

## Structure and Absolute Configuration of *N*-*tert*-Butyl-1-methyl-3,3-diphenylpropylamine (Terodiline) Hydrochloride, C<sub>20</sub>H<sub>28</sub>N<sup>+</sup>.Cl<sup>-</sup>

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**Abstract.**  $M_r = 317.9$ , orthorhombic,  $P2_12_12_1$ ,  $a = 13.392$  (7),  $b = 15.658$  (9),  $c = 9.127$  (5) Å,  $V = 1913.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.103$  (1),  $D_m$  [flotation in CHCl<sub>3</sub>/C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>] = 1.102 (1) Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.196$  mm<sup>-1</sup>,  $F(000) = 688$ ,  $T = 293$  K, 1657 diffractometer reflections gave a final  $R = 0.040$ . The dihedral angle between the two phenyl planes is 71.5 (4)° and the aliphatic chain is maximally extended. The absolute configuration determined from integrated Weissenberg photographs (Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å) is *S* at the asymmetric C atom. The structure is held together by N–H...Cl hydrogen bonds.

**Introduction.** Terodiline is an anticholinergic drug which in addition has calcium antagonistic properties. This combination of two different mechanisms has been suggested to be of clinical value and the drug has shown favourable results in the treatment of patients with urinary bladder instability (Rud, Andersson, Boye & Ulmsten, 1980). The racemic mixture of terodiline has now been separated and we here report the structure and the absolute configuration of the (–) form.

**Experimental.** The title compound was crystallized from an ethanol–diisopropyl ether solution. Systematic absences from Weissenberg diagrams:  $h00$  for  $h$  odd,  $0k0$  for  $k$  odd, and  $00l$  for  $l$  odd. One optically perfect crystal trimmed to an almost perfect sphere (diameter 0.35 mm) mounted about *c* on an automatic diffractometer (Philips Pailred). Graphite-monochromated Mo  $K\alpha$  radiation. All accessible independent reflections up to  $2\theta = 55^\circ$  recorded for the layers  $hk0$  through  $hk11$ . Lattice parameters measured using the  $h00$ ,  $0k0$  and  $00l$  reflections up to  $2\theta = 55^\circ$ . Out of the 2563 reflections recorded, 1657 considered observed [ $I > 3\sigma(I)$ ]. No decrease in the intensities of standard reflections. Lorentz–polarization correction but no absorption correction. Approximately absolute scaling by Wilson statistics. Our own program system (Bergin, 1971) used for data reduction. Structure determined using MULTAN80 (Main *et al.*, 1980). Further calculations performed with the SHELX program system (Sheldrick, 1975). Perspective drawing by the plotting program ORTEP (Johnson, 1970). Computer: Amdahl 470V/7A. Scattering factors with correction for anomalous dispersion from *International Tables for*

*X-ray Crystallography* (1974). *E* map revealed positions of 10 non-hydrogen atoms and subsequent Fourier refinement gave the coordinates of the missing 12 non-hydrogen atoms. Anisotropic least-squares refinement and subsequent difference maps revealed the positions of all 28 H atoms;  $\sum w(\Delta F)^2$  minimized. Introduction of a weighting scheme,  $w = k/[\sigma^2(F) + gF^2]$ , and further refinement of the positional coordinates of all atoms and anisotropic temperature factors of the non-hydrogen atoms gave a final  $wR = 0.039$ . H atoms given a fixed  $U = 0.05$  Å<sup>2</sup> and  $g$  of the weighting scheme was 0.0003. In the final least-squares cycle, including non-hydrogen atoms only, the maximum ratio of the shift to error was 0.06; a final difference Fourier map contained no peak higher than 0.16 e Å<sup>-3</sup>; no corrections for secondary extinction.

For the determination of the absolute configuration the crystal was transferred to an integrating Weissenberg camera where the  $hk1$  layer was recorded using Ni-filtered Cu  $K$  radiation. From densitometer measurements the net intensities were obtained for eight selected Bijvoet pairs and further calculations including Lorentz/polarization corrections gave relative  $F_o$ 's.

