

Tables for X-ray Crystallography (1974, Vol. IV). Final positional and equivalent isotropic thermal parameters are given in Table 1,* while bond lengths and angles with their e.s.d.'s are given in Table 2. An ORTEP (Johnson, 1976) diagram, Fig. 1, illustrates the numbering scheme used in the analysis. All calculations on a VAX 3600 using Glasgow GX package (Mallinson & Muir, 1985).

Discussion. The imidazole ring is fully protonated, thus forming a zwitterion. The atoms of the imidazole ring are coplanar, within experimental error, with atom C(3) deviating only 0.014 Å from this plane. Valence angles around N(2), C(5) and N(3) are typical of the protonated form, all being close to 109°.

The histidine side chain adopts an 'open' or extended conformation (Kistenmacher & Marsh, 1971) as in crystals of DL-histidine (Bennett, Davidson, Harding & Morelle, 1970) and in the two modifications of L-histidine (Madden, McGandy & Seeman, 1972; Madden, McGandy, Seeman, Harding & Hoy, 1972). This particular conformation is characterized by the large torsion angle, 179.0 (3)°, about the C(2)—C(3) bond, with the imidazole *gauche* only to the amino group and *trans* to the carboxyl. There also appears to be a rotation of the imidazole ring about the C(3)—C(4) bond whereby N(2) is directed away from N(1) with the loss of the stabilizing N(2)⋯H(N1)—N(1) intramolecular hydrogen-bond observed in other histidine structures.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55665 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1013]

An unexpected feature of the molecule is that the acetamidooxobutyl chain is not fully extended, but bends at atom C(10), with a C(9)—C(10)—N(4) bond angle of 114.3 (3)°, so that the acetamido group lies parallel to the imidazole ring. The dihedral angle between the plane of the imidazole ring and the plane of the terminal atoms of the *N*-acetylhomocarnosine chain, N(4), C(11), C(12) and O(4), is 21°. Whether this is a prerequisite for efficient crystal packing or a juxtaposition to accommodate subtle conformational interactions is unclear since neither O(4) nor N(4) appear to interact significantly with other atoms or groups. Bond lengths and angles are in close agreement with values for other histidine molecules (Kistenmacher, Hunt & Marsh, 1972).

There are strong intermolecular hydrogen bonds O(2)⋯N(2) 2.605 (3) Å [O(2)⋯H(N2) 1.62 Å] and O(1)⋯N(3) 2.712 (3) Å [O(1)⋯H(N3) 1.68 Å], subtending hydrogen valence angles of 174 and 167°, respectively. There are also weaker intermolecular hydrogen bonds between O(1) and O(4) and the interstitial water molecule.

References

- BENNETT, I., DAVIDSON, A. G. H., HARDING, M. M. & MORELLE, I. (1970). *Acta Cryst.* **B26**, 1722–1729.
 GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
 JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 KISTENMACHER, T. J., HUNT, D. J. & MARSH, R. E. (1972). *Acta Cryst.* **B28**, 3352–3361.
 KISTENMACHER, T. J. & MARSH, R. E. (1971). *Science*, **172**, 945–946.
 MADDEN, J. J., MCGANDY, E. L. & SEEMAN, N. C. (1972). *Acta Cryst.* **B28**, 2377–2382.
 MADDEN, J. J., MCGANDY, E. L., SEEMAN, N. C., HARDING, M. M. & HOY, A. (1972). *Acta Cryst.* **B28**, 2382–2389.
 MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
 O'DOWD, J. J., CAIRNS, M. T., TRAINOR, M., ROBINS, D. J. & MILLER, D. J. (1990). *J. Neurochem.* **55**, 446–452.

Acta Cryst. (1993). **C49**, 497–500

Structure of 2-Phenyl-2-dehydrosparteine

BY ANDRZEJ KATRUSIAK

Department of Crystal Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

(Received 21 October 1991; accepted 2 September 1992)

Abstract. 1,7,7a,8,9,10,11,13,14,14a-Decahydro-4-phenyl-7,14-methano-2*H*,6*H*-dipyrido[1,2-*a*:1',2'-*e*]-[1,5]diazocine, C₂₁H₂₈N₂, *M_r* = 308.47, monoclinic,

*P*2₁, *a* = 7.570 (1), *b* = 9.4313 (7), *c* = 12.485 (1) Å, β = 102.21 (1)°, *V* = 871.2 (2) Å³, *Z* = 2, *D_x* = 1.176 g cm⁻³, λ(Cu Kα) = 1.54178 Å, μ =

