ANDREEVA, N. S., ZDANOV, A. S., GUSTCHINA, A. E. & FEDOROV, A. A. (1984). *J. Biol. Chem.* **259**, 11353–11365.
BERNAL, J. D. & CROWFOOT, D. (1934). *Nature (London)*, **133**, 794–795.
BLUNDELL, T., COOPER, J. B., FOUNDLING, S. I., JONES, D. M., ATRASH, B. & SZELKE, M. (1987). *Biochemistry*, **26**, 5585 5590.
BLUNDELL, T., JENKINS, J., PEARL, L., SEWELL, T. J., COOPER, J. B., TICKLE, I. J., VEERAPANDIAN, B. & WOOD, S. P. (1990). *J. Mol Biol.* **211**, 919 941.
BLUNDELL, T. L., SEWELL, B. T. & MCLACHLAN, A. D. (1979). *Biochim. Biophys. Acta*, **580**, 24–31.
BOLIS, G. & GREER, J. (1989). *Computer-Aided Drug Design. Methods and Applications*, edited by T. J. PERUN & C. L. PROPST, pp. 297–326. New York: Dekker.
BOTT, R., SUBRAMANIAN, E. & DAVIES, D. R. (1982). *Biochemistry*, **21**, 6956–6962.
BRÜNGER, A. T., KARPLUS, M. & PETSKO, G. A. (1989). *Acta Cryst.* A**45**, 50 61.
CHEN, L. & ABAD-ZAPATERO, C. (1992). In preparation.
COOPER, J. B., KHAN, G., TAYLOR, G., TICKLE, I. J. & BLUNDELL, T. L. (1990). *J. Mol. Biol.* **214**, 199 222.
CRAVEN, B. M. (1975). *ROTRAN*. Univ. of Pittsburgh, USA.
CROWTHER, R. A. & BLOW, D. W. (1967). *Acta Cryst.* **23**, 544–548.
CYGLER, M. & ANDERSON, W. F. (1988*a*). *Acta Cryst.* A**44**, 38 45.
CYGLER, M. & ANDERSON, W. F. (1988*b*). *Acta Cryst.* A**44**, 300 308.
DAVIES, D. R. (1990). *Annu. Rev. Biophys. Biophys. Chem.* **19**, 189 215.
FITZGERALD, P. M. D. (1988). *J. Appl. Cryst.* **21**, 273 278.
FOUNDLING, S. I., COOPER, J., WATSON, F. E., CLEASBY, A., PEARL, L. H., SIBANDA, B. L., HEMMINGS, A., WOOD, S. P., BLUNDELL, T. L., VALLER, M. J., NOREY, C. G., KAY, J., BOGER, J., DUNN, B. M., LECKIE, B. J., JONES, D. M., ATRASH, B., HALLETT, A. & SZELKE, M. (1987). *Nature (London)*, **327**, 349–352.
HSU, I., DELBAERE, L. T. J., JAMES, M. N. G. & HOFMANN, T. (1977). *Nature (London)*, **266**, 140–145.
HUTCHINS, C. & GREER, J. (1991). *Crit. Rev. Biochem. Mol. Biol.* **26**, 77 127.
JAMES, M. N. G. & SIELECKI, A. R. (1983). *J. Mol. Biol.* **163**, 299 361.
KABSCH, W. & SANDER, C. (1983). *Biopolymers*, **22**, 2577 2637.
KOSTKA, V. (1985). Editor. *Aspartic Proteinases and Their Inhibitors*, Proceedings of the FEBS Advanced Course No. 84/07, Prague, Czechoslovakia. New York: Walter de Gruyter.