**Discussion.** Positional and thermal parameters are listed in Table 1,\* and selected interatomic distances and bond angles uncorrected for thermal motion in Table 2. The 26 C–H distances range between 0.79 (3) and 1.12 (3) Å with a mean value of 0.96 Å whereas the two N–H distances are 0.84 (3) and 0.87 (3) Å. The structure of the terodiline cation with the numbering scheme is shown in Fig. 1. In the phenyl ring C(1)–C(6) the bond lengths involving C(4) are short. Furthermore, this atom deviates 0.012 (5) Å from the least-squares plane. The other phenyl ring is normal with a maximum atomic deviation of 0.005 (4) Å from the best plane. The dihedral angle between the phenyl planes is 71.5 (4)°. The aliphatic chain C(14)–C(15)–N–C(17) is nearly maximally extended, the torsion angles C(7)–C(14)–C(15)–N, C(14)–C(15)–N–

\* Lists of structure factors, anisotropic thermal parameters, fractional coordinates for the H atoms and equations for mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38562 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(17), and C(15)—N—C(17)—C(19) being 177.4 (3), -172.5 (3), and 169.2 (3)° respectively, a conformation found in other diphenylpropylamines (Zanotti, Rueda & Del Pra, 1977; Zanotti, Valle & Del Pra, 1978). In this part of the molecule one angle, C(15)—N—C(17), which should be tetrahedral, is exceptionally large [123.9 (2)°]. This is certainly due to the crowded situation at the methyl groups of C(16) and C(20). Here H(16)A and H(20)B are only 1.84 (4) Å apart, which is less than the sum of the van der Waals radii.

From the calculated  $F(hk1)$  and  $F(\bar{h}k1)$  for Cu  $K\alpha$  radiation eight Bijvoet pairs exhibiting large effects of anomalous scattering by the Cl<sup>-</sup> ion were selected. Table 3 shows that the absolute configuration of the (-) form of terodiline corresponds to the atomic coordinates given in Table 1 and to the perspective drawing in Fig. 1. The configuration around the asymmetric carbon atom C(1) [here labelled C(15)] is *S* according to the sequence rule (Cahn & Ingold, 1951).

The crystal structure seen along *c* is shown in Fig. 2. The molecules are held together by infinite N—H...Cl hydrogen bonds along screw axes in the *c* direction. The geometries of the two hydrogen bonds are N...Cl(*x*, *y*, *z*) = 3.128 (2) and N...Cl(1.5 - *x*, -*y*, 0.5 + *z*) = 3.234 (2) Å, with N—H(N)A...Cl and N—H(N)B...Cl angles of 175 (2) and 167 (2)° respectively. In addition there is a C—H...Cl interaction; the distance between the hydrogen atom H(14)B and Cl(1.5 - *x*, -*y*, 0.5 + *z*) is only 2.67 (2) Å which is less than the sum of the van der Waals radii. The C(14)—H(14)B...Cl angle is 146 (2)°. There are no intermolecular distances violating ordinary packing requirements.

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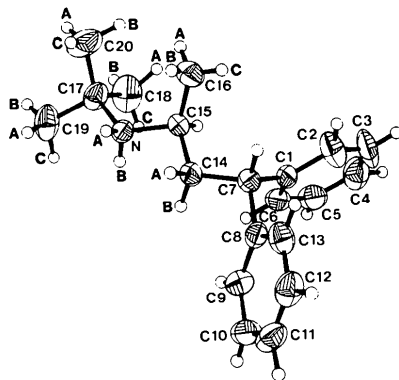


Fig. 1. Perspective drawing of the terodiline cation with the numbering of the atoms. Thermal ellipsoids are drawn at the 50% probability level. The figure shows the absolute configuration of the molecule.

Table 1. Coordinates for non-hydrogen atoms ( $\times 10^4$ ), with *e.s.d.*'s in parentheses, and equivalent isotropic temperature factors ( $\text{Å}^2 \times 10^3$ )

