Structure of 1,4-Dinitroglycoluril

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Abstract. 1,4-Dinitrotetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione, $C_4H_4N_6O_6$, $M_r = 232 \cdot 1$, triclinic, $P\bar{1}$, $a = 6 \cdot 392$ (5), $b = 6 \cdot 984$ (5), $c = 9 \cdot 228$ (6) Å, $\alpha = 103 \cdot 38$ (6), $\beta = 101 \cdot 57$ (6), $\gamma = 96 \cdot 64$ (6)°, $V = 386 \cdot 9$ (6) Å^3, $Z = 2$, $D_m = 1 \cdot 940$, $D_x = 1 \cdot 992$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 1 \cdot 749$ cm^{-1}, $F(000) = 236$, room temperature, $R = 0 \cdot 042$ for 721 unique diffractometer data with $I > 2\sigma(I)$. The molecule is made of two planes linked at a CH–CH bond; the angle between the two planes is 117·9°. The nitro substituents are in *exo* position. The regioisomerism and conformations are indicative of the mechanism of nitration of glycoluril. The molecule is chiral; the unit cell contains pairs of 'face-to-face' enantiomers. One-half of each molecule participates in an antiparallel stack mode of packing which involves no strong H bonding while the other half participates in H bonds which link adjacent stacks: $N(3)\cdots O(21) = 2 \cdot 914$ (6) Å; $N(6)\cdots O(12) = 3 \cdot 042$ (6) Å.

Introduction. Dinitroglycoluril was prepared as early as 1888 by Franchimont & Klobbie (1888, 1889). Nitro derivatives of glycoluril have recently attracted renewed interest because tetranitroglycoluril (sorguyl)* has proved to be one of the most powerful modern explosives (Boileau, Emeury & Kehren, 1975).

Dinitroglycoluril is prepared by nitration of glycoluril with nitric acid (Boileau, Emeury & Kehren, 1975), and sorguyl by reaction of dinitroglycoluril with nitric acid (HNO$_3$, N$_2$O$_5$); but so far trinitroglycoluril has not been prepared. To better understand this reactivity of glycoluril toward the nitration reaction,

and to be able to prepare new derivatives in the series, we have carried out the following structure determination.

Experimental. Crystal (0·07 × 0·1 × 0·4 mm), grown from concentrated nitric acid, mounted on a CAD-4 Enraf–Nonius diffractometer (graphite monochromator for Mo $K\alpha$). Unit-cell parameters refined by least squares on (sinθ)/λ values for 25 reflections (16 < θ < 18°). Density obtained by flotation. Intensities measured using ω–2θ scan of 0·91 to 10·06° min^{-1}, range $\Delta\omega = (0 \cdot 9 + 0 \cdot 35\tan\theta)$°, $\theta_{max} = 23$°. Intensities of three standard reflections measured every 10 000 s, remained constant within ±0·3%. 1075 unique reflections and 721 with $I > 2\sigma(I)$ used in structure determination; h: from 0 to −7; k: from −7 to 7; l: from −9 to 9.

All computations performed on a PDP 11/44 computer, *SDP* software (Frenz, 1978). Structure solved by direct methods: *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) and completed by difference Fourier methods. H atoms introduced at idealized positions in the calculation before last refinement cycles but not refined. Full-matrix least-squares refinement included anisotropic thermal parameters for non-H atoms, and minimized function $\sum w(|F_o| - |F_c|)^2$, $w = 1$. Final refinements converged with $R = 0 \cdot 042$ ($wR = 0 \cdot 051$); $S = 0 \cdot 928$; $(\Delta/\sigma)_{max} = 0 \cdot 02$. A final difference Fourier synthesis did not reveal any peak of density > 0·25 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

One of the authors (RG, Naval Research Laboratory) performed an independent X-ray diffraction analysis on a considerably smaller crystal (0·025 × 0·11 × 0·19 mm) which was much weaker in scat-

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* This compound was named after the place (Sorgues) where it was first prepared in a factory of the company SNPE (Société Nationale des Poudres et Explosifs).

tering power. Except for the use of a Nicolet $R3$ automatic diffractometer, the experimental conditions, method of structure solution, and refinement techniques were essentially identical. The numerical results of that analysis, which are slightly lower in precision, are not reported here. The discussions resulting from the two analyses have been combined in this article. Atomic parameters are given in Table 1; bond distances and bond angles in Table 2.*

Discussion. A stereoview of 1,4-dinitroglycoluril (DINGU) (Johnson, 1965) and the numbering scheme are given in Fig. 1.

