THE CRYSTAL STRUCTURE OF 8-METHOXY-*N*-TOSYL-3-TRICHLOROMETHYL-2,3,4,4a,5,6-HEXAHYDROBENZO[*f*]QUINOLINE

BY

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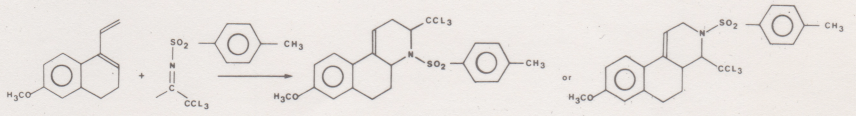
This compound crystallizes in space group $P2_1/c$ with cell constants a = 13.968, b = 19.395, c = 16.575, β = 90.37°, Z = 8. The crystal structure was determined in order to check the interpretation of NMR-spectra.

In the course of the synthesis of aza-steroids by *W. A. Zunnebeld*[1] the following reaction was used:



A B

The reaction yielded a single product; from the NMR – spectrum and a whole series of double and triple resonance experiments the structure A was established for this product and the stereochemistry determined. It was concluded that the heterocyclic ring has a pseudo boat conformation with the hydrogen atoms on both sides of the nitrogen atom at the same side of the ring and that the trichloromethyl group occupies a (pseudo) axial position. An X-ray determination of the crystal structure was undertaken in order to verify these conclusions.

Weissenberg photographs showed the crystals to be monoclinic with space group $P2_1/c$. Cell constants were obtained by measurements on a Nonius single-crystal diffractometer: a = 13.968, b = 19.395, c = 16.575 Å and β = 90.37°. The density determined by suspension is 1.45 g/cm^3; from a unit cell containing eight molecules a calculated

[1] *W. A. Zunnebeld,* Diss. Amsterdam.

density of 1.43 g/cm^3 is obtained. Therefore the crystal structure contains two crystallographically independent molecules. With an automatic Nonius single-crystal diffractometer 2687 non-zero intensities were measured at room temperature with MoKα-radiation. By means of a Wilson scaling normalized structure factors were obtained and with these a Patterson function was calculated. A procedure that searched for the vector pattern of a group of three heavy atoms (chlorine and sulphur) in the Patterson function[2] gave the positions of five of these. The remaining three heavy atoms were found in a minimum function based on one of the chlorine positions. With the chlorine and sulphur positions so obtained structure factors were computed and used in a Fourier synthesis. This revealed 38 of the light atoms, the remaining non-hydrogen atoms were found in the next Fourier synthesis. The structure smoothly refined to R = 0.085 using a block diagonal least-squares program, anisotropic temperature factors for the heavy atoms and isotropic temperature factors for the light atoms; the scattering

Table Ia

Fractional coordinates and temperature parameters ($\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$) for the heavy atoms, estimated standard deviations in parentheses

atom	x	y	z		
Cl(1)	.3564(04)	.6449(03)	.3434(04)		
Cl(2)	.1464(04)	.2178(04)	.7333(04)		
Cl(3)	.2162(05)	.5404(03)	.3127(04)		
Cl(4)	.2874(05)	.1137(03)	.7648(04)		
Cl(5)	.2044(04)	.6223(03)	.4559(03)		
Cl(6)	.2743(04)	.2327(03)	.8679(03)		
S(7)	.2514(03)	.7787(03)	.2206(03)		
S(8)	.2635(03)	.3244(03)	.5985(03)		
β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{13}$
.0046(3)	.0038(2)	.0052(3)	.0014(4)	.0014(4)	−.0002(5)
.0040(3)	.0058(3)	.0046(3)	−.0027(5)	.0034(4)	.0004(5)
.0098(5)	.0022(2)	.0074(4)	.0009(5)	−.0010(4)	.0004(7)
.0103(5)	.0027(2)	.0061(3)	−.0024(5)	.0020(4)	−.0025(7)
.0072(4)	.0032(2)	.0039(2)	.0006(4)	.0017(4)	.0019(5)
.0080(4)	.0039(2)	.0030(2)	−.0020(5)	.0013(4)	.0011(5)
.0032(3)	.0032(2)	.0030(2)	.0008(4)	.0005(3)	.0007(4)
.0033(3)	.0032(2)	.0028(2)	−.0017(4)	.0015(4)	−.0011(4)

[2] *H. van der Meer*, Diss. Amsterdam.

