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# The Crystal and Molecular Structure of the Steroid $C_{26}H_{34}O_2NBr$

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The structure of 3$\beta$-bromoacetoxy-16$\alpha$-ethyl-16$^2$-cyano-16$^2$,21-cyclo-5$\alpha$-pregna-17,21-diene has been determined by the heavy atom method, and has been refined by block-diagonal least squares to a final $R$ of 0·047 for the 1717 observed reflexions. The absolute configuration has also been established. It is concluded from the analysis that this steroid has the 16$\beta$-hydrogen configuration, but previous optical dispersion studies have shown that its Cotton effect is strongly negative. This structure, therefore, seems to be the first authentic example of a cisoid diene which is in contrast to the helicity rule. The unit cell is orthorhombic, $P2_12_12_1$, with $a=13·484$, $b=22·730$, $c=7·760$ Å, and $Z=4$.

## Introduction

Optical rotatory dispersion studies have produced valuable information on the structure, configuration and conformation of many compounds. The most important information is derived from the phenomenon called the 'Cotton effect' (Crabbé, 1965), in the spectral region close to that of maximal absorption of optically active chromophores. The optically active cisoid diene group is of great structural interest due to the correlation between the sign of the Cotton effect and the chirality or skewness of the diene system. The relationship as described by Moscowitz, Charney, Weiss & Ziffer (1961) is that the sign of the Cotton effect of skewed cisoid dienes is positive if the diene is twisted in the form of a right-handed helix, Fig. 1($a$), and negative if it has a left-handed twist as shown in Fig. 1($b$).

The steroid 3$\beta$-acetoxy-16$\alpha$-ethyl-16$^2$-cyano-16$^2$,21-cyclo-5$\alpha$-pregna-17,21-diene (I) was synthesized by Engel & Lessard (1963, 1970) and was assigned the 16$\beta$-hydrogen configuration from stereochemical and spectroscopic considerations. However, the compound exhibits a strong negative Cotton effect, indicative, according to Moscowitz *et al.*, of a left-handed skewed diene system and thus a 16$\alpha$-hydrogen configuration. Engel, Salvi & Ruest (1970) suggested a possible cause for the exception to the helicity rule of skewed dienes of this type. In order to establish firmly the configuration and to check if the helicity rule for skewed dienes has in fact broken down in the particular case, the crystal structure analysis of 3$\beta$-bromoacetoxy-16$\alpha$-ethyl-16$^2$-cyano-16$^2$,21-cyclo-5$\alpha$-pregna-17,21-diene (II) has therefore been undertaken.

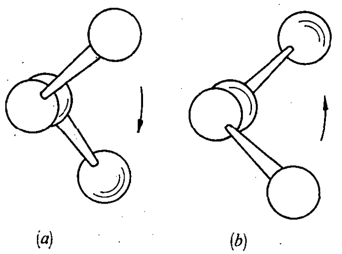
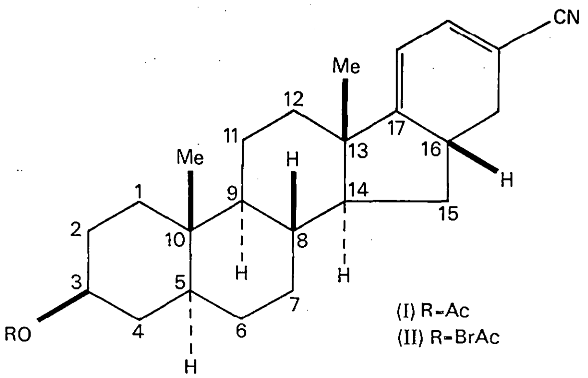


Fig. 1. The helicity of cisoid diene groups for ($a$) positive, and ($b$) negative Cotton effects.



## Crystal data

Crystals of 3$\beta$-bromoacetoxy-16$\alpha$-ethyl-16$^2$-cyano-16$^2$,21-cyclo-5$\alpha$-pregna-17,21-diene, $C_{26}H_{34}O_2NBr$, are orthorhombic with the following unit-cell data:

| | | | |
|---|---|---|---|
| $a$ | 13·484 (4) Å | $D_m$ | 1·323 g.cm$^{-3}$ |
| $b$ | 22·730 (4) | $D_x$ | 1·319 |
| $c$ | 7·760 (4) | $\mu$(Cu) | 27·60cm$^{-1}$ |
| $U$ | 2378·4 Å$^3$ | $\mu$(Mo) | 18·54 |
| $Z$ | 4 | $F$(000) | 992 |
| F.W. | 472·5 | Space group | $P2_12_12_1$ |

The density was measured by flotation in an aqueous solution of KI. The X-ray measurements were carried out with a prismatic crystal of dimensions 0·15 × 0·23 × 0·33 mm, which was grown from an ether–hexane solution at room temperature.

