

The Molecular and Crystal Structures of Two Reaction Products $C_9H_{13}N_3O_6$ and $C_9H_{13}N_3O_5$ with Unexpected Tropane Skeletons

BY H. SCHENK AND P. BENCI

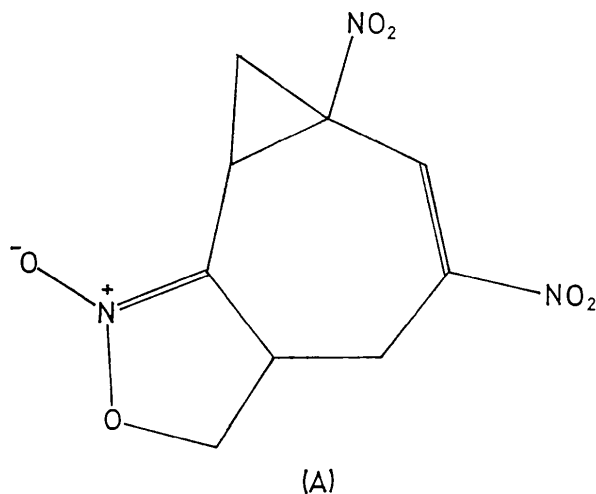
Laboratory for Crystallography, University of Amsterdam, Nieuwe Prinsengracht 126, Amsterdam, The Netherlands

(Received 17 April 1971)

$C_9H_{13}N_3O_6$ and $C_9H_{13}N_3O_5$ both crystallize in the monoclinic system, space group $P2_1/c$ with cell constants $a=13.304$, $b=6.350$, $c=13.364$ Å, $\beta=105.30^\circ$ and $a=6.423$, $b=6.937$, $c=24.416$ Å, $\beta=99.88^\circ$ respectively. The molecules could be identified as 1,3-dinitro-6-hydroxymethylene-3,4-methanonortropane and its *N*-hydroxy derivative. The corresponding bond lengths of both molecules are equal within the limits of accuracy. The piperidine ring of the tropane skeleton is in the envelope conformation. The nitro group coupled to the cyclopropane group is in a conformation in which an oxygen atom is pointing towards the cyclopropane group; an extended Hückel calculation of the rotation barrier in nitrocyclopropane is in agreement with this feature.

Introduction

Symmetric trinitrobenzene takes up three methylene groups from diazomethane at -80°C . The resulting reaction product was proved to have the molecular structure A (van Velzen, Kruk & de Boer, 1971), the stereochemistry of which could not be established. Treatment of A with NaBH_4 in ethanol gives a 'tetrahydro product' I with composition $C_9H_{13}N_3O_6$ (Fig. 1). By reduction of I with CuO in hydrochloric acid a compound II with composition $C_9H_{13}N_3O_5$ was obtained (van Velzen, Kruk, Spaargaren & de Boer, 1971). Although many details of both structures were known, it appeared to be impossible to determine the molecular structure of the two compounds by spectroscopic techniques. For this reason an X-ray structure analysis was started.



Experimental

Crystals of I and II are monoclinic and their axes were chosen so that the extinctions for both were $h0l$ with

$l=2n+1$ and $0k0$ with $k=2n+1$: space group $P2_1/c$. The cell constants were calculated by means of a least-squares procedure with data measured from zero-layer Weissenberg diagrams taken at room temperature with $\text{Cu K}\alpha$ radiation and calibrated with Al powder lines. They are:

I: $a = 13.304$ (1) Å	II: $a = 6.423$ (1) Å
$b = 6.350$ (1)	$b = 6.937$ (1)
$c = 13.364$ (1)	$c = 24.416$ (1)
$\beta = 105.30$ (2)°	$\beta = 99.88$ (1)°

From density determinations it appeared that both unit cells contain four molecules.

The intensities were collected by means of a Nonius Automatic Single Crystal Diffractometer. Some details of the data collection are: $\text{Cu K}\alpha$ radiation; θ - 2θ scan; maximum θ : 68.5° ; high intensities were reduced by attenuation filters; the background intensity was measured at both sides of the reflexion during half the scanning time. A reflexion was considered significant if the net count exceeded twice the standard deviation. No absorption correction was applied, since the dimensions of both crystals were sufficiently small.

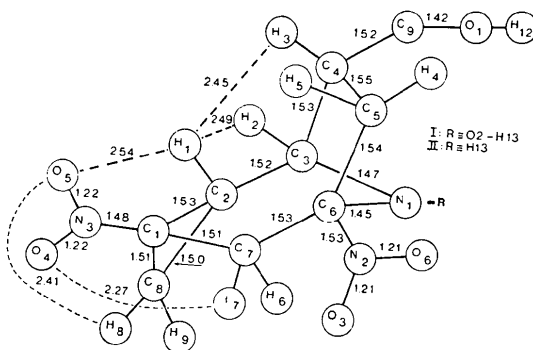


Fig. 1. Mean values of corresponding bond lengths of both molecules and numbering of the atoms. Some small intramolecular $\text{H}\cdots\text{O}$ and $\text{H}\cdots\text{H}$ distances are indicated.

