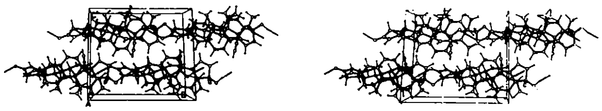

Fig. 3. Stereo packing diagram, viewed down **a**. Hydrogen bonds are indicated.

the *trans* and *gauche* ethyl-group conformers. This is supported by our molecular-mechanics calculations. Both conformers may be found in solution. At the receptor site the ethyl group can adjust itself to its most favourable orientation.

Fig. 3 shows the molecular packing in a stereoview down **a**. The steroid molecules are hydrogen bonded head to tail forming two symmetrically independent chains parallel to **b** for both molecules I and II given by: O(17)→O(3′) (x, $1+y$, z) with distances $O\cdots O' = 2{\cdot}903\,(4)$ and $2{\cdot}840\,(4)$, $O—H = 0{\cdot}97\,(4)$ and $1{\cdot}04\,(2)$, $H\cdots O' = 1{\cdot}95\,(4)$ and $1{\cdot}94\,(4)$ Å and angles $O—H\cdots O' = 167\,(3)$ and $174\,(3)°$ respectively. The torsion angle C(16)—C(17)—O(17)—H is different for the two molecules, 17 (2)° for I and 73 (3)° for II. All other intermolecular contacts are at normal van der Waals separations.

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References

Allinger, N. C. & Flanagan, H. L. (1983). *J. Comput. Chem.* **4**, 399–403.

Duax, W. L. (1986). 10th Eur. Crystallogr. Meet., Wroclaw, Poland. Collected Abstracts, pp. 30–31.

Duax, W. L., Fronckowiak, M. D., Griffin, J. F. & Rohrer, D. C. (1982). In *Intramolecular Dynamics*, edited by J. Jortner & B. Pullman, pp. 508–524. Dordrecht: Reidel.

Geerestein, V. J. van, Duisenberg, A. J. M., Duitz, M. H. G., Kanters, J. A. & Kroon, J. (1987). *Acta Cryst.* C**43**, 2402–2405.

Geerestein, V. J. van, Kanters, J. A. & Kroon, J. (1987). *Acta Cryst.* C**43**, 2398–2401.

Griffin, J. F., Duax, W. L. & Weeks, C. M. (1984). *Atlas of Steroid Structure*, Vol. II. New York: IFI/Plenum.

Losert, W., Casals-Stenzel, J. & Buse, M. (1985). *Arzneim.-Forsch.* **35**, 459–471.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS*86. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

Spek, A. L. (1982). In *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1988). C**44**, 332–334

Structure of (1α,2α,4α,6α)-3,7-Dibenzoyl-3,7-diazatricyclo[4.1.0.0^{2,4}]heptane

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Abstract. $C_{19}H_{16}N_2O_2$, $M_r = 304{\cdot}35$, orthorhombic, $P2_12_12_1$, $a = 21{\cdot}150\,(3)$, $b = 11{\cdot}666\,(2)$, $c = 12{\cdot}633\,(2)$ Å, $V = 3117{\cdot}0\,(9)$ Å^3, $Z = 8$, $D_x = 1{\cdot}30$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 6{\cdot}03$ cm^{-1}, $F(000) = 1280$, room temperature, $R = 0{\cdot}0968$ for 1296 reflections with $I > 2{\cdot}5\sigma(I)$. The molecule exists in an *exo, endo* modification having two non-equivalent aziridine N atoms. The central five-membered ring is planar, and the two three-membered rings are *cis* to each other.

Introduction. The stereochemical analysis of a *cis*-diaziridinocyclopentane derivative has been recently carried out (Majchrzak, Kotełko & Lambert, 1983) by means of ^{1}H and ^{13}C NMR and IR spectra. The authors report that the molecule exists in an *exo, endo* modification which might be the first known example of the interconversion of two diastereotopic amine NH groups within the same molecule.

The present X-ray structure determination was undertaken to ascertain the stereochemistry at both N atoms, and provide X-ray evidence for the structure of the molecule.

Experimental. Colourless crystals from chloroform; crystal dimensions ~0·2 × 0·2 × 0·2 mm. Hilger–Watts Y290 diffractometer; unit-cell dimensions from 12 reflections with $\theta_{\max} = 45{\cdot}1°$; intensity by $\omega/2\theta$ scan technique; total of 2660 reflections recorded to $\sin\theta/\lambda = 0{\cdot}5559$ Å^{-1}; $0 \le h \le 23$, $0 \le k \le 12$, $0 \le l \le$