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## Data collection

Preliminary examination of the crystal and space group was done with precession photographs. The unit-cell constants were derived from the $2\theta$ measurements of the high-order axial reflexions, determined with a narrow slit at a 1° take-off angle for Cu radiation ($\lambda$, $K\alpha_1 = 1{\cdot}54050$, $K\alpha_2 = 1{\cdot}54434$ Å), on a Picker diffractometer. The integrated intensities for Ni-filtered Cu radiation were measured, in a right-handed system of axes, by the $\theta$–$2\theta$ continuous scan method with **c** along the $\varphi$-axis, at a take-off angle of 3°. The scan range was 2° for reflexions within $2\theta = 30°$, 2·4° up to $2\theta = 90°$, and 3·0° up to $2\theta = 130°$. As observed for other steroid structures, the intensities dropped rapidly on increasing $2\theta$ and there was little to be gained by extending the data measurements beyond this cut-off point. The $2\theta$ scan speed was 2°/min and the background was measured for 20 secs at the start and end of each scan. The intensity of the 220 reflexion was monitored at frequent intervals throughout the data collection and used for scaling. At the end, all the strong reflexions were remeasured with a low current setting. The total number of non-equivalent permissible reflexions scanned was 2322 of which 1717 or 73·9 % were observed above threshold. The net intensity counts were reduced to the same relative scale, and corrected for the Lorentz and polarization effects. They were also corrected for absorption, at a later stage, using the approximation of Busing & Levy (1957) with a 6 × 6 × 6 point grid. The calculated transmission factors were in the range 0·56 to 0·74.

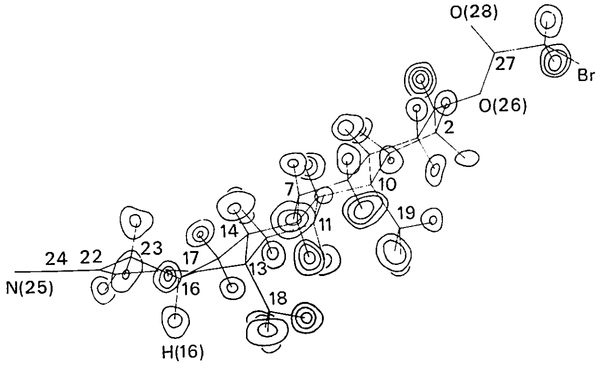

Fig. 2. The difference electron density map showing the hydrogen atoms. Contours start at 0·2 e.Å$^{-3}$ then at intervals of 0·1 e.Å$^{-3}$.

## Structure determination

The position of the Br atom was determined from an unsharpened Patterson synthesis. Two successive cycles of structure factor and electron density calculations were sufficient to reveal the positions of the other 29 non-hydrogen atoms of the molecule. The $R$ index for the trial structure was 0·19. The refinement was carried out by block-diagonal least-squares employing only the observed reflexions. The 34 hydrogen atoms were located from a difference map which was computed when $R$ was 0·09, and their peak electron density values were in the range 0·23 to 0·51 e.Å$^{-3}$. A composite drawing of this map is presented in Fig. 2.

At a later stage, the absolute configuration was established by carrying out the refinement with the two

Table 1. *Fractional coordinates, vibration tensor components* (Å$^2$) *for the expression* $T = \exp[-2\pi^2\ (U_{11}a^{*2}h^2 \ldots + 2U_{23}b^*c^*kl + \ldots)]$, *and their e.s.d.'s (all quantities* $\times 10^4$*)*

