The Crystal and Molecular Structure of Cholest-4-en-3-one

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The title steroid is monoclinic with $a = 14.634$ (5), $b = 7.862$ (5), $c = 10.674$ (5) Å, $\beta = 105.1$ (2)°, $Z = 2$, space group $P2_1$. The structure was determined by a new multisolution tangent refinement program incorporating a negative quartet test, and refined by full-matrix least squares to a final R of 0.049 for 1292 independent reflexions measured on a four-circle diffractometer. Rings B, C and D are *trans*-fused and the side chain is in the extended configuration.

Introduction

Cholest-4-en-3-one is an important synthetic intermediate in many steroid transformations. It has been shown to be involved in the metabolic pathways from cholesterol to 5α-cholest-7-en-3β-ol and 5β-cholestanol (Banthorpe & Charlwood, 1974) but does not itself exhibit important biological properties. The 4-en-3-one moiety is, however, a feature of many steroid hormones (Fieser & Fieser, 1959).

Experimental

The compound (m.p. 80–81°) was prepared by the Oppenauer oxidation of cholesterol and was recrystallized from methanol. Microanalysis yielded the following results:

	% C	% H
Found	84.20	11.40
Calculated for $C_{27}H_{44}O$	84.38	11.45.

The crystals were colourless needles elongated along **b**. From oscillation and Weissenberg photographs (Cu $K\alpha$ radiation, $\lambda = 1.542$ Å), the space group $P2_1$ was indicated by the systematic absences $0k0, k = 2n+1$. The density was measured in aqueous sodium chloride solution. Crystal data are listed in Table 1.

Table 1. *Crystal data*

Molecular formula: $C_{27}H_{44}O$	
M.W. 384.3	
Space group: $P2_1$	
$a = 14.634$ (5) Å	
$b = 7.862$ (5)	$D_m = 1.08$ g cm^{-3}
$c = 10.674$ (5)	$D_c = 1.08$ for $Z = 2$
$\beta = 105.1$ (2)°	$\mu = 0.32$ cm^{-1}
$V = 1185.74$ Å^3	$F(000) = 428$

The cell parameters were obtained by a least-squares analysis of the settings of 25 reflexions measured on a Phillips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å, graphite-monochromated) and a crystal $0.3 \times 0.4 \times 0.15$ mm. The intensities of 1583 reflexions in the range $3° < \theta < 22°$ were recorded by the ω–2θ scan technique (scan width $1.2° \theta$, scan speed $0.04° \theta s^{-1}$). The background was counted on both sides of the peak for one half of the peak scan time. The intensities of three standard reflexions measured every hour remained constant to within 2% of their mean values. Lorentz–polarization corrections were applied. No absorption correction was made. 1292 reflexions, considered observed when $F > 1.650\sigma(F)$, were used in the analysis.

Solution and refinement

The structure was solved by a new multisolution tangent refinement program written for the NOVA and ECLIPSE minicomputer with 32 k 16-bit word core storage (Sheldrick, 1976). Previous attempts with *MULTAN* and *SHELX* on a Univac 1106 computer failed. 128 permutations were generated by means of the starting set shown in Table 2.

Table 2. *Reflexions used in the starting set with allowed phases*

h	k	l	E	$\varphi(°)$
2	0	1	3.178	0
−15	0	4	3.840	0
1	1	1	3.038	0
−9	3	5	3.628	45, 135
0	0	7	3.690	0, 180
2	0	2	3.703	0, 180
−10	3	5	2.560	45, 135, 225, 315
0	7	1	2.089	45, 135, 225, 315

After the phases of the 126 largest E values ($E >$ 1·615) had been found, a negative quartet test (De Titta, Edmonds, Langs & Hauptman, 1975) and $R(\alpha)$ test (Roberts, Petterson, Sheldrick, Isaacs & Kennard, 1973) were applied. The 'best' phase sets were then expanded to 320 reflexions with $E > 1·200$. The phase set ranked second by both tests produced the most easily interpreted E map; of the top 31 peaks 26 corresponded to correct atomic positions. Three atoms were missing, but two of these could be found by reflexion of spurious peaks in a pseudo-mirror plane at $y \simeq 0·30$. The time for the direct methods job, including computation of E maps, was 20 min on ECLIPSE.