4.86 cm⁻¹, $F(000) = 336$, $T = 292$ K, final $R = 0.037$ for 1242 observed reflections. The quinolizidine moieties (rings *A/B* and *C/D*) both have *trans* configurations, piperidine ring *A* is intermediate between half-chair and sofa, rings *B*, *C* and *D* assume chair, boat and chair conformations, respectively. The phenyl substituent is 46.6° to the plane of the slightly conjugated bond system N(1)—C(2)=C(3). The crystal is isostructural with the crystals of 2-(*p*-tolyl)-2-dehydrosparteine and the conformation of the molecules of these substances is nearly identical; however, significant differences are observed in their densities and stabilities.

Introduction. This X-ray determination of the structure of 2-phenyl-2-dehydrosparteine, hereafter referred to as (I), follows the determination of 2-(*p*-tolyl)-2-dehydrosparteine (II) (Małuszyńska, Boczoń & Kałuski, 1986), $\Delta^{1(2)}$ -dehydro-2-phenylsparteinium diperchlorate (Boczoń, Kałuski & Małuszyńska, 1987) and our previous crystallographic studies on sparteine derivatives (Katrusiak, Figas, Kałuski & Lesiewicz, 1989; Szymczak, 1983). Despite very similar molecular structures for (I) and (II), the stabilities of the crystals of these substances are different. Crystals of (II) were reported to be unstable (Małuszyńska, Boczoń & Kałuski, 1986), while crystals of (I) are stable and no changes in their form could be detected after they were exposed to air for several months. We were also interested in the conformational differences between molecules of (I) and (II), and in the configuration of (I), which could be changed through the possible inversion of N(16).

Experimental. Crystals of (I) suitable for X-ray analysis were obtained from ethanol solution. Colourless elongated plates, crystal dimensions 0.5 × 0.4 × 0.3 mm. Syntex *P*₂ diffractometer, graphite-monochromated Cu *K*α radiation, unit-cell parameters from least-squares fit to 15 reflections (12.0 < 2θ < 49°), 2θ-θ scan method, variable scan speed (2.0–29.3° min⁻¹) depending on reflection intensity. 1437 reflections up to 2θ_{max} = 115° were measured: *h* 0 to 8, *k* 0 to 10, *l* -13 to 13. No systematic variation in intensity was observed for one control reflection monitored every 200 current measurements; Lp corrections. 1242 reflections with $I \geq 1.96\sigma(I)$ were considered observed. The structure was solved by direct methods with *SHELXS86* (Sheldrick, 1986) and the absolute configuration of the molecule was assigned, according to a previous determination of the absolute configuration of naturally occurring sparteine derivatives, as 7*S*,9*S* (Klyne, Scopes, Thomas, Skolik, Gawroński & Wiewiórowski, 1974). The positions of all H atoms were recalculated from the geometry of the molecule after each cycle of refinement, all the H atoms were

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
N(1)	0.0603 (3)	0.2820	0.7624 (2)	0.037
C(2)	0.0040 (4)	0.1907 (4)	0.6723 (2)	0.039
C(3)	-0.1556 (4)	0.1257 (5)	0.6509 (3)	0.049
C(4)	-0.2934 (4)	0.1403 (5)	0.7211 (3)	0.056
C(5)	-0.2547 (4)	0.2745 (5)	0.7894 (3)	0.051
C(6)	-0.0541 (4)	0.2846 (5)	0.8439 (2)	0.044
C(7)	-0.0098 (5)	0.4166 (5)	0.9162 (3)	0.048
C(8)	0.1867 (4)	0.4068 (5)	0.9787 (2)	0.047
C(9)	0.3006 (4)	0.4094 (5)	0.8921 (2)	0.040
C(10)	0.2536 (4)	0.2821 (5)	0.8163 (3)	0.041
C(11)	0.2744 (4)	0.5526 (4)	0.8290 (2)	0.038
C(12)	0.4487 (4)	0.6375 (5)	0.8477 (3)	0.053
C(13)	0.4233 (5)	0.7803 (5)	0.7899 (3)	0.064
C(14)	0.2700 (5)	0.8605 (5)	0.8231 (3)	0.056
C(15)	0.1009 (5)	0.7702 (4)	0.8024 (3)	0.051
N(16)	0.1322 (3)	0.6365 (4)	0.8636 (2)	0.041
C(17)	-0.0362 (4)	0.5558 (5)	0.8504 (3)	0.047
C(18)	0.1277 (4)	0.1727 (4)	0.5938 (2)	0.040
C(19)	0.2088 (4)	0.2869 (5)	0.5533 (3)	0.047
C(20)	0.3169 (5)	0.2658 (5)	0.4770 (3)	0.058
C(21)	0.3457 (5)	0.1304 (5)	0.4425 (3)	0.061
C(22)	0.2646 (5)	0.0163 (5)	0.4811 (3)	0.059
C(23)	0.1572 (5)	0.0367 (5)	0.5568 (2)	0.048