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
Cl	8530 (1)	-118 (1)	622 (1)	56 (1)
N	8586 (2)	340 (2)	3957 (2)	37 (1)
C(1)	7623 (2)	3008 (2)	4883 (3)	39 (2)
C(2)	8112 (3)	3782 (2)	5046 (4)	66 (2)
C(3)	8120 (4)	4194 (2)	6426 (5)	84 (3)
C(4)	7644 (3)	3844 (3)	7588 (4)	68 (3)
C(5)	7185 (3)	3080 (3)	7434 (4)	60 (2)
C(6)	7169 (2)	2661 (2)	6097 (3)	45 (2)
C(7)	7571 (2)	2604 (2)	3370 (3)	39 (2)
C(8)	6579 (2)	2822 (2)	2626 (3)	40 (2)
C(9)	5686 (2)	2451 (2)	3075 (3)	34 (2)
C(10)	4797 (3)	2656 (3)	2379 (4)	58 (2)
C(11)	4783 (3)	3240 (3)	1249 (3)	60 (2)
C(12)	5666 (3)	3609 (2)	801 (4)	61 (2)
C(13)	6544 (3)	3406 (2)	1494 (3)	51 (2)
C(14)	7721 (2)	1630 (2)	3353 (3)	38 (2)
C(15)	8669 (2)	1299 (2)	4076 (3)	37 (2)
C(16)	9608 (3)	1642 (2)	3408 (5)	65 (2)
C(17)	9304 (3)	-283 (2)	4689 (3)	51 (2)
C(18)	9384 (3)	-53 (3)	6300 (3)	77 (3)
C(19)	8814 (3)	-1147 (2)	4515 (4)	66 (2)
C(20)	10314 (3)	-284 (3)	3888 (6)	87 (3)

Table 2. Intramolecular bond distances (Å) and angles (°) with estimated standard deviations in parentheses

C(1)—C(2)	1.385 (4)	C(11)—C(12)	1.377 (5)
C(2)—C(3)	1.415 (6)	C(12)—C(13)	1.373 (4)
C(3)—C(4)	1.354 (6)	C(8)—C(13)	1.380 (4)
C(4)—C(5)	1.352 (5)	C(7)—C(14)	1.539 (4)
C(5)—C(6)	1.385 (4)	C(14)—C(15)	1.522 (4)
C(1)—C(6)	1.376 (4)	C(15)—C(16)	1.496 (4)
C(1)—C(7)	1.520 (4)	C(15)—N	1.510 (3)
C(7)—C(8)	1.531 (4)	N—C(17)	1.525 (4)
C(8)—C(9)	1.392 (4)	C(17)—C(18)	1.518 (4)
C(9)—C(10)	1.387 (4)	C(17)—C(19)	1.512 (5)
C(10)—C(11)	1.379 (5)	C(17)—C(20)	1.538 (5)
C(2)—C(1)—C(6)	117.9 (3)	C(9)—C(10)—C(11)	120.5 (3)
C(2)—C(1)—C(7)	118.9 (3)	C(10)—C(11)—C(12)	119.2 (3)
C(6)—C(1)—C(7)	123.1 (2)	C(11)—C(12)—C(13)	120.1 (3)
C(1)—C(2)—C(3)	119.9 (3)	C(8)—C(13)—C(12)	121.8 (3)
C(2)—C(3)—C(4)	120.6 (3)	C(7)—C(14)—C(15)	116.2 (2)
C(3)—C(4)—C(5)	119.4 (3)	C(14)—C(15)—C(16)	113.7 (2)
C(4)—C(5)—C(6)	121.1 (4)	C(14)—C(15)—N	104.2 (2)
C(1)—C(6)—C(5)	121.1 (3)	N—C(15)—C(16)	112.9 (3)
C(1)—C(6)—C(7)	110.5 (2)	C(15)—N—C(17)	123.9 (2)
C(1)—C(7)—C(14)	114.6 (2)	N—C(17)—C(18)	108.5 (3)
C(8)—C(7)—C(14)	109.2 (2)	N—C(17)—C(19)	104.6 (2)
C(7)—C(8)—C(9)	121.5 (2)	N—C(17)—C(20)	110.3 (3)
C(7)—C(8)—C(13)	120.6 (3)	C(18)—C(17)—C(19)	110.1 (3)
C(9)—C(8)—C(13)	117.9 (3)	C(18)—C(17)—C(20)	113.5 (3)
C(8)—C(9)—C(10)	120.4 (3)	C(19)—C(17)—C(20)	109.3 (3)

Table 3. Ratios of calculated and observed structure factors of *hkl* reflections for which the effect of anomalous dispersion is most marked

<i>h k l</i>	$ F_c(hkl) / F_c(\bar{h}k1) $	$ F_o(hkl) / F_o(\bar{h}k1) $
11 2 1	1.12	1.19
8 3 1	0.78	0.75
12 4 1	1.10	1.11
1 5 1	0.84	0.84
12 6 1	0.82	0.77
1 7 1	1.18	1.14
8 8 1	0.83	0.81
1 12 1	1.15	1.14