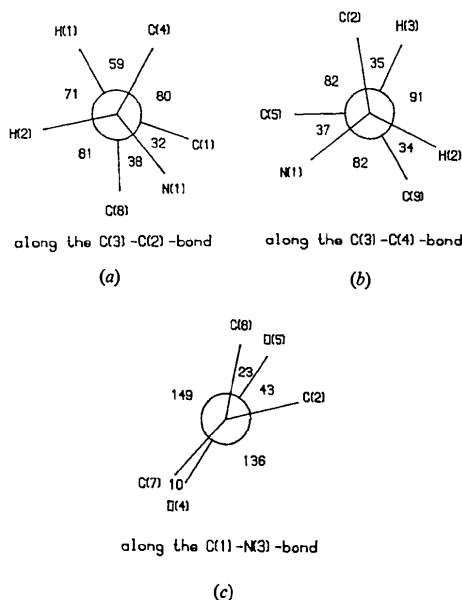


Fig. 2. Some Newman projections of molecule II. The corresponding angles in Newman projections of molecule I are similar.

Structure determination and refinement

The positions of all non-hydrogen atoms in both compounds were found using automatic programs (Schenk, 1969) based on the symbolic addition method (Karle & Karle, 1966).

The refinement was carried out by means of a block-diagonal least-squares program using the weighting scheme of Cruickshank (1961) and atomic form factors from *International Tables for X-ray Crystallography* (1962). At a later stage of the refinement, difference syntheses yielded all hydrogen atoms of both structures with peak heights between 0.4 and 0.7 e.Å⁻³.

The final refinement cycles were carried out with positional parameters for all atoms, anisotropic thermal parameters for the heavy atoms, and isotropic thermal parameters for hydrogen. The refinements were terminated when *R* was 4.6% for 1833 independent reflexions of structure I and 4.8% for 1380 independent reflexions of structure II. In both refinements approximately 10 reflexions were omitted which apparently suffered from extinction.

The final parameters of the heavy atoms and the hydrogen atoms are given in Tables 1 and 2 respec-

Table 1. Final parameters of the heavy atoms with their *e.s.d.*'s

The positional parameters *x*, *y* and *z* are given in fractions multiplied by 10⁴. The anisotropic thermal parameters *u_{ij}* have been multiplied by 10³.