Two cycles of least-squares refinement including all non-hydrogen atoms (isotropic) yielded $R = 0·139$. At this stage, several of the H atoms were located in a difference map. Theoretical positions of all the H atoms were calculated and the latter were included in constrained refinement with C–H 1·08 Å and with one common isotropic temperature factor assigned to each H atom type (–CH_2– and CH_3–; the methine H was assigned the same U as that of the former). These temperature factors were allowed to vary during the subsequent four cycles in which the heavy atoms were refined anisotropically. The average shift:error ratio was 0·01 and a final difference map revealed no peaks of height $> 0·05$ e Å^{-3}. The final R was 0·049 and R_w was 0·045 with $w = 1/\sigma^2$. An analysis of variance indicated that the latter weighting scheme was satisfactory.* An attempt to establish the absolute configuration with Hamilton's (1965) criterion failed. Scattering factors were those of Cromer & Mann (1968). Tables 3, 4 and 5 list the final atomic coordinates and temperature factors. The isotropic temperature factors of the H atoms refined to $U = 0·079$ (methylene) and $U = 0·107$ Å^2 (methyl).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31620 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
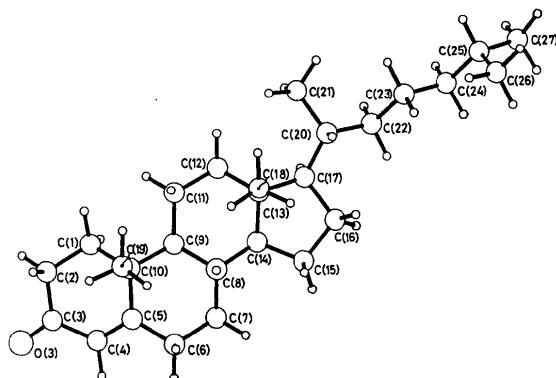

Fig. 1. View of the molecule.

Description of the structure and discussion

Bond lengths and angles are listed in Tables 6 and 7 respectively. Fig. 1 is a perspective view of the mole-

Table 3. *Fractional atomic coordinates* ($\times 10^4$) *and their e.s.d.'s for the heavy atoms*

	x	y	z
O(3)	−1776 (3)	2939 (12)	9007 (5)
C(1)	132 (5)	4798 (11)	7868 (6)
C(2)	−501 (5)	4676 (13)	8806 (7)
C(3)	−1055 (4)	3065 (14)	8646 (6)
C(4)	−664 (4)	1600 (13)	8117 (5)
C(5)	181 (4)	1597 (10)	7830 (5)
C(6)	604 (4)	−26 (11)	7503 (6)
C(7)	989 (4)	166 (11)	6305 (5)
C(8)	1664 (4)	1653 (10)	6424 (5)
C(9)	1144 (3)	3289	6640 (5)
C(10)	763 (3)	3224 (11)	7871 (5)
C(11)	1727 (4)	4886 (10)	6594 (5)
C(12)	2116 (4)	4999 (11)	5388 (5)
C(13)	2679 (3)	3398 (10)	5247 (4)
C(14)	2022 (4)	1881 (10)	5216 (5)
C(15)	2542 (4)	389 (11)	4790 (6)
C(16)	3056 (4)	1193 (11)	3846 (6)
C(17)	2939 (3)	3165 (11)	3944 (5)
C(18)	3587 (3)	3297 (12)	6393 (4)
C(19)	1569 (4)	3195 (14)	9153 (5)
C(20)	3789 (4)	4142 (11)	3688 (5)
C(21)	3734 (5)	6062 (12)	3862 (7)
C(22)	3891 (3)	3754 (12)	2306 (5)
C(23)	4885 (3)	4025 (12)	2151 (5)
C(24)	4963 (3)	3763 (11)	779 (4)
C(25)	5936 (3)	4093 (11)	563 (5)
C(26)	6687 (4)	2920 (12)	1367 (6)
C(27)	5891 (4)	3936 (13)	−878 (5)