The molecule consists of two planes connected at the C(7)—C(8) bond. The dihedral angle between the two planes is 117·9°. There are three possible isomers for a dinitroamino derivative of this ring system, with (1,3), (1,4) and (1,6) substitution patterns. In Fig. 1, the nitro substituents are located in positions 1 and 4; this is a confirmation of the assignment made by spectroscopy of the regioisomerism in nitration of glycoluril by nitric acid. Whereas each half of the heterocycle is almost planar, the nitro substituents directly bonded to the ring onto N atoms 1 and 4, are in *exo* position (bent away from the concave side of the bicyclo system by a dihedral angle of ∼7°).

The skeleton of the molecule compares well with that of glycoluril (Blessing & De Titta, 1986) and of 7,8-dimethylglycoluril (Himes, Hubbard, Mighell & Fatiadi, 1978) (Table 3).

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* Lists of anisotropic thermal parameters, torsional angles, bond distances to H, least-square planes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44596 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
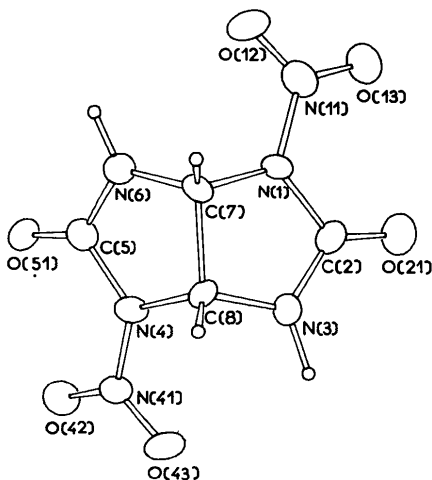

Fig. 1. *ORTEP* (Johnson, 1965) plot for DINGU showing the atom-numbering scheme.

Table 1. *Positional parameters and their e.s.d.'s*

$$B_{eq} = \tfrac{4}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$$

	x	y	z	$B_{eq}(\text{Å}^2)$
N(3)	0·3191 (9)	0·3768 (8)	0·0959 (6)	2·1 (1)
C(2)	0·489 (1)	0·2819 (9)	0·1062 (7)	1·9 (1)
O(21)	0·6415 (7)	0·2965 (7)	0·0496 (5)	2·3 (1)
N(1)	0·4516 (8)	0·1515 (8)	0·2010 (6)	2·0 (1)
N(11)	0·5844 (9)	0·0243 (8)	0·2414 (6)	2·0 (1)
O(12)	0·5193 (7)	−0·0769 (7)	0·3211 (5)	2·7 (1)
O(13)	0·7527 (7)	0·0230 (7)	0·2016 (5)	2·9 (1)
C(7)	0·246 (1)	0·1564 (9)	0·2479 (7)	1·7 (1)
N(6)	0·2735 (9)	0·2297 (8)	0·4107 (6)	2·1 (1)
C(5)	0·239 (1)	0·419 (1)	0·4587 (7)	1·8 (1)
O(51)	0·2493 (8)	0·5129 (7)	0·5879 (5)	2·8 (1)
N(4)	0·1909 (9)	0·4849 (7)	0·3247 (6)	2·2 (1)
N(41)	0·1184 (9)	0·6616 (8)	0·3135 (7)	2·3 (1)
O(42)	0·1342 (8)	0·7881 (7)	0·4328 (6)	3·2 (1)
O(43)	0·0504 (8)	0·6729 (7)	0·1831 (5)	2·8 (1)
C(8)	0·165 (1)	0·3308 (9)	0·1820 (7)	1·9 (1)
H(C7)	0·1557	0·0255	0·2151	4*
H(C8)	0·0000	0·2929	0·1113	4*
H(N6)	0·2910	0·1250	0·4707	4*
H(N3)	0·2910	0·4570	0·0273	4*

* Starred atoms were not refined.