LATTMAN, E. E. & LOVE, W. E. (1972). *Acta Cryst.* B**26**, 1854 1857.
MILLER, M., JASKOLSKI, M., RAO, J. K. M., LEIS, J. & WLODAWER, A. (1989). *Nature (London)*, **337**, 576–579.
Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Determination Software*. Version 5.0. MSC, The Woodlands, Texas, USA.
NAVIA, M. A., FITZGERALD, P. M. D., MCKEEVER, B. M., LEU, C.-T., HEIMBACH, J. C., HERBER, W. K., SIGAL, I. S., DARKE, P. L. & SPRINGER, J. P. (1989). *Nature (London)*, **337**, 615 620.
NORTHROP, J. H. (1946). *J. Gen. Physiol.* **30**, 177–184.
RAO, G. K. M., ERICKSON, J. W. & WLODAWER, A. (1991). *Biochemistry*, **30**, 4663 4671.
ROSSMANN, M. G. (1972). Editor. *The Molecular Replacement Method*. New York: Gordon and Breach.
RÜCHEL, R. (1981). *Biochim. Biophys. Acta*, **659**, 99 113.
SALI, A., VEERAPANDIAN, B., COOPER, J. B., FOUNDLING, S. I., HOOVER, D. J. & BLUNDELL, T. L. (1989). *EMBO J.* **8**, 2179–2188.
SHAM, H. L., BOLIS, G., STEIN, H. H., FESIK, S. W., MARCOTTE, P. A., PLATTNER, J. J., REMPEL, C. A. & GREER, J. (1988). *J. Med. Chem.* **31**, 289 295.
SHERIFF, S., PADLAND, E. A., COHEN, G. H. & DAVIES, D. R. (1990). *Acta Cryst.* B**46**, 418 425.
SIELECKI, A. R., FEDOROV, A. A., BOODHOO, A., ANDREEVA, N. S. & JAMES, M. N. G. (1990). *J. Mol. Biol.* **214**, 143 170.
SIELECKI, A. R., FUJINAGA, M., READ, R. J. & JAMES, M. N. G. (1991). *J. Mol. Biol.* **49**, 671 692.
STEIGEMANN, W. (1974). PhD Thesis. Technische Univ., München, Germany.
SUGUNA, K., BOTT, R. R., PADLAN, E. A., SUBRAMANIAN, E., SHERIFF, S., COHEN, G. H. & DAVIES, D. R. (1987). *J. Mol. Biol.* **196**, 877–900.
SUGUNA, K., PADLAN, E. A., SMITH, C. W., CARLSON, W. D. & DAVIES, D. R. (1987). *Proc. Natl Acad. Sci. USA*, **84**, 7009–7013.
TANG, J., JAMES, M. N. G., HSU, I. N., JENKINS, J. A. & BLUNDELL, T. L. (1978). *Nature (London)*, **271**, 618 621.
VEERAPANDIAN, B., COOPER, J. B., SALI, A. & BLUNDELL, T. L. (1990). *J. Mol. Biol.* **216**, 1017 1029.
WLODAWER, A., MILLER, M., JASKOLSKI, M., SATHYANARAYANA, B. K., BALDWIN, E. T., WEBER, I. T., SELK, L. M., CLAWSON, L., SCHNEIDER, J. & KENT, S. B. H. (1989). *Science*, **245**, 616–621.