Table 4. *Anisotropic temperature factors of the heavy atoms* (Å$^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(3)	92 (3)	164 (6)	173 (5)	−25 (5)	83 (3)	−4 (4)
C(1)	93 (5)	75 (5)	85 (5)	0 (4)	45 (4)	11 (4)
C(2)	99 (5)	113 (7)	89 (5)	−24 (5)	45 (4)	−8 (5)
C(3)	73 (4)	124 (7)	74 (4)	−5 (5)	29 (4)	12 (6)
C(4)	54 (4)	107 (6)	65 (4)	−4 (4)	12 (3)	−14 (4)
C(5)	63 (4)	73 (5)	48 (3)	3 (3)	17 (3)	−3 (4)
C(6)	73 (4)	61 (4)	88 (4)	−2 (4)	28 (3)	−16 (4)
C(7)	82 (4)	52 (4)	85 (4)	0 (4)	41 (3)	−5 (4)
C(8)	55 (3)	37 (4)	65 (4)	4 (3)	14 (3)	1 (3)
C(9)	55 (3)	52 (4)	55 (3)	−1 (3)	16 (3)	−3 (4)
C(10)	59 (3)	65 (4)	55 (3)	−3 (4)	14 (3)	−6 (4)
C(11)	68 (4)	47 (4)	67 (4)	−7 (3)	31 (3)	−2 (4)
C(12)	61 (4)	45 (4)	69 (4)	0 (3)	21 (3)	−3 (3)
C(13)	47 (3)	48 (4)	54 (3)	3 (3)	11 (3)	0 (3)
C(14)	54 (3)	42 (4)	59 (4)	3 (3)	21 (3)	0 (3)
C(15)	78 (4)	46 (4)	84 (4)	−7 (3)	31 (3)	−2 (3)
C(16)	75 (4)	63 (4)	81 (4)	−8 (4)	36 (4)	−1 (4)
C(17)	57 (3)	55 (4)	56 (3)	−3 (3)	16 (3)	5 (3)
C(18)	56 (3)	83 (4)	58 (3)	5 (4)	7 (2)	−6 (4)
C(19)	79 (4)	114 (6)	59 (3)	−4 (4)	15 (3)	−26 (5)
C(20)	50 (3)	62 (4)	69 (4)	−6 (3)	19 (3)	−8 (3)
C(21)	84 (4)	69 (5)	91 (5)	−5 (4)	40 (4)	−10 (4)
C(22)	64 (3)	78 (5)	62 (3)	−7 (4)	26 (3)	−7 (3)
C(23)	56 (3)	74 (4)	73 (4)	−6 (4)	20 (3)	−5 (3)
C(24)	70 (3)	55 (4)	58 (3)	−5 (3)	24 (3)	−1 (3)
C(25)	60 (3)	60 (4)	66 (4)	2 (3)	22 (3)	−1 (3)
C(26)	65 (4)	94 (6)	88 (4)	16 (4)	13 (3)	15 (4)
C(27)	85 (4)	91 (5)	68 (4)	7 (4)	32 (3)	9 (4)

cule with the configuration specified by the tabulated atomic coordinates. Rings *B*, *C* and *D* are *trans*-fused. Torsion angles are listed in Table 8. The side chain is

Table 5. *Fractional atomic coordinates* (× 10³) *of the hydrogen atoms*

	x	y	z
H(11)	−32	497	690
H(12)	59	589	813
H(21)	−99	573	863
H(22)	−6	474	979
H(4)	−108	45	794
H(61)	118	−40	832
H(62)	7	−100	731
H(71)	40	36	546
H(72)	136	−99	618
H(8)	227	140	723
H(9)	53	336	583
H(111)	128	598	660
H(112)	232	491	745
H(121)	258	609	548
H(122)	153	514	454
H(14)	134	205	454
H(151)	304	−17	561
H(152)	205	−57	431
H(161)	380	85	412
H(162)	274	77	287
H(17)	238	375	320
H(181)	396	218	622
H(182)	339	315	730
H(183)	404	440	645
H(191)	200	432	917
H(192)	201	208	927
H(193)	123	326	993
H(20)	441	369	441
H(211)	376	639	486
H(212)	309	655	323
H(213)	433	662	360
H(221)	341	458	163
H(222)	370	244	208
H(231)	536	314	278
H(232)	510	531	244
H(241)	477	246	51
H(242)	446	461	15
H(25)	614	537	88
H(261)	675	310	239
H(262)	735	322	117
H(263)	651	161	111
H(271)	657	428	−102
H(272)	535	477	−145
H(273)	573	264	−118