Molecule I	<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i> ₁₁	<i>u</i> ₂₂	<i>u</i> ₃₃	2 <i>u</i> ₁₂	2 <i>u</i> ₂₃	2 <i>u</i> ₃₁
C(1)	1026 (1)	7811 (3)	1691 (2)	23 (1)	38 (1)	41 (1)	6 (2)	1 (2)	21 (2)
C(2)	1588 (2)	6796 (3)	955 (2)	27 (1)	40 (1)	36 (1)	-9 (2)	-19 (2)	16 (2)
C(3)	2755 (1)	7180 (3)	1195 (2)	26 (1)	32 (1)	36 (1)	3 (2)	-7 (2)	17 (2)
C(4)	2967 (2)	9348 (3)	787 (2)	27 (1)	42 (1)	33 (1)	2 (2)	7 (2)	11 (2)
C(5)	2755 (2)	837 (3)	1627 (2)	40 (1)	29 (1)	40 (1)	0 (2)	8 (2)	16 (2)
C(6)	2738 (2)	9371 (3)	2541 (2)	37 (1)	27 (1)	31 (1)	-5 (2)	-9 (2)	6 (2)
C(7)	1649 (2)	8917 (3)	2656 (2)	43 (1)	36 (1)	37 (1)	5 (2)	-10 (2)	34 (2)
C(8)	1061 (2)	5456 (3)	1591 (2)	32 (1)	37 (1)	52 (1)	-18 (2)	-16 (2)	26 (2)
C(9)	4069 (2)	9552 (4)	659 (2)	30 (1)	60 (1)	45 (1)	-9 (2)	17 (2)	18 (2)
O(1)	4856 (1)	9489 (3)	1618 (1)	28 (1)	83 (1)	56 (1)	-30 (2)	23 (2)	5 (1)
N(1)	3273 (1)	7526 (3)	2299 (1)	28 (1)	29 (1)	35 (1)	0 (2)	12 (1)	6 (1)
O(2)	3179 (1)	5804 (2)	2958 (1)	32 (1)	36 (1)	49 (1)	7 (2)	34 (1)	12 (1)
N(2)	3401 (2)	280 (3)	3563 (2)	70 (1)	46 (1)	38 (1)	-39 (2)	-15 (2)	3 (2)
O(3)	2952 (2)	1291 (4)	4077 (2)	122 (2)	97 (2)	67 (1)	-44 (3)	-103 (3)	50 (3)
N(3)	17 (1)	8806 (4)	1161 (2)	30 (1)	67 (1)	54 (1)	22 (2)	26 (2)	37 (2)
O(4)	-167 (2)	561 (4)	1443 (2)	66 (1)	74 (1)	85 (1)	80 (2)	30 (2)	55 (2)
O(5)	-578 (1)	7854 (4)	457 (2)	33 (1)	110 (2)	84 (2)	11 (2)	-7 (3)	-21 (2)
O(6)	4337 (2)	9975 (5)	3788 (2)	69 (1)	113 (2)	67 (1)	-50 (3)	-34 (3)	-42 (2)
Molecule II	<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i> ₁₁	<i>u</i> ₂₂	<i>u</i> ₃₃	2 <i>u</i> ₁₂	2 <i>u</i> ₂₃	2 <i>u</i> ₃₁
C(1)	2490 (5)	7168 (5)	4393 (1)	44 (2)	43 (2)	26 (1)	-4 (3)	5 (3)	4 (2)
C(2)	720 (5)	8615 (5)	4169 (1)	40 (2)	43 (2)	36 (2)	6 (3)	-1 (3)	22 (3)
C(3)	574 (5)	9336 (5)	3604 (1)	29 (1)	35 (2)	35 (2)	12 (3)	1 (3)	7 (2)
C(4)	2231 (5)	10911 (5)	3584 (1)	37 (2)	33 (2)	29 (2)	5 (3)	-2 (3)	0 (2)
C(5)	4257 (5)	9731 (5)	3564 (1)	32 (2)	35 (2)	38 (2)	-6 (3)	6 (3)	2 (3)
C(6)	3454 (5)	7648 (4)	3467 (1)	29 (1)	35 (2)	27 (1)	3 (2)	-0 (3)	1 (2)
C(7)	3856 (5)	6410 (5)	3995 (1)	40 (2)	36 (2)	32 (2)	13 (3)	4 (3)	-1 (3)
C(8)	198 (6)	6593 (6)	4338 (2)	48 (2)	53 (2)	45 (2)	-18 (4)	15 (3)	22 (3)
C(9)	1716 (6)	12190 (5)	3076 (1)	53 (2)	33 (2)	34 (2)	9 (3)	4 (3)	2 (3)
N(1)	1249 (4)	7867 (4)	3235 (1)	26 (1)	35 (1)	30 (1)	-1 (2)	-0 (2)	-5 (2)
N(2)	4591 (5)	6709 (4)	3036 (1)	43 (2)	41 (2)	35 (1)	13 (2)	-2 (3)	15 (2)
N(3)	3604 (5)	7493 (5)	4968 (1)	59 (2)	64 (2)	31 (1)	-4 (3)	4 (3)	-3 (3)
O(1)	54 (4)	13490 (4)	3132 (1)	54 (2)	39 (1)	59 (2)	21 (2)	3 (2)	-24 (2)
O(3)	6385 (5)	6186 (6)	3190 (1)	50 (2)	120 (3)	61 (2)	82 (4)	-18 (4)	11 (3)
O(4)	5522 (5)	7397 (6)	5066 (1)	62 (2)	136 (4)	42 (2)	-4 (4)	-21 (4)	-27 (3)
O(5)	2561 (6)	7878 (6)	5327 (1)	95 (2)	122 (3)	31 (1)	0 (5)	-24 (3)	33 (3)
O(6)	3686 (5)	6533 (6)	2563 (1)	63 (2)	111 (3)	35 (1)	35 (4)	-36 (3)	14 (2)

tively, together with their estimated standard deviations. Lists of structure factors can be obtained from our laboratory.

Table 2. Parameters of the hydrogen atoms with their e.s.d.'s

The coordinates are given in fractions multiplied by 10³, the thermal parameters *B* in Å².

Molecule I	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	122 (2)	689 (4)	22 (2)	1.4 (0.5)
H(2)	310 (2)	601 (4)	93 (2)	1.1 (0.5)
H(3)	250 (2)	962 (4)	10 (2)	1.3 (0.5)
H(4)	332 (2)	188 (5)	184 (2)	1.9 (0.6)
H(5)	207 (2)	152 (4)	135 (2)	1.5 (0.5)
H(6)	171 (2)	808 (4)	328 (2)	1.6 (0.5)
H(7)	132 (2)	22 (4)	275 (2)	1.7 (0.5)
H(8)	41 (2)	485 (4)	124 (2)	1.3 (0.5)
H(9)	151 (2)	476 (4)	228 (2)	1.3 (0.5)
H(10)	415 (2)	92 (5)	34 (2)	3.1 (0.7)
H(11)	420 (2)	842 (5)	19 (2)	1.7 (0.5)
H(12)	464 (3)	866 (7)	213 (3)	5.6 (1.0)
H(13)	386 (3)	531 (5)	317 (3)	3.1 (0.7)

