

Fig. 4. Side-by-side views of (a) 6-*epi*-eriolanin and (b) dehydroeriolanin (Bryan & Gilmore, 1975). The lactone rings and atoms C(6) and C(9) have been oriented similarly by a least-squares fitting procedure. Note that the 6-methacrylate chains are oriented axially on both epimers but in opposite directions *vis à vis* the common lactone-ring orientations.

directs the C(6) methacrylate group to the pseudo-axial position. In this study we again observe a 1,4-diplanar cyclohexene ring conformation; however, in this case the form is *exo*; *i.e.* C(5)=C(10) is directed away from the lactone ring. This ring flip causes the methacrylate group to assume again the pseudo-axial position. Side views of 6-*epi*-eriolanin and DE are shown in Fig. 4. The views were constructed by orienting the 6-*epi*-eriolanin molecule in such a way as to emphasize the *exo* conformation of the bicyclic ring and show the disposition of the side groups at C(6), C(5), and C(10) relative to it. The view of DE was derived from that of 6-EE by a least-squares fitting of the lactone ring and atoms C(13), C(6), C(9) of DE to the corresponding atoms of 6-EE.

Inspection of Fig. 4 indicates that epimerization at C(6) has occasioned a rather dramatic conformational isomerization of the sesquiterpene lactone ring system,

with an attendant relocation of biologically important functional groups at C(5) and C(10) *vis à vis* a fixed lactone position. It explains the difficulty in the interpretation of the PMR spectrum of 6-EE in the H(6) area since epimerization did not affect the coupling of H(6) as expected. Modeling indicates that the isomerization upon epimerization is due to crowding by the C(13) methylene and C(15) methyl which would result if epimerization were to occur without isomerization.

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cis-[1,2;3,4;5,6]-Triiminocyclohexane (*cis*-Benzene-Trisimine)

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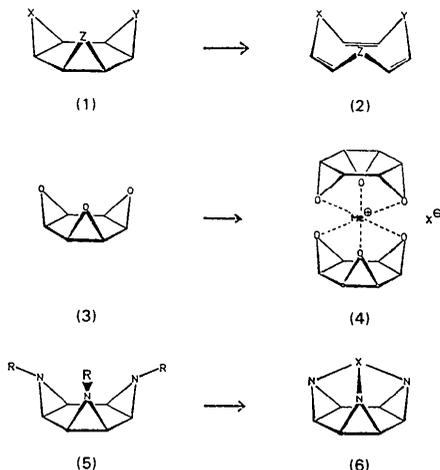
Abstract. C₆H₉N₃, *M_r* = 123.18, monoclinic, *P*2₁/*c*, *a* = 8.561 (5), *b* = 10.656 (4), *c* = 6.569 (5) Å, β = 107.70 (3)°, *V* = 570.89 (16) Å³, *Z* = 4, *D_m* = 1.44 (1), *D_c* = 1.43 Mg m⁻³. λ(Mo *K*α) = 0.71073 Å,

μ(Mo *K*α) = 0.1017 mm⁻¹, *F*(000) = 264. The structure was solved by the symbolic-addition procedure and refined to *R* = 0.040 for the 1665 observed reflexions. The molecule is asymmetric, the three aziridine rings show an outward tilt. The six-membered ring is nearly planar. Two of the three amino protons show strong

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intramolecular interactions with the free electron pair of the opposite N atom. The molecules form uninterrupted hydrogen-bonded linear chains along the [010] axis, which are alternatively parallel or antiparallel.

Introduction. The range of interesting theoretical questions presented by the class of tricarbo- and triheterocyclohexane derivatives makes it desirable to have exact structural parameters for the compounds.



Thus for a better interpretation of definite physical (*e.g.* homoconjugation, *n-n* interactions) and chemical properties [*e.g.* conditions for $3\sigma-3\pi$ isomerization [*cf.* (1) \rightarrow (2)] (Prinzbach, 1972), basicity, formation of complexes [*cf.* (3) \rightarrow (4)] (Schwesinger & Prinzbach, 1972; Schwesinger, 1978), bridging reactions [*cf.* (5) \rightarrow (6)]] of these substances we have undertaken a series of X-ray structural analyses. The first example reported recently (Littke & Drück, 1974) gave the structural data for *cis*-[1,2;3,4;5,6]-triepoxycyclohexane (*cis*-benzenetrioxide) [*cf.* (3) (Schwesinger & Prinzbach, 1972; Vogel, Altenbach & Sommerfeld, 1972)]. In the present publication we present the molecular conformation and spatial packing of the title compound (Schwesinger & Prinzbach, 1973).

