(I) = S + B + (dS)^2$, where S = scan count, B = background, interpolated from background curve, and d is an empirical constant which allows for instrumental instability taken as 0·04. Of 3992 independent reflexions 748 had $I < \sqrt{2}\sigma(I)$ and were classified as unobserved. Data were scaled together taking account of the different specimens and scan ratio. No absorption corrections were made. Lorentz and polarization factors were applied and structure amplitudes and $|E|$ values were derived.

Structure solution and refinement

Initial attempts to solve the structure were based on multisolution tangent refinement first with methods described by Kennard *et al.* (1971) and then with a program written by one of us (GMS) which incorporated quartet tests into the general methods described by Germain, Main & Woolfson (1970). Final runs with this program yielded several sensible E maps, based on 465 reflexions with $|E| \geq 1{\cdot}40$, in which two independent steroid molecules were located. Further refinement of these solutions was unsuccessful and it was concluded that the structure was displaced relative to its true position. In a difference synthesis calculated with one such 'shifted' solution it was noted that peaks occurred at positions displaced from the input set by the vector $\Delta x = 0{\cdot}40$, $\Delta z = -0{\cdot}12$. In the light of recent work on unscrambling double-image E maps (Caira, Giles, Nassimbeni, Sheldrick & Hazell, 1976), a trial model was obtained by taking the average of peak positions from the initial E map and the difference map. All non-hydrogen atom positions were located in the first difference synthesis based on this 'averaged' structure, which is shown in Fig. 1 referred to cell axes a and c. The 'shifted' E-map solution is represented by the origin shift of the axes a' and c'. Isotropic least-squares refinement, where the two independent molecules 1 and 2 were refined in alternate cycles, yielded an R of 0·165. Refinement continued with anisotropic thermal parameters for C and O. All 88 H atoms were included in the final cycles with the constraint technique described previously and rigid methyl groups (Allen, Kennard & Sheldrick, 1977). The C—H distance used was 1·08 Å, with fixed overall U values of 0·15 Å^2 for methyl H atoms and 0·10 Å^2 for the remainder. The

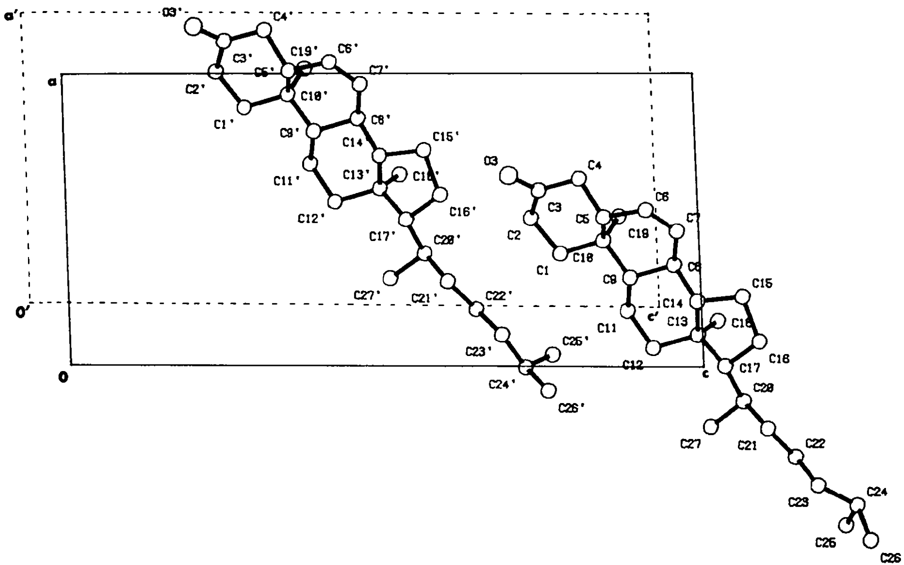

Fig. 1. One asymmetric unit projected down **b**; the true cell axes are represented by full lines, the axes represented by broken lines refer to the initial E-map solution.

Table 1. *Atom coordinates* (× 10^4)