Molecule II	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	55 (6)	941 (6)	446 (2)	1.8 (0.8)
H(2)	- 91 (6)	965 (6)	345 (2)	1.1 (0.8)
H(3)	236 (5)	1164 (5)	393 (1)	0.5 (0.6)
H(4)	492 (6)	1011 (6)	324 (2)	1.9 (0.8)
H(5)	531 (7)	959 (7)	392 (2)	2.4 (1.0)
H(6)	351 (7)	498 (7)	390 (2)	2.5 (0.9)
H(7)	535 (6)	643 (5)	418 (1)	1.2 (0.7)
H(8)	- 34 (6)	636 (5)	471 (1)	1.3 (0.7)
H(9)	- 27 (7)	587 (7)	404 (2)	2.6 (1.0)
H(10)	137 (6)	1158 (5)	274 (1)	1.1 (0.7)
H(11)	297 (7)	1298 (6)	303 (2)	2.2 (0.9)
H(12)	- 80 (11)	1325 (10)	283 (3)	7.8 (1.9)
H(13)	53 (6)	681 (5)	326 (1)	1.0 (0.7)

Discussion

Molecular structure of I, II and A

The structural formula of compound I turned out to be 1,3-dinitro-6-hydroxymethylene-*N*-hydroxy-3,4-methanonortropane where the conventional tropane numbering is used. In this paper an arbitrary numbering of atoms is used (see Fig. 1). Compound II appeared to be 1,3-dinitro-6-hydroxymethylene-3,4-methanonortropane.

The stereochemistry of compound A could now be established. It must be such that the cyclopropane group and the methylene group are situated at the same side of the 7-membered ring.

Chemistry

According to van Velzen *et al.* (1971) the reaction of product A with NaBH₄ in methanol proceeds *via* an intermediate structure in which the double bond in the seven-membered ring is reduced and the five-membered ring is opened, resulting in a nitroso group and a primary alcohol group. The nitroso group then reacts with the HCNO₂ group, thus forming the tropane skeleton.

The difficulties encountered in interpreting the nuclear magnetic resonance spectra were caused by the appearance of an uncoupled proton-signal, which afterwards could be ascribed to H(2). The dihedral angles of this proton with H(1) and H(3) are approximately 70 and 90° respectively [see Fig. 2(a), (b)]. According to the Karplus-rule these angles correspond to very small coupling constants, which explains the appearance of the singlet H(2)-signal.

Accuracy of the results

From Table 3 it can be seen that the differences between corresponding bond lengths of the two molecules are all of the order of magnitude of the e.s.d.'s, calculated from the least-squares refinement. Thus the e.s.d.'s appear to be representative of the accuracy of the results.

Table 3. Bond lengths of both molecules in Å

The mean values of corresponding bond lengths are given in Fig. 1, together with some other intramolecular distances.

	Molecule I	Molecule II
C(1)–C(2)	1.526 (0.003)	1.531 (0.005)
C(1)–C(7)	1.510 (0.003)	1.511 (0.005)
C(1)–C(8)	1.503 (0.003)	1.509 (0.005)
C(1)–N(3)	1.484 (0.003)	1.480 (0.004)
C(2)–C(3)	1.520 (0.003)	1.518 (0.005)
C(2)–C(8)	1.501 (0.003)	1.497 (0.005)
C(2)–H(1)	0.98 (0.02)	0.87 (0.04)
C(3)–C(4)	1.534 (0.003)	1.532 (0.005)
C(3)–N(1)	1.471 (0.002)	1.473 (0.004)
C(3)–H(2)	0.99 (0.03)	0.98 (0.04)
C(4)–C(5)	1.549 (0.003)	1.545 (0.005)
C(4)–C(9)	1.526 (0.003)	1.514 (0.004)
C(4)–H(3)	0.98 (0.02)	0.97 (0.03)
C(5)–C(6)	1.540 (0.003)	1.539 (0.004)
C(5)–H(4)	0.99 (0.03)	1.00 (0.04)
C(5)–H(5)	0.99 (0.02)	1.02 (0.04)
C(6)–C(7)	1.524 (0.003)	1.533 (0.004)
C(6)–N(1)	1.451 (0.003)	1.441 (0.004)
C(6)–N(2)	1.530 (0.003)	1.527 (0.004)
C(7)–H(6)	0.97 (0.03)	1.03 (0.05)
C(7)–H(7)	0.96 (0.03)	0.99 (0.04)
C(8)–H(8)	0.96 (0.03)	1.04 (0.04)
C(8)–H(9)	1.05 (0.03)	0.89 (0.05)
C(9)–O(1)	1.426 (0.003)	1.422 (0.005)
C(9)–H(10)	0.98 (0.03)	0.92 (0.04)
C(9)–H(11)	1.00 (0.03)	1.00 (0.04)
N(2)–O(3)	1.207 (0.004)	1.205 (0.004)
N(2)–O(6)	1.216 (0.004)	1.206 (0.004)
N(3)–O(4)	1.222 (0.003)	1.215 (0.005)
N(3)–O(5)	1.218 (0.003)	1.221 (0.005)
N(1)–O(2)	1.430 (0.002)	
N(1)–H(13)		0.87 (0.04)
O(1)–H(12)	0.97 (0.04)	0.86 (0.06)
O(2)–H(13)	0.92 (0.92)	