Table 2. *Interatomic distances (Å) and angles (°) in DINGU*

Values reported in the left and right columns are related by a non-crystallographic molecular twofold symmetry axis.

N(1)—C(7)	1·468 (9)	N(4)—C(8)	1·462 (7)
N(1)—C(2)	1·434 (10)	N(4)—C(5)	1·405 (9)
C(2)—N(3)	1·336 (9)	C(5)—N(6)	1·353 (9)
N(3)—C(8)	1·435 (9)	N(6)—C(7)	1·437 (8)
C(2)—O(21)	1·198 (9)	C(5)—O(51)	1·205 (8)
N(1)—N(11)	1·360 (8)	N(4)—N(41)	1·386 (8)
N(11)—O(12)	1·229 (9)	N(41)—O(42)	1·220 (7)
N(11)—O(13)	1·205 (8)	N(41)—O(43)	1·218 (8)
C(7)—C(8)	1·574 (9)		

C(7)—N(1)—C(2)	114·2 (5)	C(8)—N(4)—C(5)	114·9 (5)
N(1)—C(2)—N(3)	104·8 (6)	N(4)—C(5)—N(6)	105·0 (5)
C(2)—N(3)—C(8)	116·0 (6)	C(5)—N(6)—C(7)	115·1 (6)
N(3)—C(8)—C(7)	104·3 (5)	N(6)—C(7)—C(8)	104·1 (5)
C(8)—C(7)—N(1)	100·2 (5)	C(7)—C(8)—N(4)	100·1 (5)
C(7)—N(1)—N(11)	120·6 (6)	C(8)—N(4)—N(41)	117·2 (6)
C(2)—N(1)—N(11)	125·2 (6)	C(5)—N(4)—N(41)	126·2 (5)
O(12)—N(11)—O(13)	126·0 (6)	O(42)—N(41)—O(43)	127·7 (6)
N(1)—N(11)—O(12)	114·5 (6)	N(4)—N(41)—O(42)	117·2 (6)
N(1)—N(11)—O(13)	119·4 (6)	N(4)—N(41)—O(43)	115·0 (5)
N(1)—C(2)—O(21)	125·8 (6)	N(4)—C(5)—O(51)	127·2 (6)
N(3)—C(2)—O(21)	129·4 (7)	N(6)—C(5)—O(51)	127·9 (7)

Table 3. *Comparison of bond distances (Å) in glycoluril derivatives*

	1,4-Dinitro-glycoluril	Glycoluril†	7,8-Dimethyl-glycoluril‡
C(7)—C(8)	1·574 (9)	1·562 (3)	1·581 (3)
C(8)—N(H) and C(7)—N(H)	1·436 (1)*	1·442 (2)*	1·440 (2)*
C(CO)—N(H)	1·344 (8)*	1·347 (4)*	1·338 (2)*
C=O	1·201 (4)*	1·244 (1)*	1·237 (3)*

* Mean value.
† Blessing & De Titta (1986).
‡ Himes, Hubbard, Mighell & Fatiadi (1978).

On the other hand, the introduction of a nitro group in position 1 increases the N(1)—C(2) bond length much more than the N(1)—C(7) bond length; the corresponding distances in glycoluril and in DINGU are: N(1)—C(2) 1·347 and 1·434; N(1)—C(7) 1·442 and 1·468 Å. This is easily understood because C(2) and C(7) are respectively sp^2 and sp^3 hybridized; therefore there is some double-bond character between N(1) and C(2) which does not exist between N(1) and C(7), and consequently the bond N(1)—C(7) requires more energy to lengthen. The decrease in double-bond character of C(2)—N(1) (bond-length increase) is correlated to an increase in the double-bond character of C(2)=O(21) (bond shortening from 1·244 to 1·198 Å going from glycoluril to 1,4-dinitroglycoluril).