	x	*y*	*z*		*x*	*y*	*z*
Molecule 1				Molecule 2			
O(3)	6540 (6)	7614 (7)	7043 (3)	O(3′)	11658 (7)	10028 (6)	2135 (3)
C(1)	3888 (7)	6121 (8)	7817 (3)	C(1′)	8900 (7)	8627 (7)	2904 (3)
C(2)	5098 (8)	6117 (9)	7383 (3)	C(2′)	10100 (7)	8607 (8)	2467 (4)
C(3)	6053 (8)	7101 (8)	7487 (4)	C(3′)	11101 (8)	9568 (8)	2577 (4)
C(4)	6385 (7)	7436 (8)	8145 (3)	C(4′)	11426 (7)	9945 (9)	3237 (3)
C(5)	5093 (6)	7518 (6)	8517 (3)	C(5′)	10113 (7)	10033 (7)	3602 (3)
C(6)	5332 (7)	7972 (7)	9164 (3)	C(6′)	10346 (8)	10485 (8)	4250 (4)
C(7)	4600 (6)	7669 (6)	9649 (3)	C(7′)	9612 (7)	10191 (7)	4724 (4)
C(8)	3462 (5)	6786 (6)	9595 (3)	C(8′)	8464 (6)	9324 (6)	4675 (3)
C(9)	3044 (6)	6576 (6)	8902 (3)	C(9′)	8048 (6)	9117 (6)	3984 (3)
C(10)	4296 (6)	6353 (6)	8506 (3)	C(10′)	9290 (6)	8882 (5)	3591 (3)
C(11)	1917 (6)	5667 (7)	8843 (3)	C(11′)	6917 (6)	8197 (6)	3928 (3)
C(12)	684 (6)	5997 (6)	9239 (3)	C(12′)	5692 (6)	8521 (7)	4316 (3)
C(13)	1085 (6)	6212 (5)	9914 (3)	C(13′)	6075 (6)	8746 (5)	4999 (3)
C(14)	2216 (5)	7151 (5)	9944 (3)	C(14′)	7199 (6)	9691 (6)	5018 (3)
C(15)	2367 (6)	7495 (7)	10634 (3)	C(15′)	7364 (7)	10028 (7)	5707 (3)
C(16)	906 (6)	7421 (7)	10865 (3)	C(16′)	5894 (7)	9948 (7)	5941 (3)
C(17)	28 (6)	6847 (5)	10329 (3)	C(17′)	5015 (6)	9375 (6)	5399 (3)
C(18)	1550 (7)	5074 (6)	10251 (3)	C(18′)	6545 (7)	7605 (6)	5317 (3)
C(19)	5158 (7)	5335 (6)	8772 (3)	C(19′)	10133 (7)	7847 (7)	3853 (3)
C(20)	−1166 (6)	6160 (6)	10588 (3)	C(20′)	3855 (7)	8655 (6)	5667 (3)
C(21)	−2097 (6)	6944 (6)	10956 (3)	C(21′)	2913 (7)	9432 (7)	6046 (3)
C(22)	−3057 (8)	6313 (7)	11374 (4)	C(22′)	1965 (9)	8798 (8)	6450 (4)
C(23)	−3991 (6)	7118 (6)	11713 (3)	C(23′)	1083 (7)	9593 (8)	6835 (4)
C(24)	−4900 (11)	6599 (9)	12177 (6)	C(24′)	55 (12)	9077 (9)	7242 (5)
C(25)	−5135 (15)	5508 (9)	12253 (7)	C(25′)	351 (12)	8113 (11)	7581 (6)
C(26)	−5861 (10)	7456 (10)	12455 (5)	C(26′)	−785 (11)	9945 (10)	7547 (6)
C(27)	−1994 (7)	5519 (7)	10069 (4)	C(27′)	3008 (7)	8042 (8)	5135 (4)
H(1)	3397	5283	7784	H(1′)	8410	7788	2880
H(2)	3186	6789	7658	H(2′)	8198	9289	2738
H(3)	4707	6153	6904	H(3′)	9703	8669	1989
H(4)	5651	5316	7459	H(4′)	10625	7789	2532
H(5)	7051	6791	8358	H(5′)	12097	9318	3463
H(6)	6886	8271	8151	H(6′)	11916	10784	3233
H(7)	4460	8159	8278	H(7′)	9521	10661	3306
H(8)	6149	8585	9246	H(8′)	11166	11093	4336
H(9)	4827	8070	10099	H(9′)	9841	10592	5174
H(10)	3853	5997	9810	H(10′)	8853	8543	4900
H(11)	2599	7355	8700	H(11′)	7608	9898	3782
H(12)	1582	5596	8356	H(12′)	6585	8120	3441
H(13)	2312	4840	9005	H(13′)	7318	7373	4092
H(14)	−42	5295	9213	H(14′)	4972	7814	4289
H(15)	225	6778	9046	H(15′)	5229	9297	4119
H(16)	1975	7937	9685	H(16′)	6939	10463	4751
H(17)	3027	6898	10890	H(17′)	8029	9429	5960
H(18)	2761	8368	10684	H(18′)	7757	10900	5759
H(19)	885	6898	11285	H(19′)	5875	9418	6359
H(20)	530	8282	10961	H(20′)	5514	10806	6043
H(21)	−538	7434	10022	H(21′)	4445	9961	5093
H(22)	1829	5252	10737	H(22′)	6824	7763	5805
H(23)	2409	4714	10021	H(23′)	7410	7269	5082
H(24)	723	4459	10227	H(24′)	5731	6978	5285
H(25)	5442	5506	9257	H(25′)	10438	8005	4337
H(26)	6059	5237	8507	H(26′)	11022	7746	3579
H(27)	4567	4546	8739	H(27′)	9529	7065	3820
H(28)	−723	5516	10903	H(28′)	4313	8005	5974
H(29)	−2695	7457	10623	H(29′)	2317	9956	5718
H(30)	−1471	7513	11247	H(30′)	3539	9990	6344
H(31)	−2466	5823	11719	H(31′)	1309	8265	6152
H(32)	−3668	5725	11087	H(32′)	2554	8250	6769
H(33)	−4628	7549	11361	H(33′)	547	10163	6508
H(34)	−3364	7753	11959	H(34′)	1760	10099	7137
H(35)	−4032	6319	12462	H(35′)	−585	8651	6889
H(36)	−4378	4993	12030	H(36′)	961	7530	7314
H(37)	−6124	5301	12049	H(37′)	−570	7678	7704
H(38)	−5113	5318	12749	H(38′)	911	8371	8004

Table 1 (*cont.*)

Molecule 1	x	y	z	Molecule 2	x	y	z
H(39)	−5535	8334	12364	H(39′)	−968	10673	7235
H(40)	−5885	7318	12955	H(40′)	−258	10243	7970
H(41)	−6861	7322	12244	H(41′)	−1739	9560	7663
H(42)	−1336	4952	9817	H(42′)	3652	7482	4871
H(43)	−2456	6144	9749	H(43′)	2548	8687	4826
H(44)	−2775	5009	10279	H(44′)	2226	7529	5341

weighting scheme was $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0{\cdot}025$. The final R was 0·091 with a mean shift/error of 0·013 on the final cycle.* The scattering factors of Cromer & Mann (1968) were used for C and O, and those of Stewart, Davidson & Simpson (1965) for H. Final positional parameters are in Table 1, anisotropic thermal parameters for C and O in Table 2.

