

The piperidine ring has a chair conformation, $\Delta C_s(N) = 0.4^\circ$, with torsion angles about the C—C bonds in the range $54.1 - 54.7^\circ$ and those about the C—N bonds a little larger, 58.3 and 58.5° .

The dimethyl sulphoxide molecule is nonplanar, with the S atom displaced 0.72 \AA from the plane through the O and C atoms.

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(S)- α -Methyl-N-(phenylmethyl)benzenepropanamine Hydrochloride [(S)-N-Benzyl-1-methyl-3-phenylpropylamine Hydrochloride]: Determination of Absolute Configuration

BY PETER MURRAY-RUST AND JUDITH MURRAY-RUST

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

AND DAVID HARTLEY AND JIM CLIFTON

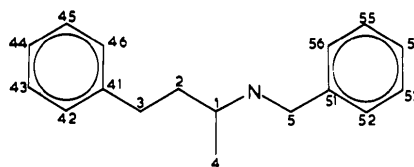
Glaxo Group Research Ltd, Ware, Hertfordshire SG12 0DG, England

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Abstract. $C_{17}H_{22}N^+.Cl^-$, $M_r = 275.82$, monoclinic, $P2_1$, $a = 5.56$ (3), $b = 9.97$ (3), $c = 14.41$ (5) \AA , $\beta = 80.42$ (2) $^\circ$ from diffractometer measurements (Cu $K\alpha$ radiation), $V = 787.8 \text{ \AA}^3$, $Z = 2$, $D_c = 1.16 \text{ Mg m}^{-3}$, $F(000) = 320$, $\mu = 2.023 \text{ mm}^{-1}$, approximate crystal dimensions $0.6 \times 0.5 \times 0.4 \text{ mm}$. Final $R = 0.044$ for 2289 observed reflexions. The absolute configuration is confirmed as *S*.

Introduction. The resolution of racemic 1-methyl-3-phenylpropylamine has been reported on three occasions by Dutch (van Dijk, Keizer & Moed, 1963), Russian (Potapov, Dem'yanovitch & Terent'ev, 1964), and Czech (Cervinka, Kroupova & Belovsky, 1968) workers. The Dutch and Czech groups attempted to establish the absolute configuration of the (+)-enantiomer by degradation to compounds with known absolute configuration but they arrived at opposite conclusions. The Russians, by studying the optical rotatory dispersion curves of (+)-1-methyl-3-phenylpropylamine and its *N*-benzyl derivative, came to the same conclusion as the Dutch group that the (+)-enantiomer has an *S* configuration.

In order to provide unequivocal evidence for this assignment the title compound (I) was prepared from (+)-1-methyl-3-phenylisopropylamine, by reductive alkylation with benzaldehyde in the presence of hydrogen and a platinum-on-carbon catalyst, followed by conversion into the hydrochloride. Recrystallization from ether–methylene chloride provided a crystal suitable for X-ray crystallography, m.p. $459\text{--}460.5 \text{ K}$, $[\alpha]_D^{21^\circ C} = -7.4^\circ$ ($c 5.7 \text{ g dm}^{-3}$, MeOH). [The change in the sign of rotation occurred on forming the hydrochloride in an analogous manner to that observed in converting (+)-1-methyl-3-phenylisopropylamine $\{[\alpha]_D +2.7^\circ$ ($c 9.5 \text{ g dm}^{-3}$ EtOH) $\}$ into (–)-1-methyl-3-phenylpropylamine hydrochloride $\{\text{m.p. } 386\text{--}387 \text{ K}, [\alpha]_D -7.2^\circ$ ($c 5.8 \text{ g dm}^{-3}$, H_2O) (van Dijk *et al.*, 1963)}.