The molecular geometry

The tropane skeleton of I and II is much more deformed than those of the known structures tropine.HBr (Visser, Manassen & de Vries, 1954), pseudotropine (Schenk, MacGillavry, Skolnik & Laan, 1967), α -chlorotropine (Vooren, Schenk & MacGillavry, 1970) and tropine-ethobromide (Benci, Stam & MacGillavry, 1971). Whereas the piperidine ring in those structures is a deformed chair, in I and II it is nearly an envelope (see Table 4, plane 1).

Table 4. Planes $AX+BY+CZ+D=0$ through two parts of the molecules

The distances of the atoms to the planes are indicated with Δ and given in Å. X , Y and Z refer to the orthogonal coordinates. The distances in italics refer to the atoms defining the planes.

Plane 1		Plane 2			
	Mol I	Mol II			
A	0.1124	-0.5706	A	0.9292	-0.0608
B	-0.8039	-0.7231	B	-0.0398	+0.1094
C	0.5840	-0.3894	C	0.3674	-0.9921
D	2.481	7.464	D	-3.458	7.781
	Δ_I	Δ_{II}		Δ_I	Δ_{II}
$C(2)$	-0.07	-0.05	$C(3)$	-0.06	-0.04
$C(3)$	+0.08	+0.06	$C(4)$	+0.09	+0.06
$C(6)$	-0.08	-0.06	$C(5)$	-0.09	-0.06
$C(7)$	+0.07	+0.05	$C(6)$	+0.06	+0.04
$C(1)$	-0.15	-0.11	$N(1)$	+0.73	+0.69
$N(1)$	+0.77	+0.80			

Angles between various parts of the tropane skeleton

		Angle between plane A and plane B		
Plane A	Plane B	Mol I	Mol II	Pseudotropine
plane 1	plane 2	111°	110°	110°
plane 1	$C(1)$, $C(2)$, $C(7)$	168	169	142
plane 1	$C(3)$, $C(6)$, $N(1)$	122	119	113
plane 2	$C(3)$, $C(6)$, $N(1)$	127	131	137

The geometries of both molecules as well as the bond angles (Table 5) and the Newman projections differ slightly because the intramolecular hydrogen bond $O(1)-H \cdots N(1)$ of structure I is lacking in II.

Table 5. Valence angles of both molecules (°)

	Molecule I	Molecule II
$C(2)-C(1)-C(7)$	119.6 (0.2)	120.5 (0.3)
$C(2)-C(1)-C(8)$	59.4 (0.2)	59.0 (0.2)
$C(2)-C(1)-N(3)$	114.1 (0.2)	114.2 (0.3)
$C(7)-C(1)-C(8)$	121.0 (0.2)	121.0 (0.3)
$C(7)-C(1)-N(3)$	115.7 (0.2)	115.1 (0.3)
$C(8)-C(1)-N(3)$	115.2 (0.2)	115.5 (0.3)
$C(1)-C(2)-C(3)$	116.3 (0.2)	115.9 (0.3)
$C(1)-C(2)-C(8)$	59.6 (0.2)	59.8 (0.2)
$C(1)-C(2)-H(1)$	115 (2)	111 (2)
$C(3)-C(2)-C(8)$	125.1 (0.2)	123.3 (0.3)
$C(3)-C(2)-H(1)$	114 (2)	120 (3)
$C(8)-C(2)-H(1)$	115 (2)	111 (3)

Table 5 (cont.)