| | x | y | z | $U_{11}$ | $U_{22}$ | $U_{33}$ | $2U_{23}$ | $2U_{13}$ | $2U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 1537(5) | 9160(2) | 1326(7) | 590(39) | 573(37) | 361(34) | 163(58) | 27(64) | 169(64) |
| C(2) | 1165(4) | 9785(2) | 1753(9) | 532(35) | 518(37) | 670(43) | 362(71) | 58(77) | 281(61) |
| C(3) | 626(4) | 9796(2) | 3450(8) | 414(32) | 403(31) | 670(44) | -58(64) | -50(67) | -42(53) |
| C(4) | 1209(4) | 9532(2) | 4872(8) | 519(36) | 448(31) | 463(36) | -89(59) | -41(64) | 57(57) |
| C(5) | 1511(4) | 8907(2) | 4431(7) | 393(31) | 400(31) | 412(33) | 13(54) | -51(57) | -78(51) |
| C(6) | 2008(5) | 8593(2) | 5921(7) | 692(41) | 427(34) | 337(32) | 69(55) | 58(67) | 48(59) |
| C(7) | 2237(5) | 7952(3) | 5500(7) | 793(47) | 508(37) | 332(33) | 44(59) | -63(71) | 172(70) |
| C(8) | 2845(4) | 7896(2) | 3873(7) | 432(32) | 463(34) | 426(34) | 13(57) | -122(60) | -171(54) |
| C(9) | 2337(4) | 8218(2) | 2353(7) | 356(29) | 513(34) | 365(31) | -4(58) | 14(51) | 45(54) |
| C(10) | 2148(4) | 8879(2) | 2753(7) | 382(30) | 411(31) | 411(33) | 182(55) | -52(56) | 92(51) |
| C(11) | 2887(5) | 8117(3) | 637(8) | 723(44) | 578(39) | 384(34) | 224(62) | 124(69) | 321(68) |
| C(12) | 3100(5) | 7461(3) | 250(8) | 805(48) | 665(39) | 310(34) | -42(63) | 216(71) | 146(75) |
| C(13) | 3639(4) | 7181(2) | 1732(8) | 459(33) | 505(34) | 385(32) | 8(59) | 79(61) | 36(54) |
| C(14) | 3019(4) | 7257(2) | 3389(7) | 489(33) | 453(31) | 339(31) | -4(55) | -57(59) | -163(53) |
| C(15) | 3475(5) | 6825(3) | 4661(8) | 759(44) | 489(34) | 434(35) | -10(62) | -428(71) | 186(67) |
| C(16) | 3835(5) | 6309(2) | 3553(9) | 586(39) | 455(34) | 612(44) | 88(64) | -191(73) | 116(57) |
| C(17) | 3723(4) | 6518(2) | 1712(8) | 462(32) | 492(34) | 468(35) | -118(62) | 125(64) | 68(54) |
| C(18) | 4696(5) | 7429(3) | 1927(9) | 570(41) | 709(42) | 753(48) | 105(80) | 47(82) | -84(65) |
| C(19) | 3146(4) | 9207(2) | 2919(9) | 426(32) | 440(31) | 695(45) | 105(66) | 71(71) | 8(54) |
| C(20) | 3655(5) | 6151(3) | 418(9) | 740(46) | 678(42) | 531(41) | -88(73) | 222(79) | 76(78) |
| C(21) | 3666(5) | 5518(3) | 755(9) | 814(49) | 521(37) | 631(45) | -178(71) | -23(86) | 188(71) |
| C(22) | 3519(4) | 5316(2) | 2338(8) | 583(38) | 432(31) | 642(43) | -16(63) | -279(71) | 140(62) |
| C(23) | 3306(5) | 5728(3) | 3787(8) | 677(41) | 531(37) | 442(37) | -2(62) | -216(72) | 79(67) |
| C(24) | 3482(6) | 4693(3) | 2621(10) | 996(55) | 552(39) | 710(51) | -173(75) | -265(94) | 172(84) |
| N(25) | 3463(6) | 4198(2) | 2877(10) | 1617(68) | 592(37) | 950(53) | -74(77) | -254(117) | 148(89) |
| O(26) | 385(3) | 10406(2) | 3886(6) | 428(22) | 471(21) | 774(30) | -248(45) | -288(45) | 140(36) |
| C(27) | -482(4) | 10617(3) | 3349(8) | 423(31) | 618(37) | 514(38) | -105(68) | -225(66) | 30(57) |
| O(28) | -1100(3) | 10339(2) | 2657(7) | 606(28) | 770(31) | 1000(39) | -591(59) | -626(56) | 245(48) |
| C(29) | -580(5) | 11269(2) | 3760(9) | 551(38) | 471(34) | 650(45) | 11(66) | -154(72) | 196(59) |
| BR(30) | -56(1) | 11711(1) | 1888(1) | 1038(6) | 882(5) | 1164(7) | 655(12) | 639(14) | 270(12) |

alternative configurations and comparing the resulting $R$ indices, as described by Ibers & Hamilton (1964). For the full set of observed reflexions, the two enantiomorphs gave $R$ indices of 0·069 and 0·081, and according to Hamilton's (1965) test the indications are significantly in favour of the first. For these calculations the anomalous dispersion corrections for Br were taken from *International Tables for X-ray Crystallography* (1962).

