Acta Cryst. (1987). C**43**, 1635–1636

The Structure of an Antigelling Agent, L-Lysyl-L-phenylalanyl-L-phenylalanine Dibromide

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(*Received* 26 *August* 1986; *accepted* 2 *February* 1987)

Abstract. $C_{24}H_{34}Br_2N_4O_4$, $M_r = 602{\cdot}4$, monoclinic, $C2$, $a = 21{\cdot}309$ (3), $b = 5{\cdot}091$ (1), $c = 26{\cdot}589$ (3) Å, $\beta = 108{\cdot}78$ (1)°, $V = 2730{\cdot}9$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}465$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 37{\cdot}94$ cm^{-1}, $F(000) = 1232$, $T = 263$ K, $R = 0{\cdot}043$ for 2373 unique observed reflections. The molecule has adopted a compact and amphipathic conformation. Peptide torsion angles: L-Lys1: $\psi = 145{\cdot}4$ (6), $\omega = -178{\cdot}3$ (7), $\omega = -178{\cdot}3$ (6), $\chi^1 = 164{\cdot}0$ (8), $\chi^{2.1} = 174{\cdot}9$ (8), $\chi^{3.1} = 167{\cdot}4$ (9), L-Phe2: $\varphi = -115{\cdot}4$ (7), $\psi = -53{\cdot}5$ (6), $\omega = 170{\cdot}4$ (6), $\chi^1 = 177{\cdot}8$ (8), $\chi^{2.1} = 81{\cdot}7$ (10), L-Phe3: $\varphi = -78{\cdot}8$ (7), $\psi_T^1 = -9{\cdot}2$ (8), $\chi^1 = -71{\cdot}5$ (9), $\chi^{2.1} = -80{\cdot}7$ (11)°. Intramolecular edge-to-face interaction between phenyl rings: phenyl(L-Phe2)—phenyl(L-Phe3) centroid separation = 5·18 (1) Å and dihedral angle = 82·4 (8)°. Intermolecular hydrogen bonds: N(L-Lys1)—H···Br1 = 3·378 (6), N(L-Lys1)—H···Br2 = 3·417 (6), N(L-Lys1)—H···Br2′ = 3·493 (6), Nζ(L-Lys1)—Br1 = 3·335 (7), Nζ(L-Lys1)—Br2 = 3·350 (7), O(L-Phe2)···H—N(L-Phe2′) = 2·923 (9) and OH(L-Phe3)—H···Br1 = 3·164 (7) Å. Intermolecular edge-to-face interactions between phenyl rings: phenyl(L-Phe3)—phenyl(L-Phe3′) centroid separation = 5·03 (1) Å and dihedral angle = 76·5 (8)°, and phenyl(L-Phe3′)—phenyl(L-Phe2) centroid separation = 5·77 (1) Å and dihedral angle = 47·3 (8)°. Finally, the atoms Cγ(L-Lys1), Cδ(L-Lys1), and Cε(L-Lys1) have large temperature factors, and there is evidence in the final difference synthesis of alternate positions for these atoms.

Experimental. Needle-shaped crystal by evaporation from aqueous solution, 0·1 × 0·1 × 0·7 mm, Nicolet $P3$ diffractometer, Ni-filtered radiation, ω-scan method, $(\sin\theta)/\lambda < 0{\cdot}58$ Å^{-1}, lattice parameters from the 2θ values of ten reflections with $33 < 2\theta < 45°$, no absorption correction, $h = -24$ to 24, $k = 0$ to 5, $l = 0$ to 30, three reflections monitored as intensity standards, intensity variation <2%. 2584 unique reflections measured, 211 excluded during refinement [$F < 3\sigma(F)$]. Bromide counter ion positions from Patterson function, other non-H atoms from Fourier syntheses based on phases defined by the two bromide counter ions. Least-squares refinement using *SHELX*76 (Sheldrick, 1976), F magnitudes and unit weights; isotropic and then anisotropic temperature factors gave $R = 0{\cdot}043$ and $S = 2{\cdot}49$ [calculated with $\sigma(F)$] with H atoms at positions calculated or located by difference synthesis. 309 parameters varied: x, y, z, U_{ij} for non-H atoms and a single U for all phenyl-ring H atoms and a single U for all other H atoms. In final cycle $(\Delta/\sigma)_{\max} = 0{\cdot}208$. Final difference synthesis $(\Delta\rho)_{\max} = 0{\cdot}70$ and $(\Delta\rho)_{\min} = -0{\cdot}68$ e Å^{-3}, which correspond to electron density difference peaks consistent with alternate positions for the atoms Cγ(L-Lys1), Cδ(L-Lys1), and Cε(L-Lys1). These alternate positions correspond to variations in the local side-chain torsion angles of approximately 180°. Of the remaining peaks in the final difference synthesis the maximum peak has $\Delta\rho = 0{\cdot}37$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Table 1* gives the atom parameters. Fig. 1 shows the molecular structure and the bromide numbering scheme drawn by *ORTEP*II (Johnson, 1976). The tripeptide numbering scheme is standard for proteins (IUPAC–IUB Commission on Biochemical Nomenclature, 1970).