(I)

Systematic absences (from precession photographs) $0k0$, k odd, indicated space group $P2_1$. Data were collected for $0-4kl$ with $\theta_{\max} = 70^\circ$ on a Stoe Stadi-2 two-circle diffractometer (graphite-monochromated Cu $K\alpha$ radiation). This gave 2431 data of which 2289 reflexions with $I > 3\sigma(I)$ were used in subsequent calculations. Lorentz and polarization corrections (but none for extinction or absorption) were applied, and the data scaled by a Wilson plot. The structure was solved by Patterson and Fourier methods with the *SHELX* 76 system of crystallographic programs (Sheldrick, 1976), which was used for all calculations. Complex neutral-atomic scattering factors were taken from

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($U_{eq} \times 10^4$, $U_{iso} \times 10^3$) with *e.s.d.*'s in parentheses

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

	x	y	z	U_{eq} or U_{iso} (\AA^2)
C(1)	-4598 (6)	-2117 (3)	-11420 (2)	426 (20)
C(2)	-4191 (6)	-984 (3)	-12131 (2)	467 (20)
C(3)	-2860 (9)	-1470 (3)	-13086 (2)	758 (30)
C(4)	-6657 (7)	-3052 (3)	-11572 (2)	565 (20)
C(5)	-5303 (6)	-2489 (2)	-9649 (2)	464 (20)
C(41)	-2323 (7)	-369 (3)	-13791 (2)	580 (20)
C(42)	-3657 (8)	-207 (4)	-14494 (2)	704 (30)
C(43)	-3164 (9)	825 (5)	-15149 (2)	811 (30)
C(44)	-1367 (9)	1705 (4)	-15110 (2)	738 (30)
C(45)	19 (8)	1567 (5)	-14418 (3)	881 (40)
C(46)	-443 (9)	544 (5)	-13760 (3)	837 (35)
C(51)	-5778 (5)	-1822 (2)	-8699 (1)	403 (20)
C(52)	-7810 (6)	-1023 (4)	-8431 (2)	546 (20)
C(53)	-8340 (7)	-500 (4)	-7530 (2)	621 (25)
C(54)	-6874 (8)	-795 (4)	-6883 (2)	686 (30)
C(55)	-4807 (9)	-1574 (5)	-7151 (2)	781 (30)
C(56)	-4259 (7)	-2092 (3)	-8055 (2)	581 (25)
N(1)	-5112 (4)	-1496 (2)	-10444 (1)	381 (20)
Cl(1)	-28 (1)	-1000*	-562 (0.4)	448 (5)
H(1A)	-6281 (90)	-3434 (51)	-12217 (30)	95 (14)
H(1B)	-7208 (60)	-3819 (30)	-11107 (19)	55 (7)
H(1C)	-8587 (156)	-2722 (90)	-11403 (48)	144 (22)
H(2A)	-3150 (56)	-2567 (28)	-11402 (18)	44 (7)
H(3A)	-5595 (81)	-509 (38)	-12265 (27)	71 (10)
H(3B)	-3275 (52)	-347 (22)	-11895 (16)	36 (6)
H(4A)	-1466 (173)	-1942 (99)	-12833 (57)	181 (20)
H(4B)	-3684 (114)	-2243 (57)	-13275 (37)	120 (19)
H(5A)	-3608 (78)	-3006 (37)	-9846 (25)	65 (10)
H(5B)	-6715 (59)	-3072 (28)	-9707 (18)	37 (6)
H(42A)	-4944 (77)	-755 (55)	-14514 (26)	90 (14)
H(43A)	-3776 (101)	783 (57)	-15766 (33)	102 (15)
H(44A)	-861 (97)	2344 (51)	-15586 (28)	90 (12)
H(45A)	1337 (154)	2392 (99)	-14320 (50)	170 (20)
H(46A)	122 (147)	457 (91)	-13117 (51)	151 (19)
H(52A)	-8770 (59)	-990 (29)	-8851 (18)	45 (7)
H(53A)	-10186 (83)	-125 (47)	-7248 (26)	68 (11)
H(54A)	-7469 (77)	-458 (36)	-6224 (25)	68 (10)
H(55A)	-3935 (75)	-1633 (41)	-6741 (24)	58 (10)
H(56A)	-2809 (90)	-2701 (53)	-8249 (30)	80 (13)
H(1)	-3949 (81)	-917 (45)	-10376 (27)	71 (11)
H(2)	-6422 (105)	-1026 (56)	-10427 (33)	79 (14)

* Fixed coordinate.