The final least-squares refinement of the accepted enantiomorph included the anomalous dispersion for Br, and weights calculated from the expression

$$w^{-1}=1+[(|F_o|-40)/40]^4$$

where $F_o=3{\cdot}6$ to 214·9. The average parameter shift in the last cycle was $0{\cdot}2\sigma$ for the non-hydrogen atoms, and the final $R$ index for the observed reflexions was 0·047. The value of $[\sum w\Delta^2/(m-n)]^{1/2}$ was 1·12. A difference map calculated at the end of the refinement showed some residual electron density between $-0{\cdot}56$ and 0·46 e.Å$^{-3}$ at the Br atomic site, and featureless background elsewhere.

The atomic scattering factor curves were those of Hanson, Herman, Lea & Skillman (1964) for C, N, O, Br, and that of Stewart, Davidson & Simpson (1965) for H.

## Results

A view of the molecule showing the accepted enantiomorph with 50% equiprobability ellipsoids as derived from the anisotropic thermal parameters, and including the numbering scheme adopted for the analysis is presented in Fig. 3. The final parameters and their estimated standard deviations as obtained from the least-squares refinement, are listed in Tables 1 and 2, where each H atom is given the same number as the C atom to which it is attached. The observed and calculated structure amplitudes are listed in Table 3, and the agreement between them is summarized in Table 4. The bond lengths and bond angles, not corrected for thermal vibration, and the torsional angles are presented in Fig. 4. The e.s.d.'s of the bonds are: C–C, 0·008–0·009; C–N, 0·009; C–O, 0·007; C–Br, 0·007 Å; and the e.s.d.'s of the angles between them are 0·4–0·6° except at C(24) where it is 0·8°. The mean values of the bond lengths and angles involving H atoms are: C–H, 0·96 Å; C–C($sp^3$)–H, 109·5; C–C($sp^2$)–H, 119·9; and H–C–H, 105·0°. There are no intermolecular contacts in the structure significantly shorter than the sum of the corresponding van der Waals radii, except for possibly C(29)···N(25), 3·10 (1); H(29, 2)···N(25), 2·67 (6); and O(28)···H(21, 1), 2·31 (6) Å.

## Discussion

The molecular geometry of the compound is well summarized by the two views presented in Figs. 2 and 3. The steroid has the basic 5α-pregnane skeleton with

Table 2. *Fractional coordinates* (× 10³) *and temperature factors* (Å²) *of the hydrogen atoms, and their e.s.d.'s*

| | x | y | z | B |
|---|---|---|---|---|
| H(1,1) | 93(4) | 887(2) | 120(7) | 4.4(1.3) |
| H(1,2) | 187(4) | 916(2) | 25(8) | 4.8(1.5) |
| H(2,1) | 169(4) | 1004(2) | 179(8) | 4.5(1.3) |
| H(2,2) | 65(4) | 992(2) | 101(7) | 4.3(1.4) |
| H(3,1) | 6(3) | 960(2) | 324(5) | 1.5(0.8) |
| H(4,1) | 81(3) | 954(2) | 595(6) | 2.6(1.1) |
| H(4,2) | 180(4) | 979(2) | 510(7) | 4.1(1.3) |
| H(5,1) | 88(3) | 866(2) | 413(6) | 2.3(1.1) |
| H(6,1) | 256(4) | 880(2) | 611(7) | 4.2(1.3) |
| H(6,2) | 162(3) | 861(2) | 689(7) | 3.0(1.1) |
| H(7,1) | 163(4) | 778(2) | 543(7) | 4.9(1.4) |
| H(7,2) | 261(5) | 780(3) | 642(8) | 6.4(1.2) |
| H(8,1) | 342(3) | 806(2) | 413(6) | 2.2(1.0) |
| H(9,1) | 165(3) | 806(2) | 232(6) | 2.0(1.0) |
| H(11,1) | 255(4) | 823(2) | -23(6) | 3.2(1.2) |
| H(11,2) | 360(4) | 836(2) | 42(7) | 4.4(1.3) |
| H(12,1) | 343(4) | 746(2) | -77(6) | 3.3(1.1) |
| H(12,2) | 245(4) | 724(2) | -7(8) | 5.0(1.5) |
| H(14,1) | 243(3) | 712(2) | 300(6) | 1.7(1.0) |
| H(15,1) | 399(4) | 701(2) | 538(8) | 5.4(1.6) |
| H(15,2) | 304(5) | 670(3) | 557(9) | 7.4(1.8) |
| H(16,1) | 457(3) | 624(2) | 384(6) | 2.9(1.1) |
| H(18,1) | 509(5) | 724(2) | 294(8) | 7.2(1.6) |
| H(18,2) | 476(5) | 779(3) | 206(9) | 8.5(2.0) |
| H(18,3) | 508(5) | 737(2) | 84(8) | 7.5(1.6) |
| H(19,1) | 358(4) | 907(2) | 382(7) | 4.5(1.4) |
| H(19,2) | 303(4) | 959(2) | 319(7) | 3.8(1.2) |
| H(19,3) | 360(6) | 922(3) | 206(10) | 9.6(2.2) |
| H(20,1) | 366(5) | 624(3) | -66(9) | 5.9(1.7) |
| H(21,1) | 372(4) | 525(2) | -25(8) | 5.0(1.5) |
| H(23,1) | 349(4) | 557(2) | 488(8) | 6.1(1.6) |
| H(23,2) | 250(4) | 578(2) | 383(7) | 3.7(1.2) |
| H(29,1) | -121(4) | 1136(2) | 384(7) | 3.8(1.3) |
| H(29,2) | -34(5) | 1131(2) | 483(8) | 6.0(1.7) |

