

intermolecular hydrogen bond between the amino N atom N(1) and the carbonyl O atom O(3) [N(1)⋯O(3) = 2.97 (1), O(3)⋯H(1) = 2.16, N(1)—H(1) = 0.85 Å, N(1)—H(1)⋯O(3) = 164°]. This type of hydrogen bond is observed in 4,4'-(3-acetamido-2-phenyl-2-propylidene)bisphenyl diacetate (Précigoux, Hospital, Miquel & Gilbert, 1985). The bond lengths in the acetamide group [N(1)—C(7) = 1.443 (7), N(1)—C(10) = 1.342 (7), C(10)—O(3) = 1.231 (7), C(10)—C(11) = 1.498 (7) Å] are very similar to those found by Précigoux *et al.* (1985). The bond angles around C(7) are in the range 102–113° and are compatible with *sp*³ hybridization.

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Structure of 15-Phenyl-14-dehydrosparteine

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Abstract. C₂₁H₂₈N₂, *M_r* = 308.47, orthorhombic, *P*₂₁₂₁, *a* = 8.959 (1), *b* = 14.137 (1), *c* = 13.934 (1) Å, *V* = 1764.8 (3) Å³, *Z* = 4, *D_x* = 1.161 g cm⁻³, λ(Cu *K*α) = 1.54178 Å, μ = 4.80 cm⁻¹, *F*(000) = 672, *T* = 292 K, final *R* = 0.040 for 1273 observed reflections and 208 refined parameters. The quinolizidine *A/B* and dehydroquinolizidine *C/D* moieties are in *trans* and *cis* configurations, respectively; rings *A*, *B*, *C* are all in chair conformations, ring *D* is intermediate between sofa and half-chair. This conformation of the molecule is stabilized by steric hindrances preventing an inversion of atom N(16). The phenyl substituent is at -32.5 (4)° to the slightly conjugated bond system C(14)=C(15)—N(16).

Introduction. 15-Phenyl-14-dehydrosparteine (I) is an isomer of 2-phenyl-2-dehydrosparteine (II) investigated most recently by spectroscopic and X-ray methods (Boczoń, 1989; Katrusiak, 1992). Other similar derivatives of sparteine investigated by X-rays include 2-(*p*-tolyl)-2-dehydrosparteine (Małuszyńska, Boczoń & Kałuski, 1986) and 2-phenylsparteine (Katrusiak, Figas, Kałuski & Lesiewicz, 1987). In the molecule of (II) the phenyl is substituted at C(2) in the outer ring *A* of the rigid

dehydroquinolizidine fragment *A/B*, with ring *A* in a half-chair and ring *B* in a chair conformation, and the junction between these rings in a *trans* configuration. In (I) the phenyl substituent is at C(15) in the outer ring *D* of the flexible dehydroquinolizidine moiety *C/D*. Owing to the possible inversion of N(16), ring *C* can assume either a chair or a boat conformation, and the junction between rings *C* and *D* can change its configuration subsequently to *cis* or *trans*, respectively. The X-ray structural determination of (II) confirmed the inversion of N(16) leading to the boat conformation of ring *C*, arising from electrostatic repulsion of the electron pairs of the N atoms. It was suggested (Boczoń, 1989) that the substitution of the phenyl ring at C(15) would constitute steric hindrances in the molecule of (I) limiting the possibilities of inversion of N(16). Because of these hindrances, and despite the electrostatic repulsion between N(1) and N(16), it was expected that an inversion of N(16) would not take place and that the molecule would preserve the all-chair conformation. This X-ray study was undertaken to confirm these assumptions.

Experimental. Crystals of (I) suitable for X-ray analysis were obtained from ethanol solution as

colourless bipyramids. A crystal of dimensions $0.40 \times 0.40 \times 0.30$ mm was used for the X-ray measurements, which were carried out on a KUMA diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The unit-cell parameters were determined from least-squares fit to setting angles for 15 reflections ($14 \leq 2\theta \leq 45^\circ$). Intensities were measured *via* the 2θ - θ scan method, with a variable scan speed (2.0 – $29.3^\circ \text{ min}^{-1}$) depending on reflection intensity. 1433 unique reflections were measured up to $2\theta = 115^\circ$; $h 0 \rightarrow 9$, $k 0 \rightarrow 15$, $l 0 \rightarrow 15$. No systematic variation in intensity was observed for one control reflection monitored every 200 current measurements. Only L_p corrections were applied. 1273 reflections with $I \geq 1.96\sigma(I)$ were considered observed. The structure was solved by direct methods with *SHELXS86* (Sheldrick, 1986). The absolute configuration of the molecule was assigned according to the previous determination of the absolute configuration of the naturally occurring sparteine derivatives as *C(7) S* and *C(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 H atoms were assigned a common isotropic temperature factor of 0.07 \AA^2 . The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(F_o)$. 236 parameters were refined. Final $R = 0.040$, $wR = 0.041$, $S = 1.08$, $(\Delta/\sigma)_{\text{max}} = 0.04$. The highest and the lowest peaks on the final ΔF map were 0.12 and -0.14 e \AA^{-3} , respectively. Most of the calculations were performed with *SHELX76* (Sheldrick, 1976), with atomic scattering parameters as incorporated in this program, on an IBM XT computer. The final atomic parameters are listed in Table 1.*

