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THE STRUCTURE OF 4-BROMO-3a-HYDROXY-7a-METHYL-OCTAHYDROINDENE-1,5-DIONE

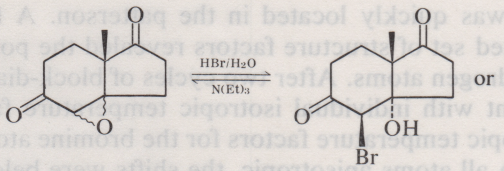
BY

H. VAN DER MEER

Laboratory of Crystallography, Nwe Prinsengracht 126, Amsterdam, The Netherlands

Introduction

An epoxide I is obtained as an intermediate in steroid synthesis[1,2]. The question is whether the methyl group and the epoxide are on the same side of the ring-system or not. If I is a *trans* epoxide one would expect compound II on treating with aqueous hydrobromic acid (hydroxyl and



I II III

methyl groups *trans* with respect to each other), whilst a *cis* epoxide will yield III (both groups in *cis* position). NMR showed a strong downfield shift of the methyl signal of 0.37 ppm, which is interpreted as an interaction between the bromine atom and the methyl group[3] and indicates the presence of II. To obtain more direct evidence an X-ray determination of the structure was undertaken.

Crystal Data

Suitable crystals were provided by Mr. *J. W. de Leeuw* of the Laboratory of Organic Chemistry, who synthesized the substance. The crystals are monoclinic; the cell constants found from Weissenberg films cali-

[1] *R. R. Crenshaw, G. M. Luke*, Tetrahedron Letters **52**, 4495 (1969).

[2] To be presented by Prof. Dr. *H. O. Huisman* at the Third International Congress on Hormonal Steroids, Hamburg, September 7–12th, 1970.

[3] *Bhacca* and *Williams*, Applications of NMR Spectroscopy in Organic Chemistry, Holden-Day Inc., 1964, p. 19.

brated with Al powder lines are $a = 7.185$ Å ± 0.001 Å, $b = 13.572$ Å ± 0.002 Å, $c = 10.713$ Å ± 0.002 Å, $\beta = 97.24° \pm 0.02°$.

The space group is P $2_1/c$ according to the systematic absences. The density determined by flotation is 1.59 g/cm^3 and shows that there are 4 molecules in the unit cell. With an automatic Nonius diffractometer 1589 independent non-zero intensities were collected below $\sin\theta/\lambda = 0.60$ Å^{-1} with CuKα radiation. The intensities were not corrected for absorption. The intensity of the repeatedly measured 540 reflection indicated an irregular decay during the collection of the measurements. A correction for this decay was applied, but this correction has to be considered as a reasonable approximation only. In addition the films showed faint streaks along the reciprocal lattice rows, which may indicate stacking faults. It may be expected that these factors will influence the accuracy of the results.

Solution of the Structure

The bromine atom was quickly located in the patterson. A fourier synthesis with a selected set of structure factors revealed the positions of all the other non-hydrogen atoms. After two cycles of block-diagonal, least-squares refinement with individual isotropic temperature factors, one cycle with anisotropic temperature factors for the bromine atom and finally four cycles with all atoms anisotropic, the shifts were below the estimated standard deviations and the R-factor had reached the value of 7.5%, a few extinctions having been removed.

A difference fourier was calculated and this showed all hydrogen atoms but one, with peak heights from 0.4 to 0.6 e/Å^3; only the hydrogen of the hydroxyl group was missing. Around the bromine atom pits of -0.7 e/Å^3 are found, which may be ascribed to absorption. In view of the remarks already made about the accuracy of the measurements and the comparatively low degree of agreement between the measured and calculated intensities at this stage, refinement of the hydrogen parameters was not attempted.

Description of the Structure

Figure 1 shows the molecule viewed along the b-axis. The coordinates and temperature factors of the non-hydrogen atoms are given in Table I. For the sake of completeness the coordinates of the hydrogen atoms, as determined from the difference fourier series, are listed in Table II.