Table Ib

Fractional coordinates and temperature parameters for the light atoms, estimated standard deviations in parentheses

atom	x	y	z	B_{iso}
O(9)	.3214(09)	.8290(07)	.2462(07)	3.7(3)
O(10)	.1905(10)	.3752(08)	.6082(08)	4.7(3)
O(11)	.2786(10)	.7224(07)	.1698(09)	4.8(3)
O(12)	.2415(10)	.2601(07)	.5620(08)	4.9(3)
O(13)	−.0418(13)	.9706(11)	.6375(12)	8.0(5)
O(14)	.5678(12)	.6017(09)	.9323(10)	7.3(4)
N(15)	.2049(11)	.7560(08)	.3013(09)	4.0(3)
N(16)	.3126(10)	.3091(08)	.6863(09)	4.3(3)
C(17)	.1593(13)	.8241(10)	.1724(11)	2.9(4)
C(18)	.3532(12)	.3632(10)	.5381(11)	3.4(4)
C(19)	.1581(14)	.8965(11)	.1707(12)	4.0(4)
C(20)	.3347(12)	.4254(10)	.5040(11)	3.3(4)
C(21)	.0854(15)	.9310(11)	.1329(12)	4.5(4)
C(22)	.4017(15)	.4529(11)	.4485(13)	4.5(5)
C(23)	.0098(13)	.8919(10)	.0975(11)	3.5(4)
C(24)	.4829(15)	.4150(12)	.4309(13)	4.8(5)
C(25)	.0089(15)	.8229(12)	.0990(12)	4.4(5)
C(26)	.5004(16)	.3516(12)	.4642(14)	5.2(5)
C(27)	.0856(14)	.7863(11)	.1377(13)	4.4(4)
C(28)	.4330(14)	.3245(11)	.5214(12)	3.8(4)
C(29)	−.0733(20)	.9304(16)	.0562(17)	7.0(7)
C(30)	.5546(18)	.4455(14)	.3658(16)	7.0(6)
C(31)	.2334(13)	.6263(10)	.3524(11)	3.7(4)
C(32)	.2655(14)	.2048(11)	.7681(12)	4.1(4)
C(33)	.1761(13)	.7976(10)	.3643(11)	3.7(4)
C(34)	.3466(13)	.3713(10)	.7304(11)	3.1(4)
C(35)	.0815(13)	.7775(10)	.4013(11)	3.3(4)
C(36)	.4347(11)	.3577(09)	.7793(10)	2.6(3)
C(37)	.0305(13)	.7210(10)	.3832(11)	3.5(4)
C(38)	.4775(13)	.2954(10)	.7853(12)	3.7(4)
C(39)	.0609(13)	.6689(11)	.3216(11)	3.8(4)
C(40)	.4420(13)	.2336(10)	.7408(10)	3.6(4)
C(41)	.1710(14)	.6739(11)	.3014(12)	4.1(4)
C(42)	.3389(13)	.2380(10)	.7068(11)	3.5(4)
C(43)	.2515(13)	.8052(11)	.4308(12)	3.8(4)
C(44)	.2691(13)	.4035(10)	.7836(12)	3.9(4)
C(45)	.2235(13)	.8678(10)	.4812(12)	4.1(4)
C(46)	.3046(15)	.4780(12)	.8070(14)	4.9(5)
C(47)	.1182(14)	.8699(11)	.5023(12)	4.1(4)
C(48)	.4121(13)	.4773(10)	.8357(11)	3.3(4)
C(49)	.0529(13)	.8284(10)	.4648(11)	3.6(4)
C(50)	.4697(13)	.4203(10)	.8224(11)	3.3(4)
C(51)	.0899(14)	.9186(11)	.5622(12)	4.7(4)
C(52)	.4476(14)	.5385(11)	.8713(13)	3.8(5)

Table Ib *(continued)*

atom	x	y	z	B_{iso}
C(53)	−.0100(16)	.9236(12)	.5812(14)	5.7(5)
C(54)	.5397(14)	.5394(11)	.8967(12)	4.4(4)
C(55)	−.0749(17)	.8778(13)	.5451(15)	5.3(5)
C(56)	.6006(16)	.4854(12)	.8888(14)	4.9(5)
C(57)	−.0489(15)	.8325(12)	.4888(13)	4.6(5)
C(58)	.5642(14)	.4254(12)	.8490(12)	4.3(4)
C(59)	.0184(18)	1.0260(15)	.6658(16)	6.9(6)
C(60)	.6565(21)	.6012(16)	.9730(19)	8.5(8)