The nitramine (N—NO$_2$) in 1,4-dinitroglycoluril may be compared with the same functional group in HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine or octogen), with respect to the N—N distance, and to the dihedral angle δ between NNO$_2$ and the heterocyclic framework (Fig. 2). The N—N distance in 1,4-dini-troglycoluril is 1·37 Å, which compares well with the same distance in α- and β-HMX (Cady, Larson & Cromer, 1963; Choi & Prince, 1972). On the other hand, the dihedral angle δ in DINGU is notably smaller than in HMX (~7 vs 15°); this may come from the possibility of conjugation of the nitro group with the cyclic urea, as well as from differences in steric repulsions within each molecule. Further studies are needed to better understand this behavior and the synthesis of other isomers by a new method, using acylation followed by nitrolysis (or nitration), is in progress (Boileau, Wimmer, Carail & Gallo, 1986).

DINGU possesses an approximate twofold symmetry axis passing through the center of the C(7)—C(8) bond and bisecting the dihedral angle of the two rings. This symmetry axis is not crystallographic, and the packing environment differs about each half. The differences in bond distances and angles related to the pseudo-twofold axis are not greater than might be expected from experimental error; however, the torsion angles, which are more easily deformed by packing forces, do show significant deviations from twofold symmetry. The largest differences are 11·0° for the C(2)—N(1)—N(11)—O(12)/C(5)—N(4)—N(41)—O(43) pair, 10·7° for C(2)—N(1)—N(11)—O(13)/C(5)—N(4)—N(41)—O(42) and 8·9° for O(21)—C(2)—N(1)—N(11)/O(51)—C(5)—N(4)—N(41). When there is a difference, the torsions on the N(1)—C(2)—N(3) side of the molecule tend more towards planar (0, 180°) values while those on the other side deviate from planarity. The 'planar' side is involved in a pair of strong H bonds, while the other is packed in an antiparallel stack (see below).

Packing (Fig. 3)

The molecule of glycoluril is chiral. The crystal contains pairs of 'face-to-face' enantiomers. Moreover, there is a symmetrically related pair of H bonds linking the carbonyl group C(2)=O(21) of the reference molecule to the amino N(3)—H(N3) of the molecule at $(1-x, -y, 2-z)$ and *vice versa*. This centrosymmetric pair of H bonds straddles a center at $(\frac{1}{2},0,1)$ and, of course, at lattice-related centers. The N(3)···O(21) distance is 2·914 (6) Å and the H(N3)···O(21) distance is 2·04 Å.

There are also several close contacts between the reference molecule and the molecule related by the symmetry operation $(1-x, -y, 1-z)$. The carbonyl C(5)=O(51) is directed toward the side of the C(2)=O(21) carbonyl in the symmetry-related molecule, with an O(51)···C(2) distance of 2·915 (7) Å. This distance is less than the sum of the usual van der Waals radii (3·1 Å). In addition, the C(5)=O(51) carbonyls of the two molecules are stacked in an
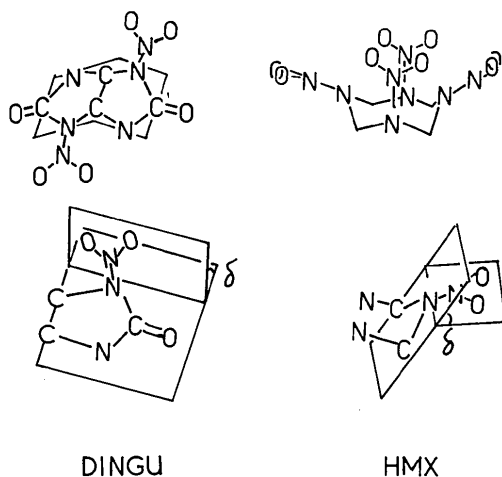