International Tables for X-ray Crystallography (1974). Weighted full-matrix least-squares refinement (including isotropic H atoms) converged at $R = 0.044$ for 2289 observed reflexions; $R_w = 0.049$ $\{R_w = \sum (|F_o| - |F_c| \cdot w^{1/2}) / \sum (|F_o| \cdot w^{1/2})$, $w = 1/[\sigma^2(F_o) + 0.010701F_o^2]\}$. In the final cycle all shifts in parameters were less than their standard deviations. R for the enantiomeric structure at this point was 0.063.

Table 2. Bond distances (\AA) and angles ($^\circ$)

C(1)–C(4)	1.521 (5)	C(43)–C(44)	1.338 (7)
C(1)–C(2)	1.516 (3)	C(44)–C(45)	1.365 (6)
C(1)–N(1)	1.518 (3)	C(45)–C(46)	1.386 (7)
C(2)–C(3)	1.529 (4)	C(51)–C(52)	1.385 (4)
C(3)–C(41)	1.491 (4)	C(51)–C(56)	1.382 (5)
C(5)–C(51)	1.505 (3)	C(52)–C(53)	1.384 (4)
C(5)–N(1)	1.503 (3)	C(53)–C(54)	1.369 (5)
C(41)–C(42)	1.361 (5)	C(54)–C(55)	1.389 (6)
C(41)–C(46)	1.393 (6)	C(55)–C(56)	1.386 (5)
C(42)–C(43)	1.392 (5)		
C(2)–C(1)–C(4)	113.0 (2)	C(46)–C(45)–C(44)	120.7 (4)
N(1)–C(1)–C(4)	110.6 (2)	C(45)–C(46)–C(41)	120.8 (4)
N(1)–C(1)–C(2)	107.8 (2)	C(52)–C(51)–C(5)	121.3 (3)
C(3)–C(2)–C(1)	111.6 (2)	C(56)–C(51)–C(5)	119.4 (2)
C(41)–C(3)–C(2)	113.1 (3)	C(56)–C(51)–C(52)	119.1 (2)
N(1)–C(5)–C(51)	112.4 (2)	C(53)–C(52)–C(51)	121.0 (3)
C(42)–C(41)–C(3)	121.4 (3)	C(54)–C(53)–C(52)	120.0 (3)
C(46)–C(41)–C(3)	121.6 (3)	C(55)–C(54)–C(53)	119.4 (3)
C(46)–C(41)–C(42)	116.9 (3)	C(56)–C(55)–C(54)	120.8 (4)
C(43)–C(42)–C(41)	121.4 (4)	C(55)–C(56)–C(51)	119.7 (3)
C(44)–C(43)–C(42)	121.3 (4)	C(5)–N(1)–C(1)	114.6 (2)
C(45)–C(44)–C(43)	118.8 (4)		

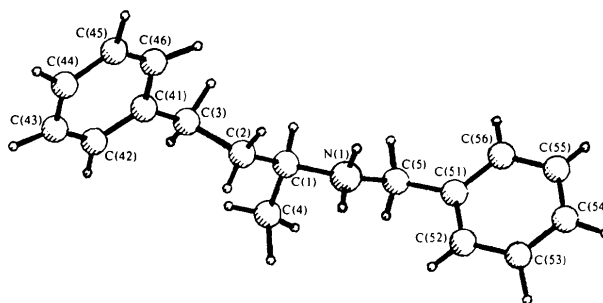


Fig. 1. Perspective view of the molecule.