The bond lengths and bond angles are shown in Fig. 2; the standard

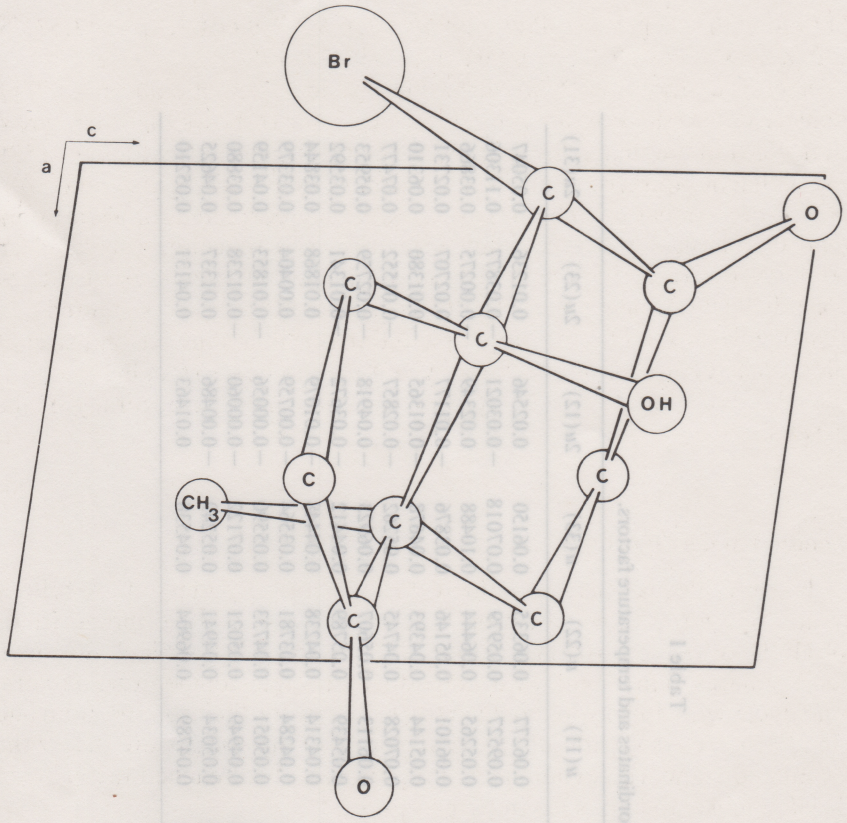


Fig. 1. View of the molecule along the *b*-axis.

deviations of the distances and angles not involving bromine are estimated as 0.015 Å and 1°, respectively. The hydrogen atoms are not included in Fig. 2; their locations are not sufficiently accurate, as may be concluded from the calculated C–H distances which fall between 0.7 and 1.3 Å. In Fig. 3a the torsional angles are given. The cyclohexane ring has a chair conformation. The five-membered ring is something in between a C_6-envelope and a half-chair, with $\Delta = -17°$ and $\phi_{max} = 45°$. The Δ and ϕ_{max} values were calculated from the expressions given by *Altona, Geise* and *Romers*[4]. The newman projection along C_5–C_6 in Fig. 3b shows the *trans*-coupling of the two rings. The distance between the methyl group and the bromine atom is C_{10}-Br = 3.34 Å, supporting the above-mentioned interpretation of the downfield shift of 0.37 ppm in

[4] *C. Altona, H.J. Geise* and *C. Romers*, Tetrahedron **24**, 13 (1968).

Table I

Coordinates and temperature factors.

atom		x	y	z	$u(11)$	$u(22)$	$u(33)$	$2u(12)$	$2u(23)$	$2u(31)$
Br		−0.0962	0.6351	0.1643	0.06277	0.06335	0.06150	0.02546	0.01236	0.05047
O	1	0.0376	0.6683	0.4906	0.09527	0.05979	0.07018	−0.03021	−0.03877	0.11306
O	2	0.6248	0.4226	0.2502	0.05265	0.06444	0.10488	0.02349	−0.00275	0.03866
O	3	0.2313	0.4472	0.4076	0.06101	0.05146	0.03876	−0.01177	0.02707	0.02731
C	1	0.0238	0.5629	0.3119	0.05144	0.04393	0.04678	−0.01365	−0.01380	0.06310
C	2	0.1166	0.6394	0.4035	0.07028	0.04745	0.05262	−0.02857	−0.01552	0.07477
C	3	0.3054	0.6813	0.3805	0.06113	0.05607	0.06923	−0.04918	−0.02759	0.05953
C	4	0.4474	0.6018	0.3491	0.05439	0.05789	0.04412	−0.03672	−0.01341	0.03592
C	5	0.3564	0.5306	0.2451	0.04314	0.04238	0.04448	−0.01079	0.01868	0.03844
C	6	0.1712	0.4888	0.2842	0.04284	0.03781	0.03564	−0.00759	0.00404	0.03379
C	7	0.1172	0.4054	0.1914	0.05051	0.04733	0.05590	−0.00056	−0.01853	0.04159
C	8	0.3124	0.3566	0.1834	0.04949	0.05021	0.07122	−0.00060	−0.01238	0.03880
C	9	0.4550	0.4351	0.2286	0.05034	0.04941	0.05249	−0.00486	0.01337	0.04625
C	10	0.3424	0.5819	0.1148	0.04789	0.06904	0.04538	0.01463	0.04131	0.05210