Suitable single crystals were prepared by recrystallization from ethanol under special conditions (Littke, 1974). Further investigations led to the crystallographic data shown in the *Abstract*. A rhombic-shaped colourless crystal of dimensions $0.55 \times 0.36 \times 0.20$ mm was mounted on an automatic CAD-4 (Enraf-Nonius) diffractometer and the intensities of 3255 symmetry-independent reflexions were measured using monochromatized Mo $K\alpha$ radiation and an $\omega/2\theta$ scan (range: $0.047 \leq \sin \theta/\lambda \leq 1.015 \text{ \AA}^{-1}$). Three control reflexions were recorded after every 20 measurements and showed no crystal decomposition. 1590 reflexions were classified as unobserved ($I \leq 2\sigma I$) and corrections were computed for absorption, Lorentz, polarization and extinction effects using XRAY 72 (Stewart,

Kruger, Ammon, Dickinson & Hall, 1972). The structure factors were scaled by Wilson's (1942) method and converted to normalized structure factors. Reflexion statistics clearly indicated a centrosymmetric crystal structure.

The signs of the phases could be determined by the symbolic-addition procedure (Karle & Karle, 1966) although this method at first presented some difficulties. Thus with the above lower limit of the average probability $P_+(\Sigma_2) = 0.98$ and the use of all normalized structure factors with $|E| > 1.3$ no sensible sets of phases could be found. Varying the origin definition did not help. In fact, expected molecular images or fragments of the same could be discerned but the results were found to be false. Only the increase of the lower *E* value limit to $|E| = 2$, with $P_+(\Sigma_2) = 0.98$, afforded sensible results. This is yet another noteworthy special case (Schenk, 1973), which shows that the symbolic-addition method fails in the frequently occurring space group $P2_1/c$ when *E* values which are too low are included. There is then a large probability that the phases are correct although the solution is false.

The set of phases for the correct solution ($10, 1, \bar{9} \cong +$, $30\bar{6} \cong +$ and $827 \cong +$ were used to fix the origin) finally enabled the determination of 193 phases (91 with positive and 102 with negative signs) and the *E* synthesis based on it led to the location of all C and N atoms. The final isotropic full-matrix least-squares refinement terminated with an *R* value of 0.111 and the subsequent anisotropic sharpening converged with *R* = 0.079. All nine H atoms were located by a difference Fourier synthesis and further refinements (C and N anisotropic, H isotropic, scale refinement, extinction correction) led to the final *R* values: *R* = 0.040, *R_m* = 0.040, *R_w* = 0.039 (weight = 1).

Table 1. Fractional coordinates of the atoms ($\times 10^4$ for non-hydrogen atoms, $\times 10^3$ for H atoms)

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	3698 (1)	5738 (1)	6963 (2)
C(2)	3861 (1)	4329 (1)	7081 (2)
C(3)	2996 (1)	3578 (1)	8334 (2)
C(4)	1982 (1)	4225 (1)	9512 (1)
C(5)	1748 (1)	5626 (1)	9300 (1)
C(6)	2595 (1)	6378 (1)	8016 (2)
N(1)	3005 (1)	4958 (1)	5022 (1)
N(2)	1196 (1)	3398 (1)	7668 (1)
N(3)	825 (1)	6112 (1)	7168 (1)
H(1)	468 (2)	621 (1)	699 (2)
H(2)	494 (1)	399 (1)	714 (2)
H(3)	357 (1)	280 (1)	898 (2)
H(4)	197 (2)	388 (1)	1085 (2)
H(5)	152 (1)	606 (1)	1049 (2)
H(6)	289 (1)	723 (1)	846 (2)
H(7)	191 (2)	490 (1)	479 (2)
H(8)	73 (1)	390 (1)	655 (2)
H(9)	23 (2)	678 (1)	730 (2)