assigned an equal isotropic temperature factor of 0.07 Å². The function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = \sigma^{-2}(F_o)$, final $R = 0.037$, $wR = 0.38$, $S = 3.8$, $(\Delta/\sigma)_{max} = 0.03$, the highest and the lowest peaks on the final ΔF map were 0.11 and -0.14 e Å⁻³. Most of the calculations were performed with *SHELX76* (Sheldrick, 1976), atomic scattering parameters as incorporated in this program, IBM XT Turbo computer. The final atomic parameters are listed in Table 1.*

Discussion. The bond lengths and valency angles are given in Fig. 1. They are in a good agreement with those observed in other sparteine derivatives. Characteristic features are reduction or widening of valency angles [e.g. C(7)—C(8)—C(9) or C(6)—C(7)—C(17)] which reflect the strains in the sparteine skeleton in the region of the fusion of two quinolizidine moieties. A small distortion in the phenyl ring, where only the valency angle C(19)—C(18)—C(23) is smaller than the ideal 120°, is similar to that observed in (II) and 2-phenylsparteine. The lengths of the C(2)—C(3) double bond and the adjacent bonds are the same, within e.s.d.'s, as the corresponding bond lengths in (II). These bond lengths and valency angles do not indicate any significant *p*- π overlap between the free-electron pair of N(1) and the double bond (Allmann, 1977; Allen, Ken-

* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55681 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU0408]

nard, Watson, Brammer, Orpen & Taylor, 1987); the bond length of C(2)=C(3) agrees with the average $C_{sp^2}=C_{sp^2}$ distance of 1.337 Å (Kennard, Watson, Allen, Isaacs, Motherwell, Peterson & Town, 1972); C(2)—C(18) corresponds well with the value of 1.49 Å commonly accepted for the $C_{sp^2}-C_{sp^2}$ single bond.

The torsion angles are given in Fig. 2. No significant differences are observed in the corresponding torsion angles of (I) and (II). The 2,3-didehydropiperidine ring *A* has an intermediate conformation between half-chair and sofa, the asymmetry param-

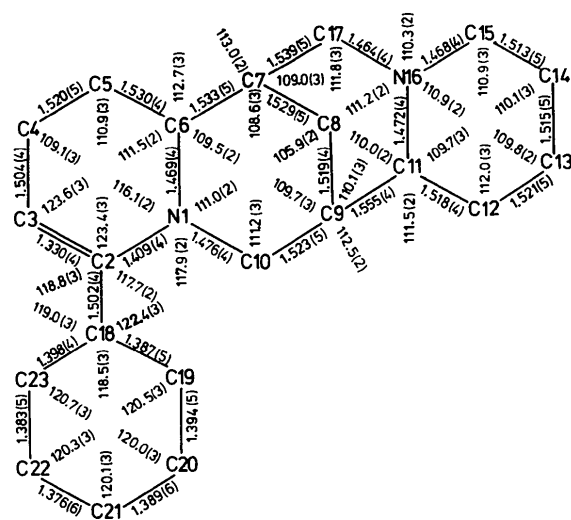


Fig. 1. Bond lengths (Å) and valency angles (°) in 2-phenyl-2-dehydrosparteine.

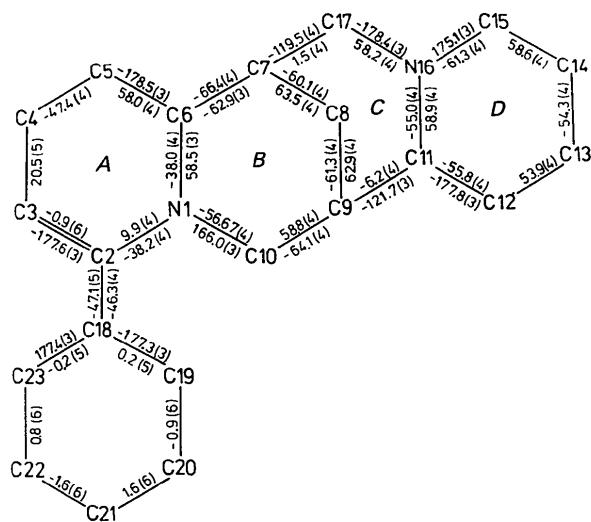


Fig. 2. Torsion angles (°) in 2-phenyl-2-dehydrosparteine. The endocyclic torsion angles are given inside the rings while the exocyclic angles are given outside the molecular contour and are defined by the bonds along the molecule contour; e.g. angle C(5)—C(6)—C(7)—C(17) is $-66.4(4)^\circ$.