Discussion. Fig. 1 shows the torsion angles in the molecule of (I). Rings *A*, *B* and *C* are in the chair conformation, and ring junction *C/D* is in *cis* configuration; the intramolecular distance $\text{N}(1) \cdots \text{N}(16)$ is $2.932(3) \text{ \AA}$. The considerable electrostatic repulsion between the electron pairs of these N atoms does not lead to the inversion of $\text{N}(16)$ in the flexible dehydroquinolizidine moiety of (I), because steric hindrances between the phenyl ring at $\text{C}(15)$ and methylene $\text{C}(8)$ restrain ring *C* to a chair conformation. The conformation of ring *D* is intermediate between sofa and half-chair and is similar to the conformation of ring *A* in (II). Inclination of the phenyl substituent at $\text{C}(15)$ to the $\text{N}-\text{C}=\text{C}$ frag-

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
N(1)	0.1200 (3)	0.8446 (2)	0.4600 (2)	0.063
C(2)	0.0847 (5)	0.7448 (3)	0.4822 (4)	0.091
C(3)	0.1178 (6)	0.6813 (3)	0.3972 (4)	0.111
C(4)	0.0327 (5)	0.7137 (3)	0.3089 (4)	0.109
C(5)	0.0654 (4)	0.8184 (3)	0.2905 (3)	0.082
C(6)	0.0301 (3)	0.8784 (2)	0.3785 (3)	0.063
C(7)	0.0531 (3)	0.9843 (2)	0.3616 (2)	0.061
C(8)	0.0067 (3)	1.0378 (3)	0.4519 (3)	0.070
C(9)	0.1141 (3)	1.0073 (3)	0.5304 (2)	0.067
C(10)	0.0954 (4)	0.9014 (3)	0.5464 (3)	0.073
C(11)	0.2745 (3)	1.0357 (2)	0.5066 (2)	0.062
C(12)	0.3040 (4)	1.1422 (3)	0.5160 (3)	0.077
C(13)	0.4717 (4)	1.1596 (3)	0.5070 (3)	0.085
C(14)	0.5422 (4)	1.0943 (3)	0.4327 (3)	0.072
C(15)	0.4678 (3)	1.0271 (2)	0.3864 (2)	0.055
N(16)	0.3202 (2)	1.0016 (2)	0.4116 (2)	0.052
C(17)	0.2109 (3)	1.0150 (3)	0.3338 (2)	0.060
C(18)	0.5382 (3)	0.9676 (2)	0.3115 (2)	0.055
C(19)	0.6461 (3)	1.0033 (3)	0.2495 (2)	0.063
C(20)	0.7140 (3)	0.9463 (3)	0.1818 (3)	0.074
C(21)	0.6740 (4)	0.8525 (3)	0.1745 (3)	0.081
C(22)	0.5648 (4)	0.8155 (3)	0.2346 (3)	0.075
C(23)	0.4973 (3)	0.8730 (2)	0.3031 (2)	0.063

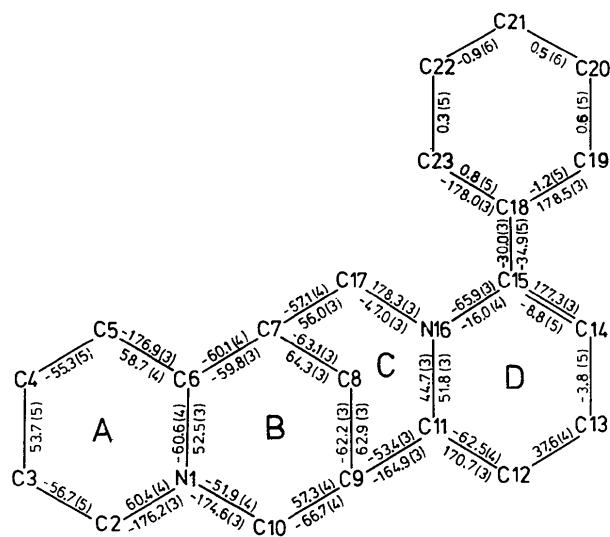


Fig. 1. Torsion angles ($^\circ$) in 15-phenyl-14-dehydrosparteine. The endocyclic torsion angles are given inside the rings while the exocyclic angles are given outside the molecular contour and are defined by the bonds along the outline of the molecule.