Table 1 contains the final fractional coordinates of all the atoms.*

Discussion. A representation of the molecule is shown in Fig. 1. It is characterized by the following features. The molecule is asymmetric. The two amino protons, H(7) and H(8), point towards the molecular axis, whereas the third, H(9), is orientated outwards. The three aziridine rings *A* [C(1)C(2)N(1)], *B* [C(3)C(4)N(2)] and *C* [C(5)C(6)N(3)] show an outward tilt and the interplanar angles made with the least-squares plane of the cyclohexane ring are *A* = 113.06, *B* = 112.04 and *C* = 103.77°. The six-membered ring formed by C(1)–C(6) is nearly planar. Whereas the positions of C(2), C(3), C(5) and C(6) coincide fairly well with the least-squares plane C(1) and C(4) are both 0.028 Å below the plane. The cyclohexane ring has a slight upward concavity along the C(1)–C(4) axis [angle between the planes C(1)C(2)C(3)C(4) and C(4)C(5)C(6)C(1) = 176.32°]. Three more planes, which are not quite coplanar with the least-squares plane of the six-membered ring, can be observed: one, given by the atoms H(1)–H(6), lies 0.47 Å below (inclination 1.18°), and two others are situated 1.20 Å [N(1)N(2)N(3), inclination 1.70°] and 1.66 Å [H(7)H(8)H(9), inclination 7.47°] above the carbon skeleton. The two protons H(7) and H(8) show strong interactions with the free electron pair of N(3) which points towards the molecular axis. The distances N(1)⋯N(3) (2.930 Å) and N(2)⋯N(3) (2.916 Å) are thus markedly shortened compared with distance N(1)⋯N(2) (3.134 Å). The values are smaller than the expected van der Waals distance (3.0 Å). The H–N interaction is obvious from the aforementioned interplanar angles of the aziridine rings: N(3) is pulled towards N(2) and N(1) and the interplanar angle of ring *C* is decreased to 103.77°. The question whether this is a case of an extremely rare three-centre hydrogen bond we want to leave unanswered, because it is a matter of definition whether or not bent H-bonds [in this case N(1)–H(7)–N(3) = 116.31, N(2)–H(8)–

N(3) = 116.31°] can be regarded as such. The distance between H(7) and H(8) is 2.055 Å. This is well within the limit of the theoretical van der Waals distance (2.4 Å). The repulsive forces therefore widen the bond angles C(2)–N(1)–H(7) and C(3)–N(2)–H(8) to 108.96 and 109.02°, respectively, and the net effect is to increase the deviation, already mentioned, from the ideal molecular symmetry. The mechanical strain is passed on to the carbon skeleton, which responds by atoms C(1) and C(4) lying a little below the ideal hexagonal plane, thus slightly puckering the cyclohexane ring along the C(1)–C(4) axis.

Intramolecular bond lengths and angles are given in Fig. 2 and Table 2.

In contrast to *cis*-benzene-trioxide (Littke & Drück, 1974) the bond lengths of bridged and unbridged C atoms in *cis*-benzene-trisimine do not show a systematic alternation. The mean value is 1.500 Å which

Table 2. Bond angles in *cis*-benzene-trisimine with standard deviations in parentheses (°)

C(6)–C(1)–C(2)	119.50 (0.13)	H(1)–C(1)–C(2)	116.6 (1.0)
C(1)–C(2)–C(3)	120.52 (0.13)	H(1)–C(1)–C(6)	114.5 (1.1)
C(2)–C(3)–C(4)	120.02 (0.12)	H(2)–C(2)–C(1)	115.8 (1.0)
C(3)–C(4)–C(5)	119.38 (0.12)	H(2)–C(2)–C(3)	113.6 (1.0)
C(4)–C(5)–C(6)	120.52 (0.12)	H(3)–C(3)–C(4)	117.0 (1.1)
C(5)–C(6)–C(1)	119.85 (0.11)	H(3)–C(3)–C(2)	114.5 (1.1)
		H(4)–C(4)–C(3)	118.0 (1.1)
C(1)–N(1)–C(2)	60.93 (0.10)	H(4)–C(4)–C(5)	115.1 (1.1)
C(3)–N(2)–C(4)	60.59 (0.09)	H(5)–C(5)–C(6)	116.2 (1.0)
C(5)–N(3)–C(6)	61.13 (0.09)	H(5)–C(5)–C(4)	116.7 (1.0)
		H(6)–C(6)–C(5)	117.6 (1.1)
		H(6)–C(6)–C(1)	115.0 (1.1)
N(1)–C(1)–C(2)	59.59 (0.09)	H(1)–C(1)–N(1)	115.2 (1.0)
N(1)–C(2)–C(1)	59.49 (0.09)	H(2)–C(2)–N(1)	113.6 (0.9)
N(2)–C(3)–C(4)	59.79 (0.09)	H(3)–C(3)–N(2)	111.3 (1.0)
N(2)–C(4)–C(3)	59.62 (0.09)	H(4)–C(4)–N(2)	113.5 (1.0)
N(3)–C(5)–C(6)	59.37 (0.09)	H(5)–C(5)–N(3)	114.5 (0.9)
N(3)–C(6)–C(5)	59.50 (0.09)	H(6)–C(6)–N(3)	116.2 (1.0)
C(6)–C(1)–N(1)	120.61 (0.11)	H(7)–N(1)–C(1)	107.4 (1.1)
C(3)–C(2)–N(1)	123.55 (0.11)	H(7)–N(1)–C(2)	109.0 (1.1)
C(2)–C(3)–N(2)	123.43 (0.11)	H(8)–N(2)–C(3)	109.0 (1.1)
C(5)–C(4)–N(2)	119.86 (0.10)	H(8)–N(2)–C(4)	106.5 (1.0)
C(4)–C(5)–N(3)	116.94 (0.10)	H(9)–N(3)–C(5)	109.8 (1.0)
C(1)–C(6)–N(3)	117.31 (0.11)	H(9)–N(3)–C(6)	110.6 (1.0)