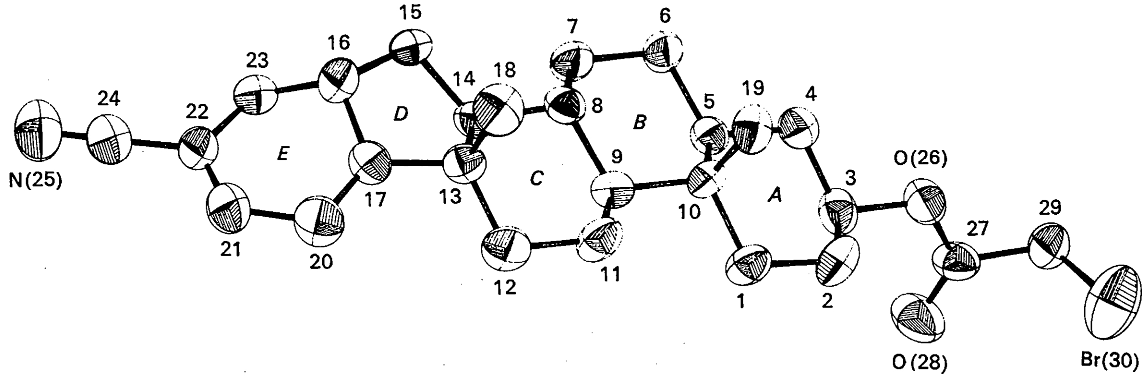

Fig. 3. A view of the accepted enantiomorph showing 50% probability ellipsoids and numbering scheme.

Table 3. *Observed and calculated structure amplitudes* ($\times 10$)
(* indicates unobserved reflexion and $|F_{th}|$ in place of $|F_o|$)

Table 4. *Agreement summary*

| Category | Limits | Number |
|---|---|---|
| | 1717 observed reflexions ($3{\cdot}6 \le \lvert F_o \rvert \le 214{\cdot}9$) $R=0{\cdot}047$ | |
| 1 | $\lvert \Delta F \rvert \le \lvert F_{th} \rvert$, or $\lvert \Delta F \rvert / \lvert F_o \rvert \le 0{\cdot}10$ | 1713 |
| 2 | $\lvert F_{th} \rvert < \lvert \Delta F \rvert \le 2 \lvert F_{th} \rvert$, or $0{\cdot}10 < \lvert \Delta F \rvert / \lvert F_o \rvert \le 0{\cdot}15$ | 4 |
| | 605 unobserved reflexions ($\lvert F_{c\max} \rvert = 7{\cdot}8$) | |
| 1 | $\lvert F_c \rvert \le 1{\cdot}0 \lvert F_{th} \rvert$ | 551 |
| 2 | $1{\cdot}0 \lvert F_{th} \rvert < \lvert F_c \rvert \le 1{\cdot}5 \lvert F_{th} \rvert$ | 53 |
| 3 | $1{\cdot}5 \lvert F_{th} \rvert < \lvert F_c \rvert \le 2{\cdot}0 \lvert F_{th} \rvert$ | 1 |
| | $\lvert F_{th} \rvert$ = threshold amplitude = 3·1 to 6·6 | |

rings *A*, *B*, *C*, and *D* *trans*-connected. Substituents C(18), C(19), and O(26) are on the *β* or upper side of the molecule, while C(23), *i.e.* C($16^1$), is on the *α* or lower side. This configuration automatically necessitates that atom H(16) should be on the *β* side where indeed it has been located from the difference map as shown in Fig. 2. The stereoid therefore has the 16*β*-hydrogen configuration but exhibits a strong negative Cotton effect, thus indicating a contradiction to the helicity rule.