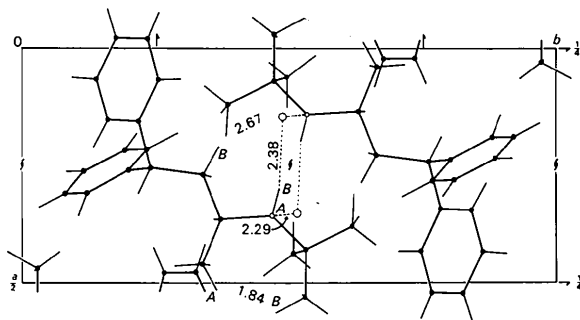


Fig. 2. Molecular packing viewed along *c* showing half of the unit cell. The H...Cl<sup>-</sup> distances of the two N-H...Cl hydrogen bonds are indicated by dashed lines. The short H...Cl<sup>-</sup> contact H(14)B...Cl and the short intramolecular H...H contact H(16)A...H(20)B are indicated by dotted lines. C, N and Cl atoms are represented by small filled, small open, and large open circles respectively. Distances in Å.

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### *N,N'*-Dinitrosopentamethylenetetramine, \*C<sub>5</sub>H<sub>10</sub>N<sub>6</sub>O<sub>2</sub>

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**Abstract.**  $M_r = 186.18$ , monoclinic,  $P2_1/a$ ,  $a = 12.156$  (8),  $b = 7.397$  (5),  $c = 9.923$  (7) Å,  $\beta = 113.8$  (1)°,  $V = 816.38$  Å<sup>3</sup>,  $D_x = 1.515$ ,  $D_m = 1.525$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 392$ ,  $\lambda(\text{Cu } K\alpha) = 1.5418$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Cu } K\alpha) = 1.04$  mm<sup>-1</sup>,  $\mu(\text{Mo } K\alpha) = 0.13$  mm<sup>-1</sup>,  $R = 0.057$  for 955 observed [ $I > 3\sigma(I)$ ] reflexions. The structure comprises discrete molecules with no intermolecular interactions other than van der Waals forces.

**Introduction.** The title compound (Fig. 1) is marketed under the trade-name 'Vulcacer BN' and is used as a blowing agent in the production of microcellular materials, e.g. 'crepe' or 'sponge' rubber. The structural analysis was undertaken to ascertain whether any relationship exists between the nitroso-group dimensions and the ease of evolution of gaseous N and O during processing, and the occasionally observed instability of certain mixes involving the compound.

**Experimental.** Prismatic crystals (m.p. 480 K, decomp.) of the title compound prepared by Dr R. A. Darrall of

\* IUPAC name: 3,7-dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane.

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Imperial Chemical Industries Limited (Organics Division) by reacting hexamethylenetetramine with nitrous acid and recrystallizing the product from absolute ethanol; unit-cell dimensions obtained initially from rotation photographs and more precisely from a least-squares fit of  $2\theta$  angles on a Stoe STADI-2 diffractometer; intensities obtained from multiple-films on Weissenberg layers  $h0l \leftarrow h7l$  and  $hk0$  using filtered Cu radiation, supplemented by  $hk0 \rightarrow hk11$  layers on the diffractometer using graphite-monochromated Mo radiation with  $\omega$  scans; corrections applied for  $L_p$  effects but not for absorption, or extinction; index range  $h\ 0 \rightarrow 14$ ,  $k\ 0 \rightarrow 7$ ,  $l\ -11 \rightarrow 11$ ; structure solved using direct methods in the NRC programs (Ahmed, Hall, Pippy & Huber, 1970) modified for use on the ICL 1905E computer at the London Polytechnics Computer Unit. The  $E$  map resulting from 227 signed  $E$  values ( $E > 1.5$ ) gave all the non-H atoms; parameters refined by least-squares using initially  $B_{\text{iso}}$  and  $\sqrt{w} = 1/F_o$ , and finally  $B_{ij}$ ; calculated H positions included in structure factor calculations with  $B_{\text{iso}} = 5.0$  Å<sup>2</sup>, but not refined; indicated shifts all  $< 0.2\sigma$ ; scattering factors from *International Tables for X-ray Crystallography* (1962);  $R_w = 0.119$ .