eters (Duax & Norton, 1975) calculated for this ring are: $\Delta C_2^{2,3} = 10.0$, $\Delta C_s^2 = 12.9$ and $\Delta C_s^3 = 27.0^\circ$. Rings *B*, *C* and *D* have chair, boat and chair conformations, respectively. The configuration of the quinolizidine moieties [*i.e.* of the N(1)—C(6) junction between rings *A* and *B* and the N(16)—C(11) junction between rings *C* and *D*] is *trans*, *trans*, respectively. This conformation, adopted by the sparteine skeleton, is associated with the intramolecular electrostatic forces between the N atoms. Rings *C* and *D* form a flexible quinolizidine moiety in which ring *C* can assume either a chair conformation (*cis* configuration of the quinolizidine *C/D* rings) or, after inversion of N(16), a boat conformation and the *trans* configuration of the quinolizidine moiety. When ring *C* is present in a chair conformation, the N(1)⋯N(16) intramolecular distance is less than 3.0 Å and the repulsion between the close free-electron pairs of the N atoms is considered responsible for the inversion of N(16) and the boat conformation of ring *C*, actually observed in (I). In lupanine (*i.e.* 2-oxosparteine), despite the involvement of the N(1) free-electron pair in the strongly conjugated bonds of the N(1)—C(2)=O lactam group, ring *C* is still present in a boat conformation (Doucerain, Chiaroni & Riche, 1976); but a chair conformation of ring *C* in $\Delta^{1(6)}$ -dehydrosparteine perchlorate [positive charge on the N(1)⁺=C(6)

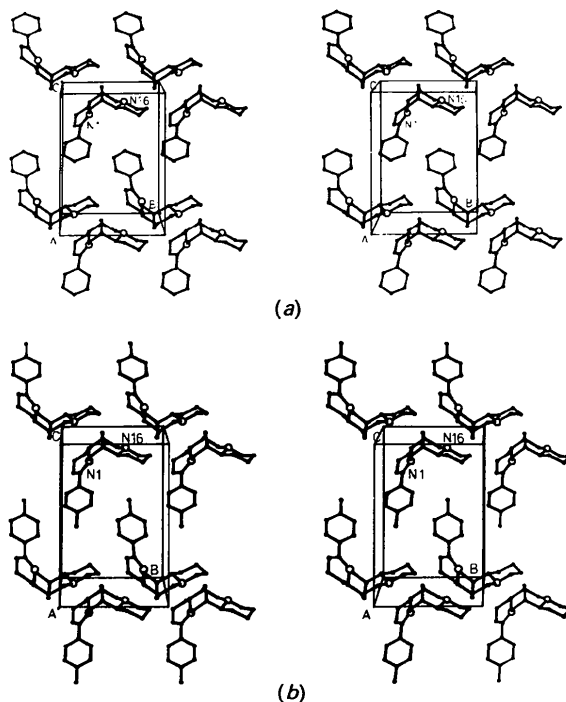


Fig. 3. A *PLUTO* (Motherwell, 1976) stereodiagram of the unit-cell contents along *a* showing the structure of (a) 2-phenyl-2-dehydrosparteine and (b) 2-(*p*-tolyl)-2-dehydrosparteine. H atoms are omitted for clarity.

bond] (Katrusiak, Kałuski, Pietrzak & Skolik, 1986) corroborates the above argument and shows the significance of the intramolecular N...N forces on the conformation of ring C. The inclination angle between the phenyl substituent and the N(1)—C(2)=C(3) group in (I) is only slightly more open than in (II); the relevant torsion angles N(1)—C(2)—C(18)—C(19) and C(3)—C(2)—C(18)—C(23) in (II) are $-43.2(8)$ and $-44.6(9)^\circ$ respectively (compare the corresponding torsion angles in Fig. 2).