ment of ring *D* can be described by the torsion angles along $\text{C}(15)-\text{C}(18)$ (Fig. 1). This inclination is smaller in (I) than in (II): the corresponding torsion angles $\text{N}(1)-\text{C}(2)-\text{C}(18)-\text{C}(19)$ and $\text{C}(3)-\text{C}(2)-\text{C}(18)-\text{C}(23)$ in (II) are $-46.3(4)$ and $-47.1(5)^\circ$, respectively. The bond lengths and valency angles in (I) are given in Fig. 2. The phenyl ring is nearly planar ($\chi^2 = 11.7$), but $\text{C}(15)$ lies markedly out of this plane by $0.042(3) \text{ \AA}$. The distortions in the

* Lists of structure factors, anisotropic thermal parameters, H-atom positions and the best plane for the phenyl ring have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55818 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1008]

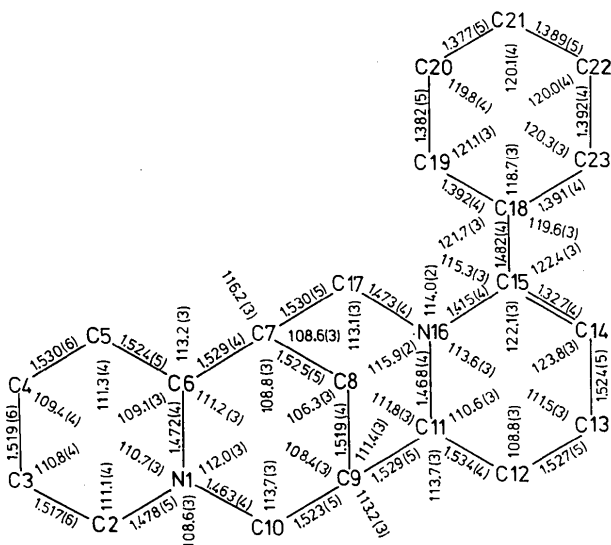


Fig. 2. Bond lengths (Å) and valency angles (°) in 15-phenyl-14-dehydrosparteine.

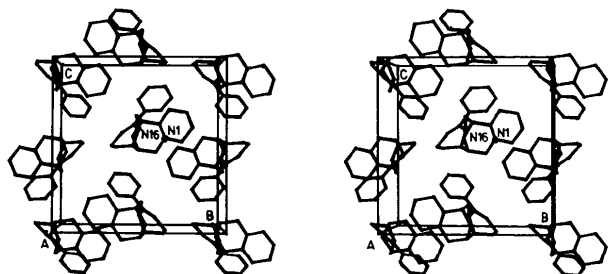


Fig. 3. A stereodiagram of the unit-cell contents along a (*PLUTO*; Motherwell, 1976). H atoms are omitted for clarity.

valency angles of the phenyl ring of (I) are similar to those observed in (II). The only significant difference between the corresponding bonds in (I) and (II) is the length of C(15)—C(18) which is markedly shorter in (I) than the analogous length C(2)—C(18) of 1.502 (4) Å in (II). This shortening of C(15)—C(18) can be correlated with the smaller inclination angle between the phenyl ring and C(14)=C(15), allowing a stronger conjugation between the adjacent bonds. The arrangement of the molecules in the crystal of (I) is presented in Fig. 3. There are no intermolecular contacts shorter than the sums of the van der Waals radii in this structure.

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7-Chloromethyl-12-methylbenz[a]anthracene

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Abstract. C₂₀H₁₅Cl, *M_r* = 290.8, monoclinic, *P*2₁/*c*, *a* = 20.449 (4), *b* = 11.473 (2), *c* = 13.025 (2) Å, β = 108.91 (1)°, *V* = 2890.9 Å³, *Z* = 8, *D_x* = 1.336 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 21.14 cm⁻¹, *F*(000) = 1216, *T* = 294 K, *R* = 0.045, *wR* = 0.049, for 3471 diffractometer data [*I_o* ≥ 3σ(*I*)]. The ring system is puckered as a result of the bulkiness of the 12-methyl group.

Introduction. 7-Chloromethyl-12-methylbenz[a]anthracene (7-CIME-12-MBA) has been found to exhibit both carcinogenic and antitumor activity (Peck, Tan & Peck, 1976), and is more carcinogenic than its non-methylated analog, 7-chloromethylbenz[a]anthracene. The crystal-structure determination of 7-CIME-12-MBA was undertaken in order to obtain reliable atomic parameters so that the structural