Bond lengths and angles in the perhydrophenanthrene moiety are comparable to those found in other stereoids. In the following discussion of bond lengths, the values quoted in parentheses are the average bond lengths given by Sutton (1965). The 21 bonds of type $C(sp^3)$–$C(sp^3)$ fall in the range 1·482 to 1·561 Å ($\sigma$= 0·008 to 0·009 Å), and their mean value of 1·528 Å is not significantly shorter than the expected average (1·537 ± 0·005 Å). However, the shortest bond C(3)–C(4), in particular, is significantly shorter than expected and it is of interest to note that it occurs in the neighbourhood of the considerably elongated C(3)–O(26) bond of length 1·463 Å (1·426 ± 0·005 Å). The four bonds of type $C(sp^2)$–$C(sp^3)$ are of lengths 1·491 to 1·523 Å, and their mean of 1·509 Å is about average (1·510 ± 0·005 Å). The C(20)–C(21) single bond occurring between two double bonds is 1·464 Å (1·465 ± 0·005 Å), and similarly the C(22)–C(24), between a double and a triple bond, is of length 1·434 Å (1·426 ± 0·005 Å). The two C–C double bonds have a mean length of 1·318 Å which is slightly but not significantly shorter than the usual value (1·336 ± 0·005 Å).

In the bromoacetoxy group, O(26)–C(3) is significantly longer and O(26)–C(27) is significantly shorter than normally found. Comparable values, however, have been observed in another steroid acetate side chain by Braun, Hornstra & Leenhouts (1970). The C(27)–O(28) double bond of 1·174 Å and the C(29)–Br(30) single bond of 1·902 Å are both shorter than the corresponding values of 1·233 and 1·938 Å given by Sutton (1965). The difference is at least partly due to the omission of corrections for thermal vibration, where these corrections are expected to be larger at the extremities than in the middle of the molecule.

The mean interbond angle in rings *A*, *B*, and *C* is 111·2° which is considerably greater than the normal tetrahedral angle of 109·4°, but such an increase is characteristic of steroids as noted by Geise, Altona & Romers (1967) and arises from an overall flattening of the rings. The angles in the five-membered ring *D* are very similar to the corresponding angles in the seven steroids reported by Braun, Hornstra & Leenhouts (1969). The angle C(14)–C(13)–C(17) of only 99·3° is indicative of the strain imposed at the *C*/*D* junction.

The torsional angles for rings *A* and *B* are considerably lower than the 60° value of an undistorted system, and are somewhat lower than those calculated by Bucourt & Hainaut (1965) for cyclohexanes and quoted in parentheses in Fig. 4(*c*). The mean deviations in the amplitudes of the observed and calculated torsional angles are −2·0 and −1·3° for rings *A* and *B* respectively, and the maximum deviations are −4·2 and −4·9° for C(1)–C(2) and C(1)–C(10), respectively. Both rings are thus more flattened than predicted, but still have the normal chair conformation with the seats of the chairs defined by atoms [C(1), C(3), C(4), C(10)], and [C(5), C(6), C(8), C(9)]. The mean planes through these sets of atoms, referred to the unit cell axes, are