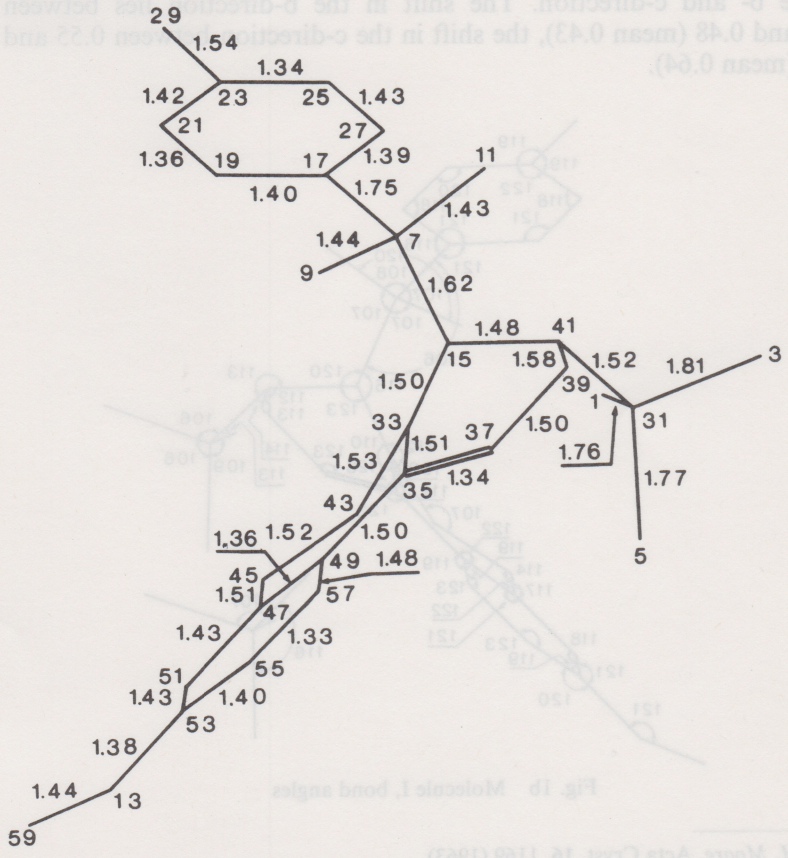


Fig. 1a Molecule I projected along [100], bond lengths and numbering of atoms.

factors of *Moore*[3] and the weighting scheme of *Cruickshank*[4] were used. The hydrogen atoms were not included.

In Table I the coordinates and temperature factors are given together with the estimated standard deviations from the least-squares refinement; the odd numbers refer to molecule I and the even numbers to the atoms of molecule II. In Figures 1 and 2 the bond distances and bond angles of the two independent molecules are shown; the precision is low. The standard deviation for a distance between light atoms is about 0.03 Å, 0.02 Å for a distance involving a heavy atom, and 2° or 1°, respectively, for the bond angles. The figures also show the numbering of the atoms.

The two independent molecules are approximately related by a reflection across a plane perpendicular to the a-axis at $x \sim \frac{1}{4}$ and a shift in the b- and c-direction. The shift in the b-direction lies between 0.37 and 0.48 (mean 0.43), the shift in the c-direction between 0.55 and 0.69 (mean 0.64).

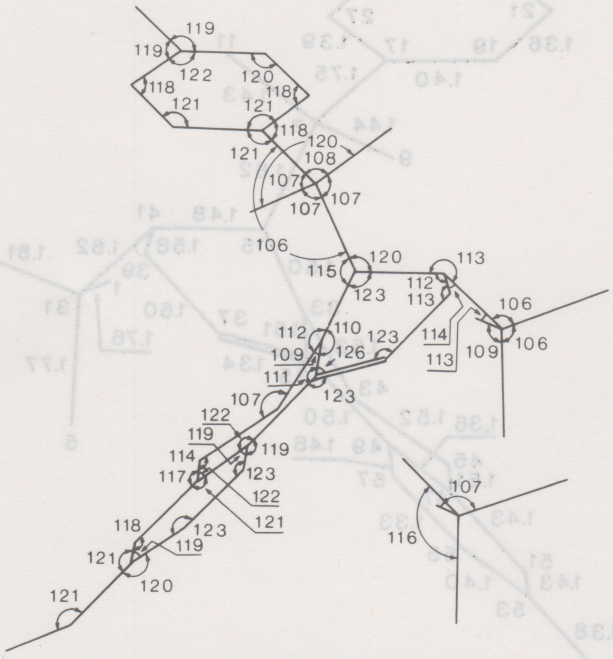


Fig. 1b Molecule I, bond angles

[3] *F. H. Moore*, Acta Cryst. **16**, 1169 (1963).