	Molecule I	Molecule II
$C(2)-C(3)-C(4)$	110.0 (0.2)	109.6 (0.2)
$C(2)-C(3)-N(1)$	114.7 (0.2)	112.1 (0.3)
$C(2)-C(3)-H(2)$	111 (2)	109 (2)
$C(4)-C(3)-N(1)$	98.1 (0.1)	101.3 (0.3)
$C(4)-C(3)-H(2)$	114 (2)	118 (2)
$N(1)-C(3)-H(2)$	109 (1)	107 (2)
$C(3)-C(4)-C(5)$	101.8 (0.2)	102.5 (0.3)
$C(3)-C(4)-C(9)$	112.8 (0.2)	112.9 (0.3)
$C(3)-C(4)-H(3)$	111 (2)	108 (2)
$C(5)-C(4)-C(9)$	113.2 (0.2)	110.6 (0.3)
$C(5)-C(4)-H(3)$	112 (2)	111 (2)
$C(9)-C(4)-H(3)$	106 (2)	112 (2)
$C(4)-C(5)-C(6)$	104.4 (0.2)	103.9 (0.2)
$C(4)-C(5)-H(4)$	110 (2)	111 (2)
$C(4)-C(5)-H(5)$	108 (2)	118 (3)
$C(6)-C(5)-H(4)$	110 (2)	108 (2)
$C(6)-C(5)-H(5)$	111 (2)	101 (3)
$H(4)-C(5)-H(5)$	112 (2)	114 (4)
$C(5)-C(6)-C(7)$	114.1 (0.2)	113.2 (0.2)
$C(5)-C(6)-N(1)$	101.6 (0.2)	104.1 (0.2)
$C(5)-C(6)-N(2)$	110.8 (0.2)	108.6 (0.3)
$C(7)-C(6)-N(1)$	113.9 (0.2)	113.7 (0.3)
$C(7)-C(6)-N(2)$	108.7 (0.2)	108.0 (0.3)
$N(1)-C(6)-N(2)$	107.6 (0.2)	109.2 (0.2)
$C(1)-C(7)-C(6)$	108.9 (0.2)	108.2 (0.3)
$C(1)-C(7)-H(6)$	112 (2)	110 (3)
$C(1)-C(7)-H(7)$	110 (1)	110 (2)
$C(6)-C(7)-H(6)$	109 (2)	111 (2)
$C(6)-C(7)-H(7)$	109 (2)	113 (2)
$H(6)-C(7)-H(7)$	108 (2)	105 (3)
$C(1)-C(8)-C(2)$	61.1 (0.2)	61.2 (0.2)
$C(1)-C(8)-H(8)$	114 (2)	115 (2)
$C(1)-C(8)-H(9)$	111 (1)	114 (3)
$C(2)-C(8)-H(8)$	117 (2)	118 (2)
$C(2)-C(8)-H(9)$	120 (2)	114 (3)
$H(8)-C(8)-H(9)$	120 (2)	120 (4)
$C(4)-C(9)-O(1)$	113.3 (0.2)	110.8 (0.3)
$C(4)-C(9)-H(10)$	110 (2)	117 (2)
$C(4)-C(9)-H(11)$	110 (2)	110 (2)
$O(1)-C(9)-H(10)$	106 (2)	108 (2)
$O(1)-C(9)-H(11)$	110 (1)	107 (2)
$H(10)-C(9)-H(11)$	108 (3)	103 (4)
$C(3)-N(1)-C(6)$	102.5 (0.1)	101.8 (0.2)
$C(3)-N(1)-O(2)$	114.2 (0.1)	
$C(3)-N(1)-H(13)$		109 (2)
$C(6)-N(1)-O(2)$	110.6 (0.2)	
$C(6)-N(1)-H(13)$		112 (2)
$C(6)-N(2)-O(3)$	117.0 (0.2)	117.2 (0.3)
$C(6)-N(2)-O(6)$	118.2 (0.2)	119.6 (0.3)
$O(3)-N(2)-O(6)$	124.8 (0.2)	123.2 (0.3)
$C(1)-N(3)-O(4)$	118.1 (0.2)	119.1 (0.3)
$C(1)-N(3)-O(5)$	118.6 (0.2)	118.6 (0.3)
$O(4)-N(3)-O(5)$	123.3 (0.2)	122.3 (0.3)
$C(9)-O(1)-H(12)$	111 (2)	100 (5)
$C(9)-O(2)-H(13)$	102 (2)	

The conformation of the nitro groups with respect to the cyclopropane groups

From Fig. 2(c) it can be seen that the oxygen atom $O(5)$ of the $C(1)$ nitro group is pointing towards the

cyclopropane group. The dihedral angles which the nitro group is making with C(8) and C(2) are 23 and 43° respectively for both compounds. This conformation is also found in 6,6-dibromo-2,3:4,5-dimethano-2,4-dinitrocyclohexanone (Stam & Evers, 1965) and a multisubstituted α -hydroxycarboxylic acid (Beintema, 1971).

In the model system nitro-cyclopropane we have calculated the internal rotation barrier with the extended Hückel method (Hoffmann, 1963), using the parameter values of van der Meer (1970). Minimum energy is obtained when one of the oxygen atoms is symmetrically above the cyclopropane ring. Rotation of the nitro group by 90° gives a barrier height of 15 kcal/mol. It should be noted that the minimum in the energy curve is rather flat.

Bond lengths

Excluding C(6)–N(2) all bond lengths are in agreement with the lengths normally found (Sutton, 1965). The C(6)–N(2) lengths are 1.530 and 1.527 Å for the molecules I and II respectively, whereas the usual value for a C–N bonded to a nitro group is 1.48 Å. The C(1)–N(3) bonds are in perfect agreement with this value. Extended Hückel calculations for the two model systems $O_2N-CH_2NH_2$ and $O_2N-CH_2CH_3$ do not provide a clue to this difference.