Table 6. *Bond lengths* (Å) *and their e.s.d.'s*

C(1)—C(2)	1·532 (6)	C(14)–C(8)	1·523 (6)
C(2)—C(3)	1·490 (7)	C(14)—C(15)	1·531 (6)
C(3)—O(3)	1·218 (5)	C(15)—C(16)	1·542 (6)
C(3)—C(4)	1·463 (7)	C(16)—C(17)	1·566 (6)
C(4)—C(5)	1·349 (6)	C(17)—C(13)	1·546 (5)
C(5)—C(6)	1·499 (6)	C(10)—C(19)	1·557 (5)
C(6)—C(7)	1·533 (6)	C(13)–C(18)	1·556 (5)
C(7)—C(8)	1·515 (6)	C(17)—C(20)	1·546 (5)
C(8)—C(9)	1·542 (6)	C(20)—C(21)	1·526 (6)
C(9)—C(10)	1·556 (5)	C(20)—C(22)	1·551 (5)
C(10)-C(1)	1·544 (6)	C(22)—C(23)	1·521 (5)
C(5)—C(10)	1·531 (6)	C(23)—C(24)	1·512 (5)
C(9)—C(11)	1·526 (6)	C(24)—C(25)	1·523 (5)
C(11)-C(12)	1·540 (6)	C(25)—C(26)	1·518 (5)
C(12)-C(13)	1·533 (6)	C(25)—C(27)	1·527 (5)
C(13)–C(14)	1·528 (6)		

Table 7. *Bond angles* (°) *and their e.s.d.'s*

C(10)-C(1)—C(2)	114·3 (4)	C(11)–C(12)–C(13)	111·1 (4)
C(1)—C(2)—C(3)	112·4 (5)	C(12)—C(13)—C(14)	107·0 (3)
C(2)—C(3)—C(4)	117·2 (4)	C(12)-C(13)-C(17)	116·8 (3)
C(2)—C(3)—O(3)	121·6 (6)	C(12)-C(13)-C(18)	109·6 (4)
C(4)—C(3)—O(3)	121·0 (6)	C(17)-C(13)-C(18)	110·0 (3)
C(3)—C(4)—C(5)	124·2 (5)	C(14)-C(13)-C(18)	112·4 (4)
C(4)—C(5)—C(10)	121·9 (5)	C(14)-C(13)-C(17)	100·9 (3)
C(4)—C(5)—C(6)	120·8 (5)	C(13)-C(14)-C(8)	115·3 (4)
C(10)-C(5)—C(6)	117·2 (4)	C(8)—C(14)—C(15)	117·9 (4)
C(5)—C(6)—C(7)	112·0 (4)	C(13)-C(14)-C(15)	104·2 (3)
C(6)—C(7)—C(8)	112·3 (4)	C(14)-C(15)-C(16)	104·2 (4)
C(7)—C(8)—C(9)	108·7 (3)	C(15)-C(16)-C(17)	106·4 (4)
C(8)—C(9)—C(10)	113·5 (4)	C(16)-C(17)-C(13)	103·6 (4)
C(9)—C(10)—C(5)	108·8 (4)	C(13)-C(17)-C(20)	119·9 (3)
C(5)—C(10)—C(1)	110·0 (3)	C(16)-C(17)-C(20)	111·9 (3)
C(1)—C(10)—C(19)	109·2 (4)	C(17)-C(20)-C(21)	113·5 (4)
C(1)—C(10)—C(9)	108·6 (4)	C(17)-C(20)-C(22)	110·6 (3)
C(9)—C(10)—C(19)	112·7 (3)	C(21)-C(20)-C(22)	109·4 (4)
C(5)—C(10)—C(19)	107·5 (4)	C(20)-C(22)-C(23)	114·0 (3)
C(7)—C(8)—C(14)	112·3 (3)	C(22)-C(23)-C(24)	113·7 (3)
C(9)—C(8)—C(14)	108·6 (3)	C(23)-C(24)-C(25)	115·6 (3)
C(10)-C(9)—C(11)	112·4 (4)	C(24)-C(25)-C(26)	112·3 (4)
C(8)—C(9)—C(11)	112·3 (3)	C(24)-C(25)-C(27)	110·0 (3)
C(9)—C(11)-C(12)	114·0 (4)	C(26)-C(25)-C(27)	110·8 (4)

Table 8. *Torsion angles* (°)

Ring *A*

C(2)—C(1)—C(10)-C(5)	45·5
C(10)-C(1)—C(2)—C(3)	−51·0
C(1)—C(2)—C(3)—C(4)	25·7
C(2)—C(3)—C(4)—C(5)	3·5
C(3)—C(4)—C(5)—C(10)	−8·1
C(4)—C(5)—C(10)-C(1)	−16·6