Table II.

Coordinates of the hydrogen atoms.

atom		*x*	*y*	*z*
H	1	0.572	0.635	0.299
H	2	−0.080	0.523	0.356
H	3	0.278	0.630	0.111
H	4	0.495	0.586	0.114
H	5	0.337	0.339	0.084
H	6	0.273	0.718	0.297
H	7	0.029	0.352	0.246
H	8	0.055	0.458	0.119
H	9	0.251	0.522	0.042
H	10	0.364	0.714	0.469
H	11	0.317	0.300	0.246
H	12	0.467	0.567	0.399

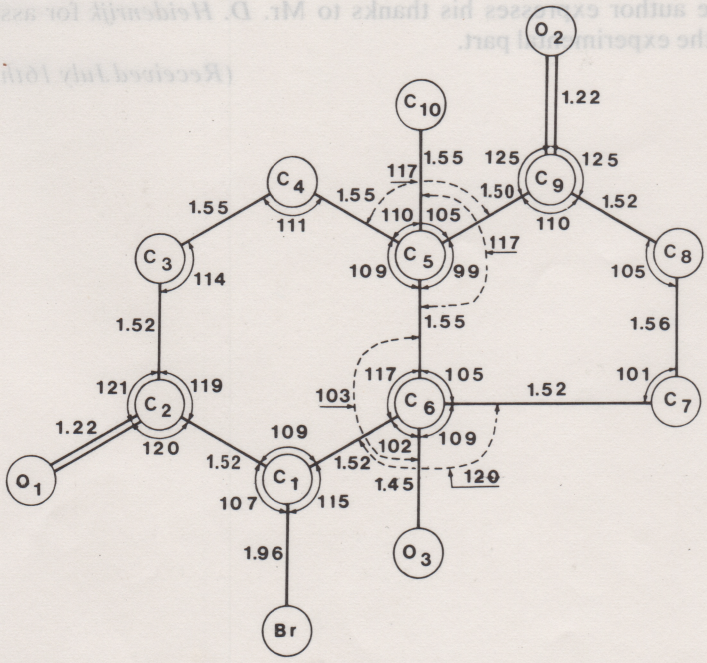


Fig. 2. Bond lengths and bond angles.

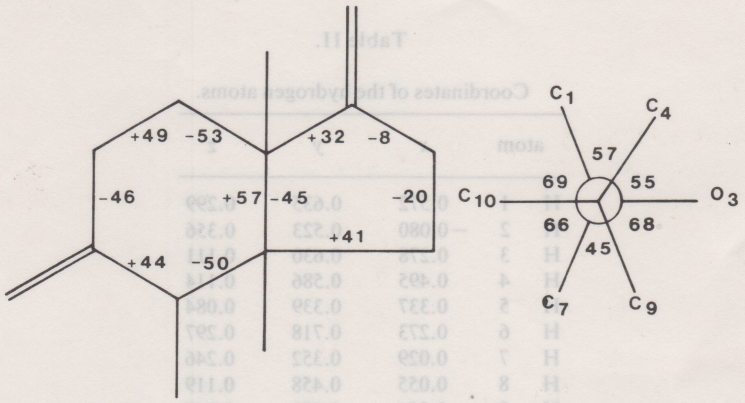


Fig. 3. a. Torsional angles of the bonds. b. Newman projection along C_5–C_6.

the NMR spectrum. The methyl group C_{10} has its hydrogen atoms neatly staggered with respect to the atoms bound to C_5.

Acknowledgement

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