[4] *D. W. J. Cruickshank*, Computing Methods and the phase problem in X-ray Crystal Analysis, Pergamon Press, Oxford 1961.

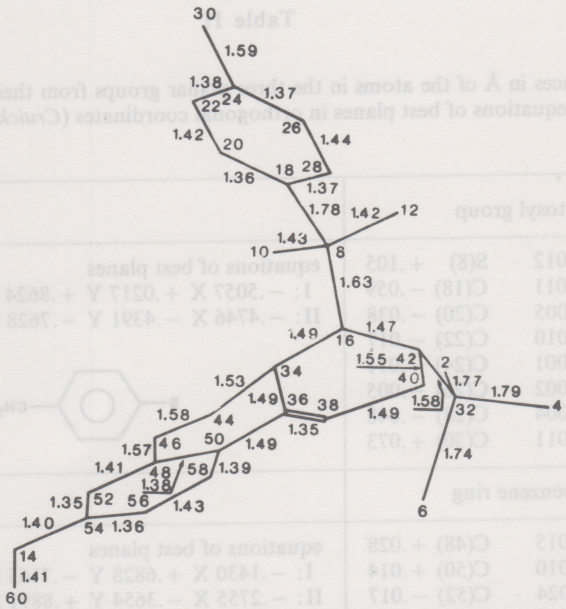


Fig. 2a Molecule II projected along [100], bond lengths and numbering of atoms

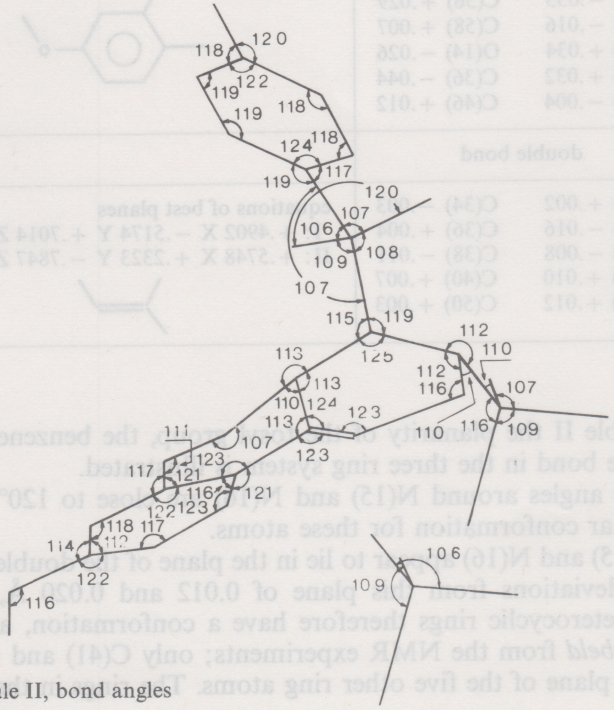
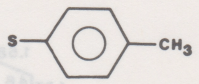
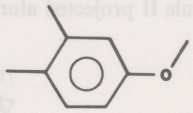


Fig. 2b Molecule II, bond angles

Table II

Distances in Å of the atoms in the three planar groups from their best planes; equations of best planes in orthogonal coordinates (*Cruickshank*[4])

tosyl group		
S(7) +.012	S(8) +.105	equations of best planes
C(17) −.011	C(18) −.059	I: −.5057 X +.0217 Y +.8624 Z −1.705 = 0
C(19) +.005	C(20) −.038	II: −.4746 X −.4391 Y −.7628 Z +12.152 = 0
C(21) −.010	C(22) −.017	
C(23) −.001	C(24) −.011	
C(25) −.002	C(26) −.005	
C(27) −.004	C(28) −.048	
C(29) +.011	C(30) +.073	
benzene ring		
C(47) −.015	C(48) +.028	equations of best planes
C(49) +.010	C(50) +.014	I: −.1430 X +.6828 Y −.7165 Z −5.342 = 0
C(51) −.024	C(52) −.017	II: −.2755 X −.3654 Y +.8891 Z −7.344 = 0
C(53) +.017	C(54) −.003	
C(55) −.033	C(56) +.029	
C(57) −.016	C(58) +.007	
O(13) +.034	O(14) −.026	
C(35) +.032	C(36) −.044	
C(45) −.004	C(46) +.012	
double bond		
C(33) +.002	C(34) −.003	equations of best planes
C(35) −.016	C(36) +.004	I: +.4902 X −.5174 Y +.7014 Z +2.583 = 0
C(37) −.008	C(38) −.011	II: +.5748 X +.2323 Y −.7847 Z +5.086 = 0
C(39) +.010	C(40) +.007	
C(49) +.012	C(50) +.003	

In Table II the planarity of the tosyl group, the benzene ring and the double bond in the three ring system is illustrated.