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13. 1296 non-zero reflections with $I > 2{\cdot}5\sigma(I)$; standard reflections 943 and $9\bar{4}3$, mean variation < 1%; graphite-monochromatized Cu $K\alpha$; no absorption correction; solution by direct methods using *MULTAN*80 (Main *et al.*, 1980), refined (*F* magnitudes) by full-matrix least squares using *SHELX*76 (Sheldrick, 1976); positions of H atoms calculated with $d(\mathrm{C-H}) = 1{\cdot}08$ Å, common isotropic temperature factor for H atoms; final $R = 0{\cdot}0968$, $wR = 0{\cdot}1097$ (the large *R* values result mainly from the very poor quality of the crystals); $w = 0{\cdot}7466/[\sigma^2(F_o) + 0{\cdot}02(F_o)^2]$; maximum $\Delta/\sigma < 0{\cdot}013$ for both positional and thermal parameters; maximum peak on final difference map $0{\cdot}297$ e Å^{-3}; atomic scattering factors from *SHELX*76.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (× 10⁴) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma)$.

	x	y	z	U_{eq}(Å^2)
N1	7579 (3)	1508 (5)	8495 (5)	753
C2	7373 (3)	806 (6)	7628 (5)	673
C3	7866 (3)	329 (6)	6872 (6)	417
N4	8511 (2)	622 (4)	7179 (4)	495
C5	8200 (3)	1295 (5)	6371 (6)	686
C6	7917 (3)	2425 (6)	6784 (6)	790
C7	7392 (3)	2089 (6)	7544 (6)	925
C8	8151 (3)	1624 (6)	9013 (5)	588
O9	8403 (3)	2554 (4)	9082 (4)	578
C10	8407 (3)	593 (6)	9579 (5)	589
C11	8114 (3)	−452 (6)	9568 (6)	852
C12	8373 (4)	−1356 (7)	10104 (6)	971
C13	8930 (5)	−1233 (9)	10659 (7)	1358
C14	9228 (4)	−185 (9)	10687 (8)	848
C15	8977 (4)	735 (7)	10122 (6)	733
C16	8995 (3)	−163 (5)	6942 (5)	499
O17	8890 (2)	−1189 (4)	6971 (4)	953
C18	9622 (3)	319 (5)	6703 (5)	436
C19	10094 (3)	−440 (6)	6399 (5)	702
C20	10690 (3)	−8 (7)	6159 (5)	811
C21	10806 (3)	1163 (7)	6202 (6)	802
C22	10334 (3)	1901 (7)	6507 (7)	575
C23	9744 (3)	1476 (6)	6765 (6)	549

Table 2. *Bond lengths* (Å) *and bond angles* (°)

N1–C2	1·435 (9)	C12–C13	1·378 (14)
C2–C3	1·519 (9)	C13–C14	1·375 (15)
C3–N4	1·458 (7)	C14–C15	1·394 (13)
N4–C5	1·446 (8)	C15–C10	1·396 (10)
C3–C5	1·472 (9)	N4–C16	1·408 (7)
C5–C6	1·539 (9)	C16–O17	1·218 (7)
C6–C7	1·520 (10)	C16–C18	1·472 (8)
C7–N1	1·435 (10)	C18–C19	1·390 (8)
C7–C2	1·501 (10)	C19–C20	1·391 (9)
N1–C8	1·383 (9)	C20–C21	1·389 (12)
C8–O9	1·212 (9)	C21–C22	1·374 (11)
C8–C10	1·501 (9)	C22–C23	1·382 (10)
C10–C11	1·369 (9)	C23–C18	1·377 (9)
C11–C12	1·369 (11)		

N1–C2–C3	118·8 (5)	O9–C8–C10	121·6 (6)
C2–C3–N4	112·8 (5)	C8–C10–C11	123·1 (6)
C3–N4–C5	60·9 (4)	C10–C11–C12	120·0 (7)
C3–N4–C16	118·1 (5)	C11–C12–C13	120·9 (8)
C2–C3–C5	108·6 (5)	C12–C13–C14	119·8 (9)
C3–C5–C6	108·9 (5)	C13–C14–C15	119·8 (9)
N4–C5–C3	60·0 (4)	C14–C15–C10	119·2 (7)
N4–C5–C6	113·7 (6)	C15–C10–C8	116·8 (6)
C5–C3–N4	59·1 (4)	C15–C10–C11	120·1 (6)
C5–C6–C7	106·1 (6)	N4–C16–O17	120·1 (5)
C5–N4–C16	122·3 (5)	N4–C16–C18	116·8 (5)
C6–C7–N1	116·7 (6)	O17–C16–C18	123·1 (5)
C6–C7–C2	108·8 (6)	C16–C18–C19	117·4 (5)
C2–C7–N1	58·5 (4)	C18–C19–C20	118·7 (6)
C7–N1–C2	63·1 (5)	C19–C20–C21	120·5 (7)
C7–C2–C3	107·6 (6)	C20–C21–C22	119·9 (7)
C7–C2–N1	58·5 (5)	C21–C22–C23	119·9 (7)
C2–N1–C8	133·1 (6)	C22–C23–C18	120·5 (6)
C7–N1–C8	126·3 (6)	C23–C18–C16	122·1 (5)
N1–C8–O9	120·4 (6)	C23–C18–C19	120·4 (5)
N1–C8–C10	117·6 (6)		

Discussion. The final atomic coordinates are listed in Table 1,[*] bond lengths and bond angles in Table 2. A view of the molecular structure with the atomic numbering is shown in Fig. 1. The arrangement of molecules in the unit cell is shown in Fig. 2.