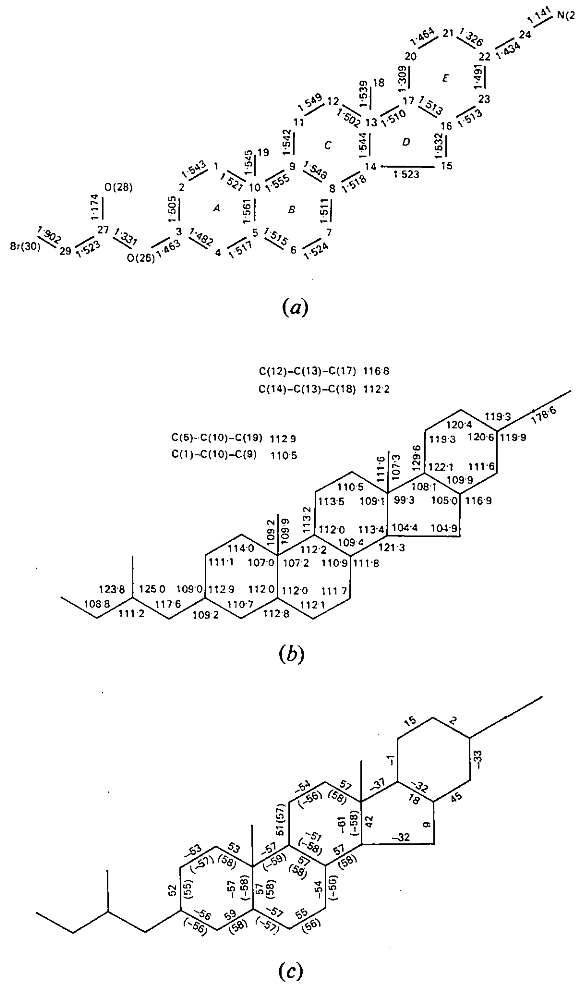

Fig. 4. (*a*) Bond lengths (Å), (*b*) angles (°), (*c*) observed torsional angles (°) and the calculated values in parentheses.

$$0{\cdot}6946\,X+0{\cdot}7114\,Y-0{\cdot}1067\,Z=16{\cdot}1419 \tag{1}$$

and

$$0{\cdot}7796\,X+0{\cdot}6227\,Y-0{\cdot}0671\,Z=13{\cdot}9648 \tag{2}$$

where $X$, $Y$, $Z$ are in Å. The four atoms of each set are coplanar and their $\chi^2$ values are only 0·04 and 0·01, respectively. Atoms C(2) and C(5) of ring *A* are at distances 0·63 and −0·69 Å from plane 1, while atoms C(10) and C(7) of ring *B* are at distances 0·72 and −0·64 Å from plane 2.

Owing to the strain imposed by the junction of the neighbouring cyclopentane unit, the conformation of ring *C* is that of a distorted chair. The mean plane of atoms [C(8), C(11), C(12), C(14)] forming the seat of this chair is

$$-0{\cdot}9850\,X-0{\cdot}1603\,Y-0{\cdot}0641\,Z=-6{\cdot}8348 \tag{3}$$

and its $\chi^2$ of 16·7 indicates that the four atoms are non-planar. Atoms C(9) and C(13) of ring *C* are at distances 0·62 and −0·70 Å from plane 3. Torsional angles of ring *C* are considerably different from those calculated by Bucourt & Hainaut (1965), but the latter were exclusive of deformations imposed by substituents like ring *D*.

The perhydrophenanthrene group is convex towards the protruding methyl substituents C(18) and C(19) as shown in Fig. 2. This shape is also evident, as described by Schomaker, Waser, Marsh & Bergman (1959) from consideration of the deviations of the atoms on the upper side from their mean plane, and of those on the lower side from their mean plane. The two mean planes of atoms [C(2), C(4), C(6), C(8), C(10), C(11), and C(13)] on the β side, and of atoms [C(1), C(3), C(5), C(7), C(9), C(12), and C(14)] on the α side are nearly parallel with a dihedral angle of only 1° between them. The deviations of these atoms from their respective mean planes are presented in Fig. 5. The methyl atoms C(18) and C(19) are at distances −1·48 and −1·71 Å from the mean plane on the β side, and at distances −1·96 and −2·16 Å from that on the α side. Fig. 5 shows clearly that atoms C(1), C(10), C(5), C(8), C(9), C(11) in the middle of the group are all on the same side of their respective planes as the methyl groups, while the outside atoms C(2), C(3), C(4), C(6), C(7), C(14), C(15), C(13), C(12) are on the opposite side of their respective planes.

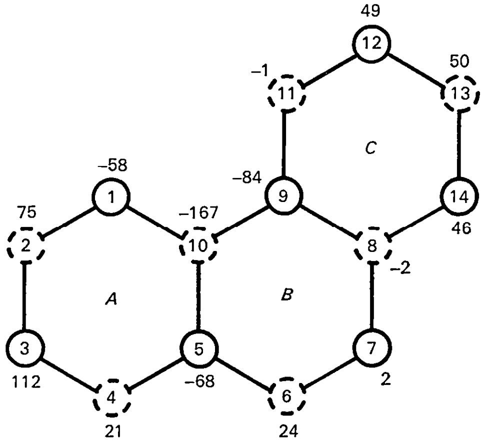

Fig. 5. Distances (× 10³ Å) of the α atoms (solid circles) and of the β atoms (dotted circles) from their respective mean planes. Atoms C(18) and C(19) are on the negative side of these planes.