Discussion

Final bond lengths and valence angles for the two independent molecules are given in Tables 3 and 4. The geometry is in good agreement with expected values with an overall mean distance for C_{sp^3}—C_{sp^3} of 1·535 and C_{sp^3}—C_{sp^2} of 1·494 Å. The two terminal methyl groups of the 17β side chain [C(25), C(26)] are less well defined and have been omitted from the averaging. The mean differences between corresponding distances and angles in the two molecules are 0·010 Å and 0·8° (both $\sim 1\sigma$) respectively.

Fig. 1 shows one asymmetric unit projected down **b**. The conformations of the two molecules are almost identical except for a change in the orientation of methyl C(25) at the end of the extended side chain. The similarity is shown by the intra-annular torsion angles (ω) for the four rings listed in Table 5 for the B, C and D rings and in Table 6 for the A ring. The mean difference in ω values for molecules 1 and 2 is 1·0° over all rings, but is significantly greater for ring A (2·3°) than for the other rings (0·3, 0·5, 0·8° respectively).

This appears to be the first reported X-ray study of a 3-keto-Δ^6-steroid and the conformation of ring B is of special interest. The ring has an almost symmetrical substitution pattern except for the axial methyl group C(19), and adopts a slightly distorted half-chair conformation. All torsion angles show small expansions (1–7°, Table 5) over the minimum-energy values for unsubstituted cyclohexene (Bucourt & Hainaut, 1965). The mean torsion angle ($\bar{\omega}$) in the ring is 34·1° (molecule 1) and 33·8° (molecule 2), showing the increased puckering over free cyclohexene ($\bar{\omega} = 30{\cdot}3°$). The asymmetry parameter $\Delta C_2^{6,7}$ (Duax & Norton, 1975), which measures the deviation of the ring from the ideal C_2 conformer, is 4·3° in molecule 1 and 3·7° in molecule 2. This asymmetry is largely due to the opening of the torsion angle ω(10–5–6–7) to a mean value of −20·8°. The Δ^6 bond is planar within the limits of experimental error, with C(9) and C(10) respectively 0·34 below and 0·36 Å above the plane (mean for both molecules). These results are very similar to those obtained by Peck, Langs, Eger & Duax (1974*a*) for the 1,4,6-androstatriene-3,17-dione–*p*-bromophenol complex, *viz* $\bar{\omega} = 32{\cdot}8°$, $\Delta C_2^{6,7} = 2{\cdot}4°$, ω(10–5–6–7) = −21·0°, with displacements of C(9) and C(10) from the Δ^6 plane at −0·36 and +0·41 Å.

The conformation of ring A in its present environment is fundamental to an understanding of the rapid rate of 2-condensation with the benzaldehyde observed for III by Barton *et al.* (1960), and also the preference for 2 rather than 4-condensation. In order to introduce a quantitative aspect we have examined ring-A conformations, determined by X-ray diffraction, for steroids which have identical, or nearly identical, substitution patterns to those used in the chemical study. The relevant X-ray studies for which some numeric data are presently available were obtained from the files of the Crystallographic Data Centre (Kennard, Watson, Allen, Motherwell, Town & Rodgers, 1975) and are summarized in formulae IV–VIII. Both the chemical and crystallographic substitution patterns are given, together with the reaction rate (r) as a percentage of the rate for Δ^8-lanostenone ($r = 100$). Except for VII they are either identical or differ only in the 17β-substituent, variation of which is known to have a minimal effect on reaction rates (Barton *et al.*, 1960). The 7α-methyl group in VII should also have a relatively small effect since all 1,3 and 1,5 interactions are with H atoms rather than with other methyl groups, which could lead to significant conformational distortion (Geise, Altona & Romers, 1967; Allen, Isaacs, Kennard & Motherwell, 1973; Allen, Kennard & Sheldrick, 1977). For this reason, structures where the 17 substituent is a keto group, *e.g.* 5α-androstan-3,17-dione (Coiro, Giglio, Lucano & Puliti, 1973; Peck, Langs, Eger & Duax, 1974*b*) and 4α,8α,14β-trimethyl-18-nor-5α,13β-androst-9(11)-ene-3,17-dione (Ward, Templeton & Zalkin, 1973) were excluded, as well as structures with 17α substituents such as the 3-oxo-

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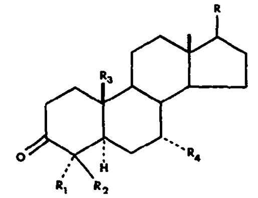
* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32229 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

lanosta-8,24-diene (Lanfredi, Tiripicchio & Camellini, 1975).