Hydrogen bonding

Structure I has an intramolecular hydrogen bond O(1)–H...N(1) of 2.798 Å in good agreement with known bonds of the same type (Hamilton & Ibers, 1968). The crystal structure of I is composed of strings of molecules, which generate the twofold screw axis. Successive molecules in a string are connected by O(2)–H...O(1) hydrogen bonds of 2.659 Å (see Table

6 and Fig. 3). The relative positions of different strings are determined by van der Waals forces only (see Table 6).

Table 6. Intermolecular short atom–atom distances

O–H distances are given <2.80 Å, H–H distances <2.55 Å and O–O and O–N distances <3.1 Å.

Molecule I		Equivalent position of atom B			Distance
Atom A	Atom B				
O(1)	O(2)	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	2.66 Å
O(1)	H(13)	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	1.74
O(3)	H(10)	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	2.67
O(4)	H(6)	$-x$	$-\frac{1}{2}+y$	$-z$	2.70
O(5)	H(5)	$-x$	$2-y$	$-z$	2.72
H(10)	H(11)	$1-x$	$1-y$	$-z$	2.51
H(12)	H(13)	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	2.39
Molecule II					
O(1)	O(6)	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.02 Å
O(1)	H(13)	x	$1+y$	z	2.34
O(3)	H(13)	$1+x$	y	z	2.67
O(3)	H(9)	$1+x$	y	z	2.73
O(4)	H(3)	$1-x$	$2-y$	$1-z$	2.68
O(5)	H(5)	$1-x$	$2-y$	$1-z$	2.73
O(6)	H(11)	x	$-1+y$	z	2.78
O(6)	H(4)	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	2.49
O(6)	H(12)	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	2.27
N(1)	O(3)	$-1+x$	y	z	3.13
N(1)	H(12)	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	2.58
H(3)	H(6)	x	$1+y$	z	2.43
H(8)	H(8)	$-x$	$1-y$	$1-z$	2.36

In structure II no intramolecular hydrogen bond appears, and only two weak intermolecular hydrogen bonds are present. Molecules related by the screw axis are connected by an O(2)–H...O(6) hydrogen bond of 3.016 Å. Within these strings of molecules a second hydrogen bond N(1)–H(13)...O(1) of 3.131 Å connects molecules which are related by the translation **b**. In an X-axis projection (Fig. 4) the hydrogen bonding is indicated.

The differences in hydrogen bonding between both structures is reflected in the melting points, which are 196–198°C for I and 165–166°C for II.

The authors thank Professor C. H. MacGillavry and Dr C. H. Stam for critical reading of the manuscript, Professor Th. J. de Boer and Mr K. van Velzen

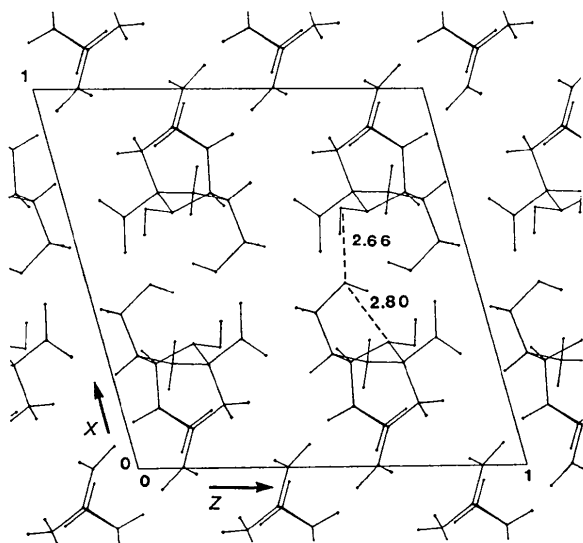


Fig. 3. *b* axis projection of structure I. The hydrogen bonds are indicated by dashed lines.

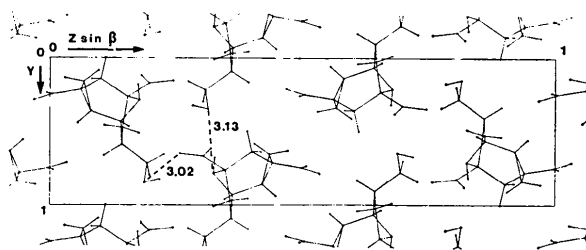


Fig. 4. *a* axis projection of structure II. Hydrogen bonds are indicated by dashed lines.

for providing the samples and Mr D. Heijdenrijk for his valuable assistance in the X-ray experiments.