Table 3. Torsion angles ($^\circ$); *e.s.d.*'s about 0.3 $^\circ$

C(4)–C(1)–C(2)–C(3)	-76.1	C(42)–C(41)–C(46)–C(45)	0.0
N(1)–C(1)–C(2)–C(3)	161.2	C(41)–C(42)–C(43)–C(44)	0.0
C(4)–C(1)–N(1)–C(5)	62.1	C(42)–C(43)–C(44)–C(45)	0.0
C(2)–C(1)–N(1)–C(5)	-173.9	C(43)–C(44)–C(45)–C(46)	0.0
C(1)–C(2)–C(3)–C(41)	-177.2	C(44)–C(45)–C(46)–C(41)	0.0
C(2)–C(3)–C(41)–C(42)	-103.7	C(5)–C(51)–C(52)–C(53)	174.7
C(2)–C(3)–C(41)–C(46)	76.0	C(56)–C(51)–C(52)–C(53)	0.0
N(1)–C(5)–C(51)–C(52)	58.3	C(5)–C(51)–C(56)–C(55)	-174.6
N(1)–C(5)–C(51)–C(56)	-126.6	C(52)–C(51)–C(56)–C(55)	0.0
C(51)–C(5)–N(1)–C(1)	180.0	C(51)–C(52)–C(53)–C(54)	-1.2
C(3)–C(41)–C(42)–C(43)	180.0	C(52)–C(53)–C(54)–C(55)	2.5
C(46)–C(41)–C(42)–C(43)	0.0	C(53)–C(54)–C(55)–C(56)	-2.2
C(3)–C(41)–C(46)–C(45)	180.0	C(54)–C(55)–C(56)–C(51)	0.0

Atomic parameters are given in Table 1 and bond distances and angles in Table 2.*

Discussion. The structure consists of cations and chloride ions held together by two weak hydrogen bonds (N—H...Cl) of 3.15 Å. The absolute configuration is confirmed as *S*. The backbone of the molecule is almost fully extended (Fig. 1 and Table 3) and the maximum deviation from perfect staggering is 17°. The phenyl ring [C(41)] can be seen to be nearly perpendicular to the chain. This structure will be used as a reference for determining the absolute configuration and conformations of pharmacologically active molecules containing a 1-methyl-3-phenylpropylamine moiety and in particular that of the four

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36227 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

enantiomers present in the antihypertensive drug, labetalol [Trandate®] (Brittain, Drew & Levy, 1981).

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Tetramethylenefurazan *N*-Oxide at 125 K

BY MICHAEL J. BARROW.

Department of Chemistry, Edinburgh University, West Mains Road, Edinburgh EH9 3JJ, Scotland

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Abstract. C₆H₈N₂O₂, *M_r* = 140.1, orthorhombic, *Pbca*. At 125 K: *a* = 9.54, *b* = 12.61, *c* = 10.69 Å (e.s.d.'s 0.3% assumed), *U* = 1286.0 Å³, *Z* = 8, *D_c* = 1.45 Mg m⁻³, Cu *K*α radiation (Ni filter), λ = 1.5418 Å, μ(Cu *K*α) = 0.889 mm⁻¹. A partially disordered structure has been refined to *R* = 4.2% using 800 photographic (microdensitometer) intensities. A recent X-ray structure analysis of trimethylenefurazan *N*-oxide [Barnes, Barrow, Harding, Paton, Ashcroft, Crosby & Joyce (1979). *J. Chem. Res. (S)*, pp. 314–315] revealed angle strain in the five-membered carbocyclic ring and an unusually long O(1)–N(2) bond, 1.494 (3) Å, in the furazan ring. The structure of the title compound shows that addition of a further methylene group alleviates the angle strain in the carbocycle and the O(1)–N(2) bond shortens to 1.465 (4) Å.

Introduction. Trimethylenefurazan *N*-oxide (1*a*), which had hitherto been believed unstable, has recently been synthesized and its molecular geometry established by X-ray crystallography (Barnes *et al.*, 1979). The main

structural features of (1*a*) are an unusually long O(1)–N(2) bond, 1.494 (3) Å, and angle strain in the five-membered carbocyclic ring. The O(1)–N(2) distance implies an incipient weakening of this bond and might be related with the observation of thermal decomposition to the bis(nitrile oxide) (2), though the thermolytic ring fission of (1*a*) is not unusually facile (Barnes *et al.*, 1979). The next member in the series, tetramethylenefurazan *N*-oxide, (1*b*), is markedly more resistant to thermal decomposition (Paton, 1981) and was investigated by X-ray crystallography to determine the structural consequences of increasing the size of the carbocyclic ring.