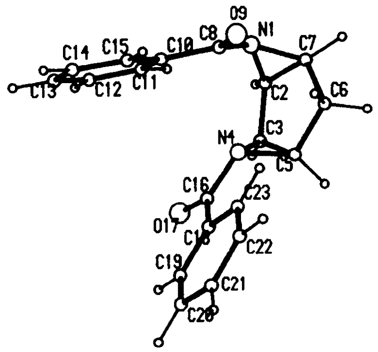

Fig. 1. Molecular structure down the *x* axis showing the atomic numbering scheme.

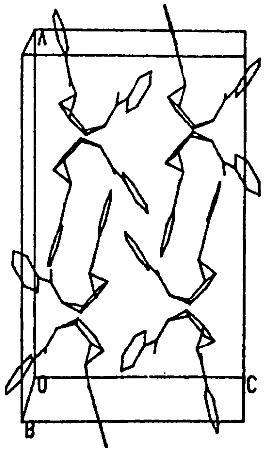

Fig. 2. Arrangement down the *y* axis of the molecules in the unit cell.

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[*] Lists of structure factors and thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44363 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The central five-membered ring is planar, the maximum distance from the best plane being 0·017 (9) Å. The two three-membered rings are *cis* to each other, while the angles formed by them with the central plane differ considerably [107·3 (6) and 111·9 (6)° for N1, C2, C7 and N4, C3, C5 respectively]. In addition the stereochemistry of two N centres is different. The N1—C8 and N4—C16 bonds are inclined at 48·8 (6) and 144·1 (6)° to the planes of the three-membered rings, giving evidence for the *exo,endo* modification of the molecule. Thus, in the crystal, the molecule is not symmetrical. The molecules are linked by van der Waals forces only.

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References

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Majchrzak, M. W., Kotełko, A. & Lambert, J. B. (1983). *Org. Magn. Reson.* **21**, 706–710.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure of Tris(2-hydroxyethyl)ammonium 3,5-Dinitrobenzoate

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Abstract. $C_6H_{16}NO_3^+.C_7H_3N_2O_6^-$, $M_r = 361{\cdot}31$, monoclinic, $P2_1/n$, $a = 12{\cdot}929$ (3), $b = 7{\cdot}160$ (2), $c = 18{\cdot}131$ (4) Å, $\beta = 105{\cdot}55$ (2)°, $V = 1617{\cdot}0$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}484$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 9{\cdot}87$ cm^{-1}, $F(000) = 760$, $T = 298$ K. $R = 0{\cdot}0480$ for 2621 unique observed reflections. In the acid–base complex the H atom of 3,5-dinitrobenzoic acid (DNB) is transferred to the N atom of tris(2-hydroxyethyl)amine (TEA). In the TEA residue, the conformation about the three C—C bonds is *gauche*, causing encapsulation of the transferred H atom. This H atom forms a weak trifurcated *intra*molecular H bond with the terminal O atoms. *Inter*molecular O—H···O hydrogen bonds link screw-axis-related TEA residues into an infinite chain along **b**. The two remaining TEA O—H donors are hydrogen bonded to the O atoms of the carboxyl groups of two DNB residues that are situated on opposite sides of the TEA chain.

Introduction. Several acid–base complexes between phenols and tertiary amines have been investigated in solution and in the solid state by infrared, nuclear quadrupole resonance methods and dipole measurements with the aim of studying the proton transfer of the system O—H···N ←→ O$^-$···H—N$^+$ (Ratajczak & Sobczyk, 1969; Grech, Kalenik, Malarski & Sobczyk, 1983; Zundel & Fritsch, 1984; Huyskens & Zeegers-Huyskens, 1964). According to the Huyskens & Zeegers-Huyskens (1964) model the proton transfer equilibrium constant $K_{\rm PT}$ can be related to the $\Delta {\rm p}K_a$ value *via*

$$\log K_{\rm PT} = c'\Delta {\rm p}K_a + c''$$

where $\Delta {\rm p}K_a$ is the difference of the acid dissociation constants of the base and the acid, and c' and c'' are constants depending on the chosen series of complexes and the environment respectively. Only a few structure determinations have been performed on these types of complexes consisting of a proton donor and a proton acceptor. Clearly, there are two types of such complexes, depending on whether the H bond is *inter*- or *intra*molecular. In the complex pentachlorophenol–aniline (van Bellingen, Germain, Piret & Van Meerssche, 1971) the acidic proton is transferred to the base with the formation of an *inter*molecular N$^+$—N···O$^-$H bond. In the complexes of triethanolamine (TEA) with 2-(methylphenoxy)acetic acid (Starova, Frank-Kamenetskaya, Fundamenskii, Semenova & Voronkov, 1981) and 4-chlorophenylthioacetic acid (Shklover, Gridunova, Struchkov, Voronkov, Kryukova & Mirskova, 1983) the N—H$^+$ group is involved in weak *intra*molecular H-bond interactions with the O atoms of

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