As can be seen in Fig. 3, crystals of (I) and (II) are essentially isostructural. This can also be observed by comparing the unit-cell dimensions: parameters *a* are identical, *b* is only slightly longer in (I) than in (II), but *c* is 1.2 Å longer in (II) than in (I), which corresponds to the orientation of the methyl substituent in structure (II) (Fig. 3*b*) [the unit-cell dimensions of (II) are $a = 7.569(3)$, $b = 9.381(1)$, $c = 13.684(4)$ Å, $\beta = 105.81(2)^\circ$ (Małuszyńska, Boczoń & Kałuski, 1986)]. The comparison of structures (I) and (II) gives a volume of 31.2 Å³ for the methyl substituent in (II). This volume is much larger than the volume of 21.5 Å³ given by Kitajgorodski (1976), which was calculated from the molecular-fragment volumes (23.5 Å³ per methyl substituent minus 2.0 Å³ per H atom in an aromatic ring). It is also reflected in the density of crystals of (II) ($D_x = 1.147$ g cm⁻³) which are less dense by over 2.5% than the crystals of (I). It appears that the poor stability of the crystals of (II) (Małuszyńska, Boczoń & Kałuski, 1986) is connected with the less-dense packing of the molecules in that structure. No intermolecular contacts shorter than the sum of the van der Waals radii are observed for the structures of (I) and (II).

We are grateful to Dr Wł. Boczoń for suggesting this study and providing the sample of the title compound.

References

- ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. 1–19.
- ALLMANN, R. (1977). In *Monoatomic Rings, Chains and Macromolecules of Main Group Elements*, edited by A. RHEINGOLD, p. 30. Amsterdam: Elsevier.
- BOCZOŃ, WŁ., KAŁUSKI, Z. & MAŁUSZYŃSKA, H. (1987). *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **35**, 541–550.
- DOUCERAIN, P. H., CHIARONI, A. & RICHE, C. (1976). *Acta Cryst.* **B32**, 3213–3215.
- DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*. New York: Plenum Press.
- KATRUSIAK, A., FIGAS, E., KAŁUSKI, Z. & LESIEWICZ, D. (1989). *Acta Cryst.* **C45**, 1758–1760.
- KATRUSIAK, A., KAŁUSKI, Z., PIETRZAK, P. & SKOLIK, J. (1986). *J. Cryst. Spectrosc. Res.* **16**, 191–206.
- KENNARD, O., WATSON, D. G., ALLEN, F. H., ISAACS, N. W., MOTHERWELL, W. D. S., PETERSON, R. C. & TOWN, W. G. (1972). Editors. *Molecular Structures and Dimensions*, Vol. 41. Utrecht: Oosthoek.
- KITAJGORODSKI, A. I. (1976). *Kryształy Molekularne*, p. 28. Warszawa: PWN.
- KLYNE, W., SCOPES, P. N., THOMAS, R. N., SKOLIK, J., GAWROŃSKI, J. & WIEWIÓROWSKI, M. (1974). *J. Chem. Soc. Perkin Trans. 1*, pp. 2565–2570.
- MAŁUSZYŃSKA, H., BOCZOŃ, WŁ. & KAŁUSKI, Z. (1986). *J. Cryst. Spectrosc. Res.* **16**, 687–694.
- MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for crystal structure determination. Univ. of Göttingen, Germany.
- SZYMCZAK, A. (1983). MSc thesis, Adam Mickiewicz Univ., Poznań, Poland.

Acta Cryst. (1993). **C49**, 500–504

Structure of 1-{4-[2-(Diethylamino)ethoxy]phenyl}-2-(4-methoxyphenyl)-1-phenylethan-1-ol, the Non-Steroidal Antiestrogen MER25

BY M. B. HOSSAIN, J. SYMERSKY, S. C. NEELY AND D. VAN DER HELM

Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, USA

AND R. A. MAGARIAN

Department of Medicinal Chemistry, College of Pharmacy, University of Oklahoma Health Science Center, Oklahoma City, Oklahoma 73190, USA

(Received 24 December 1991; accepted 21 July 1992)

Abstract. C₂₇H₃₃NO₃, $M_r = 419.6$, monoclinic, $P2_1/a$, $a = 22.833(6)$, $b = 9.370(3)$, $c = 11.434(4)$ Å, $\beta = 110.71(8)^\circ$, $V = 2288.2$ Å³, $Z = 4$, $D_x = 1.22$ g cm⁻³,

$\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 5.8$ cm⁻¹, $F(000) = 904$, $T = 138$ K, $R = 0.049$ for 3265 observed reflections. The molecule of MER25 assumes an extended con-