Table 2. *Anisotropic temperature factors* (Å^2 × 10^3)

The temperature factor exponent takes the form: $[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Molecule 1						
O(3)	146 (5)	143 (5)	110 (4)	18 (4)	31 (4)	−5 (5)
C(1)	84 (4)	120 (6)	71 (4)	−6 (4)	−1 (3)	−4 (4)
C(2)	94 (5)	131 (6)	83 (4)	−10 (5)	12 (4)	1 (5)
C(3)	84 (4)	109 (6)	92 (5)	12 (4)	17 (4)	4 (4)
C(4)	75 (4)	107 (5)	103 (5)	2 (5)	17 (4)	2 (4)
C(5)	73 (4)	68 (4)	86 (4)	3 (3)	3 (3)	−9 (3)
C(6)	75 (4)	76 (4)	99 (5)	−18 (4)	5 (4)	−16 (3)
C(7)	63 (3)	77 (4)	89 (4)	−26 (4)	0 (3)	−15 (3)
C(8)	56 (3)	66 (4)	69 (3)	−4 (3)	−1 (3)	−9 (3)
C(9)	63 (3)	73 (4)	71 (3)	−2 (3)	−2 (3)	−11 (3)
C(10)	66 (3)		77 (4)	−3 (3)	−7 (3)	−5 (3)
C(11)	73 (4)	88 (5)	83 (4)	−20 (4)	−2 (3)	−22 (4)
C(12)	76 (4)	80 (5)	77 (4)	−9 (3)	−2 (3)	−9 (3)
C(13)	64 (3)	50 (3)	76 (3)	4 (3)	−1 (3)	−6 (3)
C(14)	63 (3)	55 (3)	68 (3)	1 (3)	−4 (3)	−5 (3)
C(15)	80 (4)	83 (4)	59 (3)	−3 (3)	−5 (3)	−5 (3)
C(16)	85 (4)	80 (4)	68 (3)	−8 (3)	−1 (3)	−10 (4)
C(17)	60 (3)	61 (4)	73 (3)	−3 (3)	3 (3)	−1 (3)
C(18)	95 (5)	50 (4)	116 (5)	16 (4)	9 (4)	11 (3)
C(19)	86 (4)	67 (4)	100 (5)	−2 (4)	0 (4)	12 (3)
C(20)	62 (3)	62 (4)	94 (4)	3 (3)	5 (3)	1 (3)
C(21)	73 (4)	69 (4)	93 (4)	−3 (3)	11 (3)	1 (3)
C(22)	97 (5)	67 (4)	137 (6)	14 (4)	36 (4)	9 (4)
C(23)	71 (4)	74 (4)	97 (4)	9 (4)	16 (3)	1 (3)
C(24)	148 (7)	90 (6)	253 (9)	52 (7)	117 (7)	46 (6)
C(25)	309 (11)	82 (7)	378 (11)	−7 (8)	257 (9)	−37 (8)
C(26)	127 (6)	120 (7)	181 (8)	8 (7)	61 (6)	28 (6)
C(27)	91 (5)	89 (5)	115 (5)	−20 (4)	4 (4)	−26 (4)
Molecule 2						
O(3′)	152 (5)	131 (5)	136 (5)	−1 (4)	55 (4)	−24 (5)
C(1′)	80 (4)	86 (5)	82 (4)	0 (4)	1 (3)	−2 (4)
C(2′)	89 (5)	92 (5)	99 (5)	−4 (4)	7 (4)	−6 (4)
C(3′)	93 (5)	107 (6)	107 (5)	12 (5)	28 (4)	8 (5)
C(4′)	87 (5)	120 (6)	101 (5)	−11 (5)	13 (4)	−21 (5)
C(5′)	79 (4)	78 (5)	91 (4)	−2 (4)	3 (3)	−20 (4)
C(6′)	93 (5)	106 (6)	100 (5)	−35 (4)	7 (4)	−25 (4)
C(7′)	76 (4)	90 (5)	99 (5)	−36 (4)	−6 (4)	−14 (4)
C(8′)	64 (3)	67 (4)	73 (4)	−8 (3)	−9 (3)	−13 (3)
C(9′)	57 (3)	67 (4)	79 (4)	−3 (3)	−4 (3)	−5 (3)
C(10′)	74 (4)	53 (3)	75 (4)	0 (3)	−8 (3)	−1 (3)
C(11′)	78 (4)	82 (5)	74 (4)	−11 (3)	−2 (3)	−23 (3)
C(12′)	70 (4)	85 (5)	74 (4)	−8 (3)	−6 (3)	−15 (3)
C(13′)	73 (3)	56 (4)	63 (3)	4 (3)	−4 (3)	0 (3)
C(14′)	69 (3)	60 (4)	69 (3)	−2 (3)	−5 (3)	−10 (3)
C(15′)	88 (4)	98 (5)	68 (4)	−16 (4)	−3 (3)	−12 (4)
C(16′)	91 (4)	76 (4)	78 (4)	−15 (3)	3 (3)	−11 (4)
C(17′)	76 (4)	59 (4)	72 (4)	−3 (3)	2 (3)	5 (3)
C(18′)	106 (5)	48 (4)	99 (4)	16 (3)	3 (4)	18 (3)
C(19′)	88 (4)	79 (5)	89 (4)	3 (4)	−11 (3)	20 (4)
C(20′)	84 (4)	66 (4)	84 (4)	−1 (3)	4 (3)	−11 (3)
C(21′)	87 (4)	74 (4)	99 (5)	−4 (4)	22 (4)	−1 (4)
C(22′)	125 (6)	86 (5)	124 (6)	13 (5)	41 (5)	7 (5)
C(23′)	89 (5)	99 (5)	105 (5)	−3 (4)	23 (4)	−2 (4)
C(24′)	194 (9)	85 (6)	162 (8)	3 (6)	87 (7)	18 (6)
C(25′)	163 (8)	181 (9)	271 (10)	126 (8)	102 (8)	81 (7)
C(26′)	170 (8)	112 (7)	220 (9)	−20 (7)	102 (7)	−4 (7)
C(27′)	90 (5)	90 (5)	124 (5)	−12 (5)	9 (4)	−23 (4)