DINGU   HMX

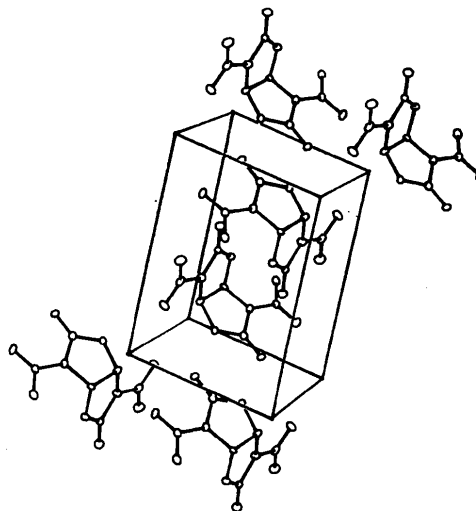Fig. 2. Dihedral angle δ in DINGU and HMX.

Fig. 3. Packing diagram showing pairs of 'face-to-face' enantiomers.

electrostatically favorable anti-parallel fashion with C(5)···O(51) non-bonded contacts of 3·172 (7) Å.

In other directions, the only contacts less than van der Waals contacts are between O and H atoms. The amino H(N6) atom, a potential H-bond donor, approaches the nitro O(12) atom $(1-x, 1-y, 1-z)$, at a distance of 2·33 Å; this is significantly shorter than the O···H van der Waals distance (2·6 Å), but it would be considered a very weak hydrogen bond. Other close approaches are: carbonyl O(21) to H(C8) $(x-1, y, z)$, 2·25 Å; nitro O(13) to H(C7) $(x-1, y, z)$ 2·55 Å; nitro O(43) to H(C7) $(x, y-1, z)$ 2·41 Å; and nitro O(42) to H(N6) $(x, y-1, z)$ 2·37 Å.

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Structure of (5S)-9(10→5)abeo-1-Estrene-3,10,17-trione

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Abstract. $C_{18}H_{22}O_3$, $M_r = 286·37$, monoclinic, $P2_1$, $a = 11·337$ (1), $b = 6·436$ (1), $c = 11·751$ (2) Å, $\beta = 112·98$ (1)°, $V = 789·4$ (2) Å^3, $Z = 2$, $D_x = 1·205$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·753$ cm^{-1}, $F(000) = 308$, $T = 291$ K, $R = 0·0421$ for 972 observed reflections. The title compound is a synthetic steroid and exhibits a 9(10→5)abeo skeleton; the carbon at position 5 becomes a spiro center with absolute configuration S.

Introduction. Treatment of the quinol (1) (Bieri, Prewo, Briansó & Piniella, 1985) under acidic conditions (p-toluenesulfonic acid) affords the title compound (2) (72% yield) as described by Planas, Tomas & Bonet (1987). Its structure could not be solved by means of spectroscopic and analytical information. The present X-ray structure determination was undertaken to determine unambiguously the connectivity of the molecule and to confirm the absolute configuration at C5 which was assumed to be S according to the proposed reaction mechanism.
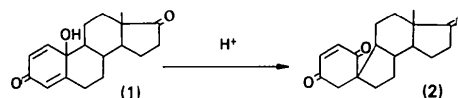
Experimental. Pale-yellow crystals obtained by slow evaporation from an acetone/petroleum ether solution. Parallelepiped crystal with dimensions 0·29 × 0·23 × 0·13 mm. Lattice parameters refined from 25 reflections in the range 5 < 2θ < 20°. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation. 1516 independent reflections with (sinθ)/$\lambda \leq 0·592$ Å^{-1}, $-12 \leq h \leq 12$, $0 \leq k \leq 7$, $0 \leq l \leq 13$, 972 with $I \geq 2·5\sigma(I)$. One standard reflection checked every 50 measurements; no significant deviation.