The angles around N(15) and N(16) are close to 120° and indicate a planar conformation for these atoms.

N(15) and N(16) appear to lie in the plane of the double bond system with deviations from this plane of 0.012 and 0.020 Å, respectively. The heterocyclic rings therefore have a conformation, as deduced by *Zunnebeld* from the NMR experiments; only C(41) and C(42) are out of the plane of the five other ring atoms. The rings in the middle have

nearly the same conformation, C(43) and C(44) deviate by only 0.29 and 0.33 Å from the plane defined by the benzene ring of the steroid skeleton. In Figure 4 the torsion angles are shown. The Newman projections along C(35)-C(33) and C(36)-C(34) in Figure 3 illustrate how the two rings are tied together. The Newman projections along

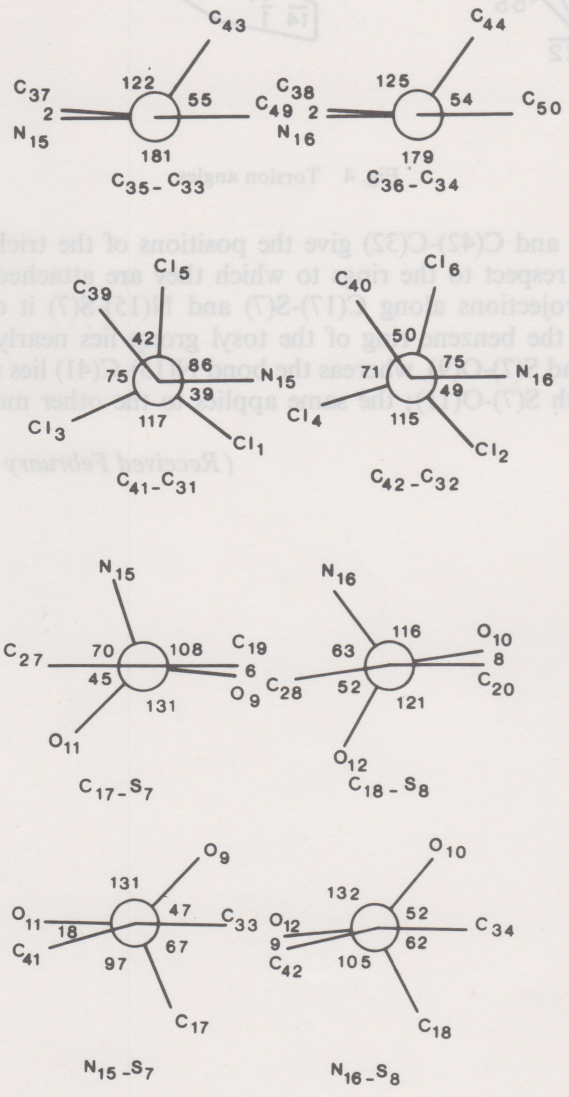


Fig. 3 Newman projections

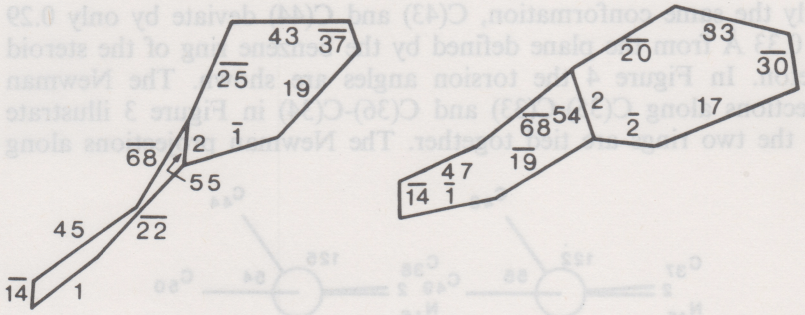


Fig. 4 Torsion angles

C(41)-C(31) and C(42)-C(32) give the positions of the trichloromethyl group with respect to the rings to which they are attached. From the Newman projections along C(17)-S(7) and N(15)-S(7) it can be concluded that the benzene ring of the tosyl group lies nearly in a plane with the bond S(7)-O(9), whereas the bond N(15)-C(41) lies more nearly in plane with S(7)-O(11); the same applies to the other molecule.

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