(IV)	*Chem*	$R = \mathrm{OH}, R_1 = R_2 = \mathrm{CH_3}, R_3 = R_4 = \mathrm{H}$. $r = 17$.
	Cryst	$R = \mathrm{OCOCH_2I}$: 17β-iodoacetoxy-4,4-dimethyl-19-nor-5α-androstan-3-one (Ferguson, McCauley, Midgley, Robertson & Whalley, 1970).
(V)	*Chem*	$R = \mathrm{OH}, R_1 = R_2 = R_3 = \mathrm{CH_3}, R_4 = \mathrm{H}$. $r = 58$.
	Cryst	$R = \mathrm{OCOCH_2I}$: 17β-iodoacetoxy-4,4-dimethyl-5α-androstan-3-one (Ferguson, McCauley, Midgley, Robertson & Whalley, 1970).
(VI)	*Chem*	$R = \mathrm{OH}, R_3 = \mathrm{CH_3}, R_1 = R_2 = R_4 = \mathrm{H}$. $r = 188$.
	Cryst	identical: 17β-hydroxy-5α-androstan-3-one.
	VI(*a*), (*b*)	Two independent molecules (Courseille, Precigoux, Leroy & Busetta, 1973).
	VI(*c*)	Hydrated form (Busetta, Courseille, Fornies-Marquina & Hospital, 1972).
(VII)	*Chem*	$R = \mathrm{OH}, R_3 = \mathrm{CH_3}, R_1 = R_2 = R_4 = \mathrm{H}$. $r = 188$.
	Cryst	$R = \mathrm{OCOCH_3}, R_4 = \mathrm{CH_3}$: 17$\beta$-acetoxy-7$\alpha$-methyl-5$\alpha$-androstan-3-one (Hazel, Rohrer, Duax & Wolff, 1976).
(VIII)	*Chem*	$R = \mathrm{OH}, R_3 = \mathrm{CH_3}, R_1 = R_2 = R_4 = \mathrm{H}$. $r = 188$.
	Cryst	R = toluene-*p*-sulphonyloxy: 17β-*p*-toluenesulphonyloxy-5α-androstan-3-one (de Graff & Romers, 1974).

Intra-annular torsion angles for the nine independent *A* rings of compounds III–VIII are listed in Table 6. With reference to Fig. 2, ω_0 refers to the twist about the 1–2 bond and ω_1–ω_5 follow cyclically anticlockwise; $\bar{\omega}$ is the mean absolute torsion angle in the ring. We have also calculated the quantities Δ_1 and Δ_2 with respect to the mirror planes which pass through C(1), C(4) and C(2), C(5) in a perfect chair, where

$$\Delta_n = \left(\sum_{i=3}^{5} |\omega_{n+i}| - \sum_{i=0}^{2} |\omega_{n+i}|\right)/3$$

and $(n + i)$ is taken modulo 6. Δ_n is thus the difference between the mean absolute torsion angles on either side of the mirror plane defined by n. For a perfect chair all $\Delta_n = 0$; in distorted rings positive Δ_n indicate a relative flattening in the area of atoms $n + 1$, $n + 2$, while a negative Δ_n indicates puckering.

The value of $\bar{\omega}$ for III(*a*), (Table 6) ($r = 645$) shows that in the present structure ring *A* is considerably flattened in comparison with $\bar{\omega}$ = 55·9° for free cyclohexane (Geise, Buys & Mijlhoff, 1971). The average over both molecules of III is $\bar{\omega}$ = 51·2°, but values for individual angles show that the flattening is chiefly in the area of C(2) and C(3), in agreement with the qualitative study of Robinson & Whalley (1963). They used models to show that the effect of the Δ^6 bond was to displace C(6) downwards relative to the saturated skeleton. The displacement produces a positive rotation of bonds about the ring junction C(5)–C(10), an opening of ω_4 and a closing of ω_1. This implies an expansion of the angle C(1)–C(2)–C(3) (114·5° in III) and prepares C(2) for rehybridization. The effect of transmission of conformational distortion across the ring junction is not so great at C(4). The value of ω_2 is indeed reduced in III but ω_3 (mean 57·0°) is increased over the free-ring value, giving an angle C(3)–C(4)–C(5) of 110·2°. This is not a complete explanation of the preference for C(2)-condensation since steric factors, as shown below, also play a large part.

The quantities Δ_1 and Δ_2 enable the effects observed in the present structure to be compared with those oc-

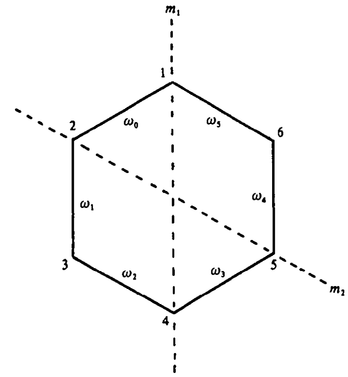


Fig. 2. Definition of *A*-ring torsion angles and planes of reference (see *Discussion*).