## Conclusions

This analysis confirms that the steroid has the 16β-hydrogen configuration; consequently, taking into account Engel & Lessard's observation that the compound has a strong negative Cotton effect, this seems to represent the first authentic example of a cisoid diene compound which is in contrast to the helicity rule. Further studies by Engel & Lessard (1970) on related compounds with the cyano group replaced by alcohol and ketonic functional groups, and by Engel, Salvi & Ruest (1970) on a related nitrile with an additional methyl group on position 21, have also shown apparent contradictions to the helicity rule.

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# Eine Wasserstoffbrücke vom Typ F-H···O: Die Kristallstruktur von $K[PHO_2(OH)].HF$*

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The 1:1 adduct of potassium acid phosphite and hydrogen fluoride crystallizes with space group $P2_1/c$, $a=6\cdot692$, $b=11\cdot040$, $c=7\cdot841$ Å, $\beta=127\cdot88°$, and $Z=4$. The structure was determined by conventional methods from 867 independent Cu $K\alpha$ intensity data measured on an automatic diffractometer. The final $R$ value was 0·056. The presence of molecular hydrogen fluoride and the hydrogen phosphite anion is evident from the hydrogen atom positions and phosphorus–oxygen bond distances (two short and similar P–O bonds at 1·502 and 1·512 Å and one long P–OH bond at 1·566 Å). The alternative structure $KF.PHO(OH)_2$ is thus rejected. Another point of interest is a strong but unusual hydrogen bond F–H···O with F···O distance of 2·383 Å.

Bei Versuchen zur Darstellung fluorophosphoriger Säure erhielt Falius (Falius, Mootz & Altenburg, 1970; hier auch eine kurze Mitteilung über die Kristallstrukturanalyse) durch Umsetzung von Fluorwasserstoff mit Kaliumhydrogenphosphit und von Kaliumfluorid mit phosphoriger Säure monokline Kristalle eines 1:1-Adduktes, für das sich zunächst drei Formulierungen mit gleicher Summenformel anboten:

$$K[PHO_2(OH)].HF \qquad (I)$$
$$KF.PHO(OH)_2 \qquad (II)$$
$$K[PHO_2F].H_2O \qquad (III)$$

Die Struktur (III) konnte auf Grund chemischer und spektroskopischer Befunde mit Sicherheit ausgeschlossen werden. Die Formeln (I) und (II) entsprechen der linken und rechten Seite des Protonenübergangs-Gleichgewichts:

$$[PHO_2(OH)]^- + HF = PHO(OH)_2 + F^- \,.$$

In verdünnter wässriger Lösung liegt dieses weitgehend auf der linken Seite, da phosphorige Säure ($K_1 = 1{,}0\,.\,10^{-2}$) etwas stärker ist als Flusssäure ($K = 6{,}7\,.\,10^{-4}$). Nach Erfahrungen mit anderen kristallinen Säure/Base-Systemen ist der Unterschied der Dissoziationskonstanten jedoch für einen sicheren Schluss auf die Situation auch im festen Zustand zu klein. Zur Entscheidung zwischen den Formeln (I) und (II) wurde daher eine Kristallstrukturanalyse unternommen, deren Durchführung und Ergebnisse im folgenden beschrieben werden.

### Experimentelles und kristallographische Daten

Kompakte farblose Kristalle des Adduktes mit gut ausgebildeten Flächen wurden beim Erkalten einer heissgesättigten methanolischen Lösung erhalten. Sie sind im Exsiccator beständig; an der Luft verwittern sie jedoch schnell und greifen beim Aufbewahren in Glasgefässen deren Oberfläche örtlich an. Für die röntgenographischen Aufnahmen und Messungen wurden sie in Paraffinöl getaucht und in dünnwandige Glaskapillaren eingeschlossen.

Oszillations- und Weissenbergaufnahmen ergaben monokline Symmetrie und die Raumgruppe $P2_1/c$. Die Gitterkonstanten wurden diffraktometrisch und durch eine Ausgleichsrechnung bestimmt zu:

$$a = 6{,}692\ (2),\ b = 11{,}040\ (2),\ c = 7{,}841\ (5)\ \text{Å},$$
$$\beta = 127{,}88\ (2)°\,.$$

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* In grösserem Zusammenhang vorgetragen auf der 11. Diskussionstagung der Sektion für Kristallkunde der Deutschen Mineralogischen Gesellschaft in Saarbrücken (Albrand, Altenburg & Mootz, 1970).

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