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34375 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

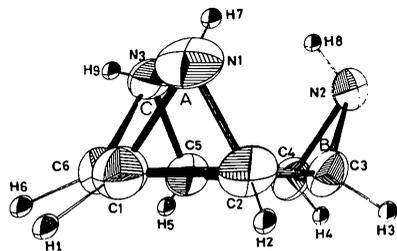


Fig. 1. Molecule of C₆H₉N₃. Thermal ellipsoids of the non-hydrogen atoms are scaled to the 50% probability level.

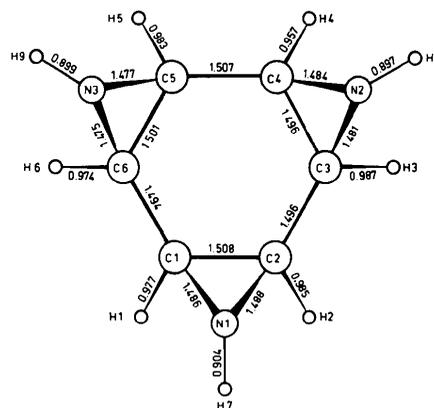


Fig. 2. Bond lengths (Å) of *cis*-benzene-trisimine. The average standard deviation for bonds between non-hydrogen atoms is 0.002 Å and for bonds involving H atoms, 0.017 Å.

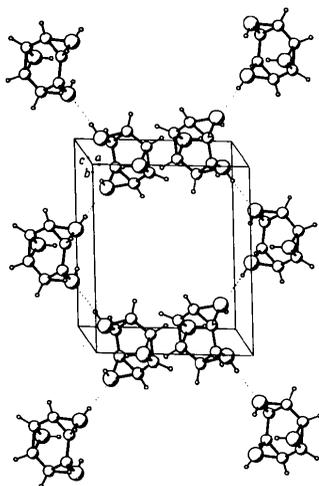


Fig. 3. Molecular packing in the crystal. For clarity only half of the molecules are presented.

approaches the expected value (1.48 Å) for an sp^2 – sp^2 C–C single bond. The H atoms H(1)–H(6), with the exception of H(5), are shifted by an average of 1.98° sideways, i.e. away from the corresponding aziridine ring. The structural parameters of *cis*-benzene-trisimine and aziridine do not show the very good agreement found between *cis*-benzene-trioxide and ethylene oxide.

The principle of spatial packing also discloses some interesting features: the outward-oriented protons [H(9)] of the molecules interact with the lone electron pairs on N(1') and N(2') of the neighbouring molecules, thereby forming uninterrupted linear chains along the [010] axis which are alternatively parallel or antiparallel depending on whether N(1') or N(2') is participating in the chain. The distances between the

intermolecular bridgehead atoms N(3)–N(1') and N(3)–N(2') (3.012 Å), as well as the flattened bond angle N–H–N of 174.78° , indicate classical H-bonds. Between the single linear strands, van der Waals interactions operate, so that the mean distance of the two 'back-to-back' oriented molecules is 3.77 Å with respect to their C atoms. The mode of the molecular packing and hydrogen bonds is given in Fig. 3.

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Chlorure de Cytidinium

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Abstract. $C_9H_{14}N_3O_5^+ \cdot Cl^-$, orthorhombic, $P2_12_1$, $a = 11.00$ (1), $b = 16.304$ (7), $c = 6.648$ (4) Å, $V = 1192.5$ Å³, $Z = 4$, $\rho_x = 1.557$ Mg m⁻³, $\rho_{exp} = 1.55$ (1) Mg m⁻³. The structure was solved by direct methods and refined by least-squares calculations with anisotropic temperature factors to $R = 0.028$. The conformation of the nucleoside about the glycosidic bond is *anti* [$\chi_{CN} = 45.7$ (4)^o]; the ribose ring is C(2')-*endo* and the conformation about C(4')–C(5') is *gauche-gauche*.

Introduction. L'évaporation lente d'une solution de chlorure de fer(II) et de cytidine (rapport 1/1; pH = 6) conduit à l'obtention de beaux monocristaux de chlorure de cytidinium.

Les intensités diffractées ont été collectées à l'aide d'un diffractomètre automatique CAD-4 Enraf–Nonius (radiation Mo $K\alpha$). 1206 réflexions, dont l'intensité satisfaisait à $I \geq 3\sigma(I)$, ont été retenues pour la détermination structurale (2106 réflexions mesurées).

La structure a été résolue par les méthodes directes à