Table 3. *Bond lengths* (Å)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
O(3)–C(3)	1·230 (11)	1·230 (12)	C(1)–C(2)	1·541 (12)	1·538 (12)
C(2)–C(3)	1·484 (13)	1·495 (13)	C(3)–C(4)	1·479 (12)	1·495 (12)
C(4)–C(5)	1·534 (11)	1·543 (12)	C(5)–C(10)	1·554 (11)	1·553 (12)
C(1)–C(10)	1·533 (10)	1·529 (11)	C(5)–C(6)	1·486 (10)	1·486 (11)
C(6)–C(7)	1·332 (11)	1·313 (12)	C(7)–C(8)	1·517 (11)	1·511 (11)
C(8)–C(9)	1·538 (10)	1·533 (10)	C(9)–C(10)	1·547 (10)	1·538 (10)
C(9)–C(11)	1·528 (11)	1·539 (11)	C(11)–C(12)	1·557 (11)	1·540 (11)
C(12)–C(13)	1·498 (9)	1·512 (10)	C(13)–C(14)	1·554 (10)	1·553 (10)
C(8)–C(14)	1·524 (10)	1·533 (10)	C(14)–C(15)	1·526 (10)	1·522 (10)
C(15)–C(16)	1·546 (11)	1·558 (11)	C(16)–C(17)	1·554 (10)	1·564 (11)
C(13)–C(17)	1·575 (10)	1·557 (10)	C(13)–C(18)	1·553 (11)	1·541 (11)
C(10)–C(19)	1·541 (11)	1·544 (11)	C(17)–C(20)	1·541 (10)	1·542 (11)
C(20)–C(21)	1·527 (11)	1·543 (12)	C(21)–C(22)	1·514 (12)	1·488 (12)
C(22)–C(23)	1·512 (13)	1·526 (14)	C(23)–C(24)	1·487 (15)	1·486 (15)
C(24)–C(25)	1·288 (16)	1·350 (17)	C(24)–C(26)	1·507 (17)	1·467 (17)
C(20)–C(27)	1·538 (12)	1·553 (12)			

Table 4. *Bond angles* (°)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
C(2)–C(1)–C(10)	113·3 (6)	114·5 (6)	C(1)–C(2)–C(3)	114·4 (8)	114·5 (8)
O(3)–C(3)–C(2)	121·2 (8)	120·8 (8)	O(3)–C(3)–C(4)	121·7 (9)	120·7 (9)
C(2)–C(3)–C(4)	117·0 (8)	118·5 (8)	C(3)–C(4)–C(5)	110·5 (7)	109·9 (7)
C(4)–C(5)–C(6)	113·5 (6)	113·0 (7)	C(4)–C(5)–C(10)	111·8 (7)	112·8 (7)
C(5)–C(6)–C(7)	124·0 (7)	123·9 (7)	C(6)–C(5)–C(10)	112·2 (6)	111·9 (8)
C(6)–C(7)–C(8)	122·7 (7)	123·6 (8)	C(7)–C(8)–C(9)	110·3 (6)	109·9 (6)
C(7)–C(8)–C(14)	112·9 (6)	114·2 (6)	C(9)–C(8)–C(14)	108·7 (5)	108·0 (5)
C(8)–C(9)–C(10)	111·2 (6)	111·2 (6)	C(8)–C(9)–C(11)	110·7 (6)	110·3 (6)
C(10)–C(9)–C(11)	116·0 (6)	115·4 (6)	C(1)–C(10)–C(5)	106·1 (6)	106·8 (6)
C(1)–C(10)–C(9)	111·6 (6)	112·4 (6)	C(5)–C(10)–C(9)	105·3 (6)	105·8 (6)
C(1)–C(10)–C(19)	109·9 (7)	108·0 (6)	C(5)–C(10)–C(19)	112·2 (6)	112·2 (5)
C(9)–C(10)–C(19)	111·5 (6)	111·7 (6)	C(9)–C(11)–C(12)	111·9 (7)	112·1 (7)
C(11)–C(12)–C(13)	112·3 (6)	112·8 (6)	C(12)–C(13)–C(14)	108·4 (6)	107·2 (6)
C(12)–C(13)–C(17)	117·4 (6)	117·4 (6)	C(14)–C(13)–C(17)	98·4 (5)	99·0 (6)
C(12)–C(13)–C(18)	111·6 (6)	109·8 (6)	C(14)–C(13)–C(18)	111·6 (6)	112·4 (6)
C(17)–C(13)–C(18)	108·7 (6)	110·6 (6)	C(8)–C(14)–C(13)	112·5 (6)	113·0 (6)
C(8)–C(14)–C(15)	119·5 (6)	118·2 (6)	C(13)–C(14)–C(15)	105·2 (6)	104·6 (6)
C(14)–C(15)–C(16)	103·7 (6)	103·3 (6)	C(15)–C(16)–C(17)	106·8 (6)	106·5 (6)
C(13)–C(17)–C(16)	104·3 (5)	103·6 (6)	C(13)–C(17)–C(20)	119·9 (6)	118·7 (6)
C(16)–C(17)–C(20)	111·5 (6)	110·5 (6)	C(17)–C(20)–C(21)	111·6 (6)	110·9 (7)
C(17)–C(20)–C(27)	112·3 (6)	111·0 (6)	C(21)–C(20)–C(27)	109·8 (6)	109·1 (6)
C(20)–C(21)–C(22)	115·1 (7)	115·3 (7)	C(21)–C(22)–C(23)	113·5 (7)	113·9 (8)
C(22)–C(23)–C(24)	118·0 (8)	119·6 (9)	C(23)–C(24)–C(25)	126·3 (12)	120·2 (11)
C(23)–C(24)–C(26)	114·0 (9)	113·5 (9)	C(25)–C(24)–C(26)	117·9 (12)	115·8 (12)

curring in IV–VIII. If we exclude the study of VIII (de Graaff & Romers, 1974) then the values of Δ_1 [relative flattening C(2), C(3)] increase from −3·8 to 16·5° as r increases from 17 to 645. Compound VIII has an anomalously high value of Δ_1, and here the ring is not only flattened, but also twisted about the C_2 axis which bisects C(2)–C(3) and C(5)–C(10) in a perfect chair. This twist is indicated by the $\Delta C_2^{2,3}$ asymmetry parameter (Duax & Norton, 1975) of 9·2°; this quantity never exceeds 4·9° in III–VII. There is evidence that this C_2 symmetry is closely retained in the benzylidene steroid (II) from the structure of *cis,trans*-1,2-di(4-bromobenzylidene)cyclohexane (Groth, 1969) where $\Delta C_2^{2,3} = 2{\cdot}3°$. De Graaff & Romers (1974), who performed valence-force-field calculations on VIII, concluded that crystal packing forces were responsible for the anomalously flat A ring. The results for Δ_1 are summarized in Table 7, where appropriate averages have been taken over molecules with the same r value, and VIII has been excluded.