Related literature. The compound was synthesized according to Gorecki, Votano & Rich (1980). Related structures were reported by Wang & Burley (1987), Burley & Wang (1987), Fujii, Burley & Wang (1987), and Burley (1987). An antigelling mechanism was proposed by Burley, Wang, Votano & Rich (1987). The

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* Lists of structure-factor amplitudes, anisotropic thermal parameters, bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43769 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}(Å^2)
Br1	0·27071 (4)	0	0·17509 (3)	0·058
Br2	0·16982 (4)	0·0254 (4)	0·1217 (3)	0·048
N(*K*1)	0·3408 (3)	0·034 (2)	0·07781 (19)	0·041
C*A*(*K*1)	0·4063 (3)	0·0679 (18)	0·1204 (3)	0·038
C*B*(*K*1)	0·4602 (4)	0·098 (2)	0·0931 (4)	0·071
C*G*(*K*1)	0·5186 (6)	0·057 (4)	0·1163 (6)	0·195
C*D*(*K*1)	0·5691 (6)	0·017 (5)	0·0850 (6)	0·173
C*E*(*K*1)	0·6334 (6)	−0·002 (4)	0·1238 (4)	0·116
N*Z*(*K*1)	0·6879 (3)	0·019 (2)	0·0998 (2)	0·060
C(*K*1)	0·4007 (4)	0·3091 (18)	0·1519 (3)	0·042
O(*K*1)	0·3674 (3)	0·4991 (17)	0·12995 (19)	0·060
N(*F*2)	0·4346 (3)	0·2937 (14)	0·2034 (2)	0·036
C*A*(*F*2)	0·4345 (3)	0·504 (2)	0·2418 (2)	0·037
C*B*(*F*2)	0·4090 (4)	0·3850 (18)	0·2853 (3)	0·044
C*G*(*F*2)	0·4089 (4)	0·5764 (18)	0·3279 (3)	0·047
C*D*1(*F*2)	0·4606 (4)	0·584 (2)	0·3760 (3)	0·063
C*E*1(*F*2)	0·4601 (6)	0·759 (3)	0·4147 (4)	0·086
C*Z*(*F*2)	0·4099 (6)	0·931 (3)	0·4078 (4)	0·092
C*E*2(*F*2)	0·3578 (6)	0·928 (2)	0·3613 (4)	0·084
C*D*2(*F*2)	0·3580 (4)	0·755 (2)	0·3213 (4)	0·059
C(*F*2)	0·5045 (4)	0·6201 (16)	0·2645 (3)	0·038
O(*F*2)	0·5139 (3)	0·8579 (11)	0·2633 (2)	0·041
N(*F*3)	0·5523 (3)	0·4478 (12)	0·2854 (2)	0·036
C*A*(*F*3)	0·6222 (3)	0·525 (3)	0·3009 (2)	0·039
C*B*(*F*3)	0·6659 (4)	0·3314 (19)	0·3418 (3)	0·048
C*G*(*F*3)	0·6564 (4)	0·3586 (18)	0·3955 (3)	0·044
C*D*1(*F*3)	0·6899 (5)	0·562 (3)	0·4291 (3)	0·072
C*E*1(*F*3)	0·6814 (6)	0·591 (2)	0·4799 (4)	0·083
C*Z*(*F*3)	0·6415 (6)	0·426 (3)	0·4957 (4)	0·086
C*E*3(*F*3)	0·6090 (6)	0·236 (3)	0·4626 (4)	0·090
C*D*2(*F*3)	0·6161 (5)	0·201 (2)	0·4122 (4)	0·061
C(*F*3)	0·6443 (4)	0·540 (3)	0·2521 (3)	0·053
O(*F*3)	0·6114 (3)	0·464 (2)	0·2088 (2)	0·081
OH(*F*3)	0·7038 (3)	0·6376 (17)	0·2627 (2)	0·076

edge-to-face interaction between phenyl rings is enthalpically favorable (Burley & Petsko, 1986).

We thank Professor G. A. Petsko for his useful discussion. One of us (SKB) was supported by a Natural Sciences and Engineering Research Council of Canada postdoctoral fellowship.

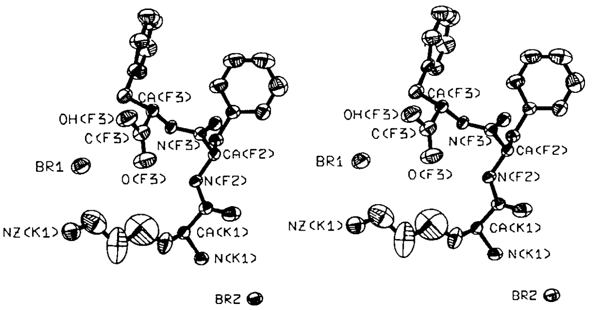

Fig. 1. Stereodrawing of the molecular structure showing the numbering scheme. The thermal ellipsoids are drawn at the 50% level.

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Acta Cryst. (1987). C**43**, 1636–1638

Structure of 4-Chloro-7*H*-benz[*de*]anthracen-7-one

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(*Received* 14 *February* 1987; *accepted* 12 *March* 1987)

Abstract. $C_{17}H_9ClO$, $M_r = 264{\cdot}7$, orthorhombic, $P2_12_12_1$, $a = 16{\cdot}153$ (6), $b = 14{\cdot}564$ (5), $c = 5{\cdot}003$ (2) Å, $V = 1177{\cdot}0$ (7) Å^3, $Z = 4$, $D_m = 1{\cdot}49$, $D_x = 1{\cdot}494$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}14$ mm^{-1}, $F(000) = 544$, $T = 298$ K, final $R = 0{\cdot}047$ for 1126 independent reflections. The title compound