References

- BEINTEMA, J. (1971). Private communication.
 BENCI, P., STAM, C. H. & MACGILLAVRY, C. H. (1971). *Tetrahedron Letters*. In the press.
 CRUICKSHANK, D. W. J. (1961). *Computing Methods and the Phase Problem*, p. 45. New York: Pergamon Press.
 HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonds in Solids*. New York: Benjamin.
 HOFFMANN, R. (1963). *J. Chem. Phys.* **39**, 1397.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
 MEER, H. VAN DER (1970). *Mol. Phys.* **18**, 401.
 SCHENK, H. (1969). *Automation of the Symbolic Addition Method*. Amsterdam-London: North Holland Publishing Company.
 SCHENK, H., MACGILLAVRY, C. H., SKOLNIK, S. & LAAN, J. (1967). *Acta Cryst.* **23**, 423.
 STAM, C. H. & EVERS, H. (1965). *Rec. Trav. chim. Pays-Bas*, **84**, 1496.
 SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. London: The Chemical Society.
 VELZEN, J. C. VAN, KRUK, C. & DE BOER, TH. J. (1971). *Rec. Trav. chim. Pays-Bas*. In the press.
 VELZEN, J. C. VAN, KRUK, C., SPAARGAREN, K. & DE BOER, TH. J. (1971). *Rec. Trav. chim. Pays-Bas*. To be published.
 VISSER, J. W., MANASSEN, J. & DE VRIES, J. L. (1954). *Acta Cryst.* **7**, 288.
 VOOREN, M., SCHENK, H. & MACGILLAVRY, C. H., (1970). *Acta Cryst.* **B26**, 1483.

Acta Cryst. (1972). **B28**, 543

Bestimmung der Wirtsstruktur von 1,4-Dichlorbutan-Harnstoff, ein Beitrag zur Bestätigung eines allgemeinen Bauprinzips für die Einschlussverbindungen des Harnstoffs und des Thioharnstoffs

VON J. OTTO

Kristallographisches Institut der Universität, 3550 Marburg, Deutschland

(Eingegangen am 25. Februar 1970 und wiedereingereicht am 25. Mai 1971)

Hermann's general structure principle of addition compounds of urea and thiourea is applied to the structures of 18 adducts with the chemical composition $X \cdot (CH_2)_n \cdot X$ -urea with $X = CH_2Cl, CH_2Br, CH_2OH$ and $COOH$. Twelve of these compounds – especially the derivatives with dialcohols – crystallize in the normal hexagonal type, while the structures of two compounds with dicarboxylic acids are not based on the ordinary structure principle. The derivatives with 1,4-dichlorobutane, 1,5-dichloropentane, 1,6-dichlorohexane and 1,6-dibromohexane possess approximately the orthorhombic cell of the ordinary hexagonal type. Hermann's principle allows exactly two host structure forms to have this cell: one, originating from the ordinary hexagonal type of rhombic deformation and a new structure with a different channel type, which has been found by structure determination of the host structure of 1,4-dichlorobutane-urea; 1,5-dichloropentane-urea and 1,6-dibromohexane-urea seem to have the same host structure. For 1,6-dichlorohexane-urea the present material permits no decision between the two possible host structure forms.

1. Einleitung

(a) *Beschreibung der normalen Wirtsstruktur-Formen in den Einschlussverbindungen des Harnstoffs und des Thioharnstoffs*

Die Aufklärung der normalen, d.h. am weitesten häufigsten gefundenen Wirtsstruktur-Form in den Harnstoff-Einschlussverbindungen durch C. Hermann (zit. in Schlenk, 1949) und auf anderem Wege durch Smith (1952) ergab, dass sich die Harnstoffmoleküle darin in Form einer *Bienenwabe* mit regelmässigen, sechskantigen, prismatischen Kanälen anordnen. Das Gleiche wurde auch für die bisher stets gefundene Wirtsstruktur der Thioharnstoff-Einschlussverbindungen festgestellt (Hermann & Renninger, 1950; Lenné, 1954).

Fig. 1 zeigt eine grob schematische Darstellung dieser Wirtsstruktur-Form. Die kurzen Striche sollen darin die Projektion der den Kanalwänden angenähert parallelen, ebenen Harnstoff- bzw. Thioharnstoffmoleküle auf eine zu den Kanalachsen senkrechte Ebene (Zeichenebene) andeuten. Die Kanalwände sind in Fig. 2 dargestellt. Man sieht, sie sind ebenfalls prinzipiell gleich gebaut.

Die normale Harnstoff-Wirtsstruktur besitzt eine der beiden enantiomorphen Raumgruppen $P6_122$ oder $P6_522$, die Thioharnstoff-Wirtsstruktur $R\bar{3}c$. Die primitive Elementarzelle ist sonach beim Harnstoff hexagonal und beim Thioharnstoff rhomboedrisch. Beide Wirtsstrukturen haben dreizählige Schraubenachsen in den Kanalkanten, beim Harnstoff mit gleichem Schrau-