Ring *B*

C(6)—C(5)—C(10)-C(9)	46·7
C(10)-C(5)—C(6)—C(7)	−48·0
C(5)—C(6)—C(7)—C(8)	52·8
C(6)—C(7)—C(8)—C(9)	−57·9
C(7)—C(8)—C(9)—C(10)	58·8
C(8)—C(9)—C(10)-C(5)	−51·8

Ring *C*

C(14)-C(8)—C(9)—C(11)	−50·0
C(8)—C(9)—C(11)-C(12)	50·7
C(9)—C(11)-C(12)-C(13)	−54·1
C(11)-C(12)-C(13)-C(14)	55·9
C(12)-C(13)-C(14)-C(8)	−60·7
C(9)—C(8)—C(14)-C(13)	57·7

Ring *D*

C(17)-C(13)-C(14)-C(15)	45·9
C(13)-C(14)-C(15)-C(16)	−34·1
C(14)-C(15)-C(16)-C(17)	8·9
C(15)-C(16)-C(17)-C(13)	18·9
C(14)-C(13)-C(17)-C(16)	−39·2

in an extended configuration. There are no significant short intermolecular contacts.

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Structural Investigations of Ylides. VIII.* Crystal and Molecular Structure of a First-Row Sulphonyl-Stabilized Ylide: N-(Trimethylammonio)toluene-p-sulphonamidate

BY A. FORBES CAMERON, FERGUS D. DUNCANSON AND DAVID G. MORRIS

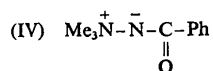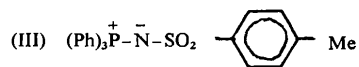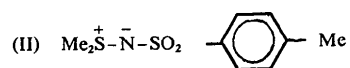*Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland*

The structure of the title compound has been determined from 2116 independent data collected on a diffractometer. The crystals are monoclinic, space group $P2_1/c$, with $Z=4$, $a=6.128$, $b=7.161$, $c=28.142$ Å, $\beta=93.66°$. The structure was solved by direct methods, and refined by least squares to a final R of 0.007. The conformation is very similar to that of several other ylides containing the imine-sulphonyl grouping, despite the presence of water of crystallization, the latter molecules being hydrogen-bonded both to the imino-nitrogen atom and to one of the sulphonyl-oxygen atoms of the ylide molecules. The $\overset{+}{N}-\overset{-}{N}$ and $\overset{-}{N}-SO_2$ lengths are respectively 1·472 (2) and 1·592 (2) Å, while the $\overset{+}{N}-\overset{-}{N}-S$ valence angle is 118·0 (1)°.

Introduction

Previous examples of ylides containing the imine-sulphonyl grouping, such as (II) (Cameron, Hair & Morris, 1973), (III) (Cameron, Hair & Morris, 1974) and similar molecules (Kálmán, 1967; Kálmán, Duffin & Kucsman, 1971; Kálmán & Sasvári, 1972), are all characterized by the presence of second row 'onium species which possess *d*-orbitals of energies such that delocalization is possible between the 'onium and imino-nitrogen atoms. It is plausible that such delocalization could compete with delocalization between the imino and sulphonyl species. However, in the ammonium imines (IV) and (V) (Cameron, Hair & Morris, 1972), delocalization of the formal negative charge on the imino-nitrogen may take place only *via* the stabilizing groups, and it has been shown that for these two compounds, the $\overset{+}{N}-\overset{-}{N}$ lengths are identical, no differences having been induced by the two considerably different stabilizing groups.

(I) $Me_3\overset{+}{N}-\overset{-}{N}-SO_2$ ⟨benzene⟩ Me

(II) $Me_2\overset{+}{S}-\overset{-}{N}-SO_2$ ⟨benzene⟩ Me

(III) $(Ph)_3\overset{+}{P}-\overset{-}{N}-SO_2$ ⟨benzene⟩ Me

(IV) $Me_3\overset{+}{N}-\overset{-}{N}-C-Ph$
                        ‖
                        O

(V) $Me_3\overset{+}{N}-\overset{-}{N}-NO_2$

In order to study the geometry of the imine-sulphonyl grouping in the absence of possible and competing

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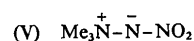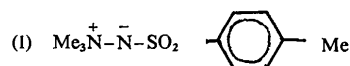
* Part VII: Cameron, Cameron, Campbell, & Johnson (1976).