Table 5. *Intra-annular torsion angles* ($\omega°$) *for rings* B, C, D

Values for ring B are compared with theoretical values of Bucourt & Hainaut (1965); $\bar{\omega}$ is the mean angle of puckering in each ring.

Ring B

Bond	Molecule 1	Molecule 2	Theoretical
5–6	−21·2	−20·5	−15
6–7	2·2	2·1	0
7–8	−15·5	−15·6	−15
8–9	48·5	48·3	45
9–10	−66·3	−66·0	−62
10–5	50·7	50·1	45
	$\bar{\omega}$ = 34·1	33·8	30·3

Ring C

Bond	Molecule 1	Molecule 2
8–9	−56·8	−57·2
9–11	54·4	55·0
11–12	−54·7	−55·0
12–13	54·9	54·8
13–14	−59·3	−59·6
14–8	60·1	61·4
	$\bar{\omega}$ = 56·7	57·1

Ring D

Bond	Molecule 1	Molecule 2
13–14	46·3	48·1
14–15	−35·2	−35·6
15–16	9·1	9·0
16–17	19·6	20·5
17–13	−39·4	−40·8

The values of Δ_2 [relative flattening C(3), C(4)] are less than the Δ_1 values for all molecules except the two 4,4-dimethyl derivatives IV and V, where 4-condensation is blocked in any case. It is known that the introduction of *gem*-dimethyl groups into the cyclohexane ring induces considerable flattening (Romers, Altona, Jacobs & de Graaff, 1974). In structures like V there is a strong 1,3 interaction between β-methyl groups at C(4) and C(10); the angle C(4)–C(5)–C(10) expands and ω_3 contracts (see for example Allen, Kennard & Sheldrick, 1977; Allen, Isaacs, Kennard & Motherwell, 1973). The conclusion is that C(4) is generally less well prepared for hybridization than C(2). An additional and probably more important reason for the overall preference for 2-condensation is the increased steric hindrance of C(4) over C(2). The H atoms at both sites are involved in similar 1,2-interactions with H atoms at ~2·4 Å, and with O at 2·5 and 3·0 Å. Longer-range (*i.e.* 1,3 and 1,4) interactions are, however, much more frequent and stronger for the C(4) H atoms; for example in III the closest approach of a C4(H) to a methyl C19(H) is only 2·09 Å, whereas C2(H)–C19(H) all exceed 2·27 Å and C4(H) have an additional involvement with C6(H) at 2·5 Å. However, the location of the H atoms in this structure does involve geometrical assumptions.

Although the available pertinent X-ray data are presently limited, the results show, in general quantitative terms, the effect of long-range conformational transmission on steroid A rings. It does appear (Allen & Kennard, 1977) that further correlation with the reaction-rate studies is possible by deriving suitable correction factors for torsion angles in, *e.g.*, 3-hydroxy- and 3-*p*-bromobenzoate derivatives which are more common in the X-ray literature. We also note that the

Table 7. *Values of* Δ_1, *with averages taken over molecules with the same r value*

Compound	Δ_1	r
IV	−3·8	17
V	1·2	58
VI(*a*), (*b*), (*c*), VII	5·0	188
III(*a*), (*b*)	14·6	645

Table 6. *Analysis of intra-annular torsion angles for ring A of compounds* III–VIII

Compound	ω_0	ω_1	ω_2	ω_3	ω_4	ω_5	$\bar{\omega}$	Δ_1	Δ_2	r
IV	−54·9	56·8	−54·7	50·4	−51·9	52·8	53·6	−3·8	−0·8	17
V	−50·8	48·5	−47·0	46·6	−50·8	52·6	49·4	1·2	4·0	58
VI(*a*)	−54·7	51·6	−52·8	56·6	−55·6	55·7	54·5	3·0	2·0	188
(*b*)	−51·6	48·7	−50·3	56·3	−58·8	55·9	53·6	6·8	3·3	188
(*c*)	−51·0	49·1	−51·4	56·0	−57·4	55·1	53·3	5·7	2·3	188
VII	−51·1	51·3	−54·9	58·8	−57·7	54·0	54·6	4·4	−2·2	188
VIII	−48·9	37·2	−38·7	49·9	−58·0	57·9	48·4	13·7	13·0	188
III(*a*)	−46·1	41·2	−46·6	58·0	−62·0	55·2	51·5	13·8	5·8	645
(*b*)	−43·2	37·8	−43·5	56·0	−61·3	53·8	49·3	16·5	7·7	645

$\Delta^{9(11)}$-17-keto steroid (Ward, Templeton & Zalkin, 1973), excluded from this analysis on the basis of its substitution pattern, conforms very well to the figures of Table 7. The Δ_1 value of 7·9° ($\Delta_2 = 6{\cdot}4°$) for the reaction rate *r* of ~235 may be calculated from the group rate factors given by Barton *et al.* (1960), assuming that the 17-keto group has minimal effect.

With respect to the present structure III there is independent evidence to support the results of Table 7. In the structure of 17β-hydroxy-1,4-androstadien-3-one (Duax, Norton, Pokrywiecki & Eger, 1971) the *A* ring is almost planar with $\Delta_1 = -2{\cdot}2°$. The addition of the Δ^6 bond in 1,4,6-androstatriene-3,17-dione (Peck *et al.*, 1974*a*) changes Δ_1 to +7·4°, a net change due to conformational transmission of 9·5°. A similar structural change (addition of a Δ^6 bond) relates compounds with $r = 188$ in Table 7 to the present structure. Here the change in Δ_1 is 10·1°, a value very close to that obtained for the 1,4-dienes. These figures show the real effect of conformational transmission over any flattening caused by the sp^2-hybridized C(3) atom.

The *C* ring in Δ^6-cholesten-3-one is a slightly puckered chair (Table 5), $\bar{\omega}$ averaged over both molecules being 56·9°. The effects of the Δ^6 bond can be seen in the area of C(11), C(12) which are analogous to C(3), C(2) of ring *A*. If Δ_1 is defined with respect to the plane through C(9), C(13) then we obtain a value of 4·3°. The comparable value for the 1,4,6-androstatriene (Peck *et al.*, 1974*a*) is 6·3°, while for compounds lacking the Δ^6 bond, *e.g.* VI(*a*), (*b*), (*c*) above, Δ_1 is smaller at 2·8°. Thus the net effect of the Δ^6 bond on ring *C* is less by a factor of ~3·5 than its effect on ring *A*, reflecting the greater rigidity of the doubly-fused all-sp^3 *C* ring.

The five-membered *D* ring has values of φ_m and Δ (Altona, Geise & Romers, 1968) of 46·4 and 11·8° for molecule 1 and 48·4 and 12·8° for molecule 2. These values indicate a conformation intermediate between a 13β,14α half-chair and a 13β envelope; they fall into the most heavily populated area of a φ_m–Δ plot for 165 steroids prepared by Duax & Norton (1975).

The 17β side chain is fully extended in both molecules of III, with ω values in the range 166·0–179·5°. The ill-defined methyl C(25) adopts a different orientation in the two molecules with ω(22–23–24–25) at 12° in molecule 1 and 41° in molecule 2. The methyl C(27) is oriented towards the α side of the steroid as expected (Romers, Altona, Jacobs & de Graaff, 1974).

The overall shape of the steroid ring skeleton in III is convex towards the β-methyl groups C(18) and C(19). The angles between the non-bonded vectors C(10)–C(19) and C(13)–C(18) are 16·7 and 15·3° in the two molecules, somewhat larger than expected (Geise, Altona & Romers, 1967).

The molecular packing is illustrated by the stereo pair of Fig. 3. The two independent molecules adopt almost identical orientations in the cell, the mean planes through C(1)–C(24) in the two molecules making an angle of 0·8°, with the steroid ring system some 75° to **b**. Pairs of C_8H_{17} side chains are arranged between, and parallel to, pairs of ring nuclei along **c**. Intermolecular contacts correspond to van der Waals interactions with $C\cdots C > 3{\cdot}5$ and $C\cdots O > 3{\cdot}35$ Å.

We thank Professor D. H. R. Barton FRS for suggesting the problem and supplying the crystals, the Medical Research Council for financial support and the Science Research Council for the provision of the diffractometer and for financial support to JJG. All calculations were carried out on the University of Cambridge IBM 370/165 computer with programs written by GMS; crystallographic plots were prepared with *PLUTO* developed by Dr W. D. S. Motherwell.

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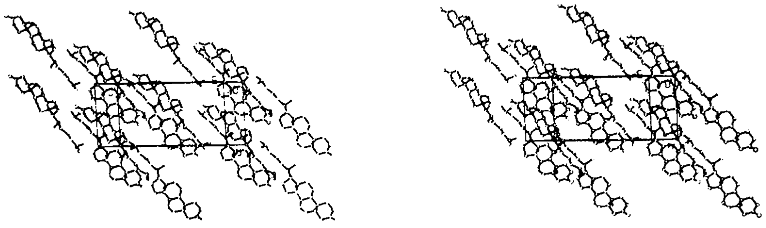

Fig. 3. Stereo view of the molecular packing.

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β-Tribenzopyrene (Naphtho[1,2,3,4-*rst*]pentaphene)

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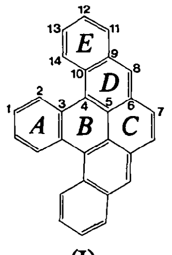
(*Received* 1 *September* 1976; *accepted* 20 *October* 1976)

β-Tribenzopyrene crystallizes in the orthorhombic system, space group $Pn2_1m$ with $a = 4·0260\,(5)$, $b = 10·693\,(3)$ and $c = 19·720\,(4)$ Å and two molecules in the unit cell. The molecule is required to have crystallographic mirror symmetry. The structure was refined to an R of 0·046 for 331 observed reflexions. The considerable strain inherent in a planar molecular model is spread out over the ring systems and is relieved by a succession of out-of-plane bendings and angular deformations such that the C atoms in the most overcrowded region have an intramolecular separation of 3·04 Å, and the separation of the hydrogens attached to these carbons is only 1·98 Å. In achieving this, ring A remains essentially planar, whereas all the other rings are forced to adopt boat conformations.

Introduction

As part of our continuing interest in overcrowded molecular structures (Ferguson & Robertson, 1963; Roberts, Brauer, Tsay & Krüger, 1974), we have examined $C_{28}H_{16}$ (I) by X-ray diffraction.



(I)

Crystal data

$C_{28}H_{16}$, FW 352·4, orthorhombic, $a = 4·0260$ (5), $b = 10·693$ (2), $c = 19·720$ (4) Å, $V = 848·95$ Å^3,