Acta Cryst. (1992). B**48**, 488–492

Crystal and Molecular Structures of Propanediamine Complexed with L- and DL-Glutamic Acid: Effect of Chirality on Propanediamine

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(*Received* 6 *August* 1991; *accepted* 13 *January* 1992)

Abstract

The structures of complexes of 1,3-diaminopropane with L- and DL-glutamic acid have been determined. L-Glutamic acid complex: $C_3H_{12}N_2^{2+}.2C_5H_8NO_4^-$, $M_r = 368.4$, orthorhombic, $P2_12_12_1$, $a = 5.199$ (1), $b = 16.832$ (1), $c = 20.076$ (3) Å, $V = 1756.6$ (4) Å^3, $Z = 4$, $D_x = 1.39$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 1.1$ cm^{-1}, $F(000) = 792$, $T = 296$ K, $R = 0.044$ for 1276 observed reflections. DL-Glutamic acid com-

0108-7681/92/040488-05$06.00

plex: $C_3H_{12}N_2^{2+}.2C_5H_8NO_4^-$, $M_r = 368.4$, orthorhombic, $Pna2_1$, $a = 15.219$ (2), $b = 5.169$ (1), $c = 22.457$ (4) Å, $V = 1766.6$ (5) Å^3, $Z = 4$, $D_x = 1.38$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 1.1$ cm^{-1}, $F(000) = 792$, $T = 296$ K, $R = 0.056$ for 993 observed reflections. The conformation of diaminopropane is all-*trans* in the DL complex but *trans–gauche* in the L complex. The main packing feature in the L complex is the arrangement of diaminopropane around dimers of antiparallel L-glutamic acid molecules. The diaminopropane in the DL complex is sandwiched between two antiparallel glutamic acid molecules of the same chirality and this forms the basic packing unit. This might be the dominant form of interaction between L-glutamic acid and diaminopropane in solution. The structures reveal the adaptability of the polyamine backbone to different environments and the probable reasons for their choice as biological cations.

Introduction

Polyamines are believed to be important for a variety of biological functions (Smith, 1985; Tabor & Tabor, 1984; Slocum, Swahney & Galston, 1984). Their concentration in living cells is under stringent regulation. The enzymes, ornithine decarboxylase, arginine decarboxylase and polyamine oxidase involved in the biosynthesis and metabolism of polyamines are targets for possible chemotherapy (Guiseppe & Ferioli, 1990). Spermine, spermidine, putrescine and cadaverine are the most ubiquitous polyamines found, although, other amines such as propanediamine, *sym*-homospermidine, agmatine, *etc.*, are frequently encountered (Kuehn, Garay, Bagga & Phillips, 1990). Extensive biochemical literature exists on the possible functions of polyamines in living cells (Smith, 1985; Tabor & Tabor, 1984; Slocum, Swahney & Galston, 1984). However, studies on structure and interaction of these molecules are limited. Only the structures of some inorganic salts of polyamines and complexes with nucleic acids have so far been reported by other investigators (Giglio, Liquori & Puliti, 1966; Pattabi & Chandrasekar, 1982; Frederick, Williams, Ughetto, van der Marel, van Boom, Rich & Wang, 1990). We have reported the structures of complexes of putrescine and hexanediamine with aspartic and glutamic acids (Ramaswamy, Nethaji & Murthy, 1989; Ramaswamy & Murthy 1990, 1991). In this communication, we report the structures of propanediamine complexed with L- and DL-glutamic acid molecules.

Experimental

Crystals of propanediamine–L-glutamic acid complex (L complex) and propanediamine–DL-glutamic acid (DL complex) were obtained using similar protocols. An aqueous solution of the 1:2 mixture of propanediamine and glutamic acid was layered with propanol in a test tube and left undisturbed. Needle-shaped crystals appeared within a few days. Unlike some inorganic salts of polyamines, the needle-shaped crystals of the complexes were stable when exposed to the atmosphere. These crystals were characterized by X-rays from a microfocus sealed-tube generator and data were collected on an Enraf–Nonius CAD-4 four-circle diffractometer. Details are presented in Table 1.* The data for the DL complex were obtained as the average of measurements over two asymmetric units. The data were corrected for Lorentz and polarization effects; absorption was ignored. All non-H atoms were associated with anisotropic temperature factors. The positions of the H atoms were calculated by geometrical considerations and confirmed on the difference Fourier maps computed after refinement of non-H atoms. These H atoms were refined with isotropic temperature factors for a few cycles. The final coordinates and equivalent temperature factors of the non-H atoms are given in Table 2. The quantity minimized by least

Table 1. *Details of data collection and refinement*

	L Complex	DL Complex
Crystal size (mm)	0.44 × 0.16 × 0.12	0.40 × 0.20 × 0.12
Method of measuring intensities	$\omega/2\theta$	$\omega/2\theta$
No. and 2θ range ( ) of reflections used for refining lattice parameters	25 2 24	25 4 21
Max. $(\sin\theta/\lambda)$ (Å^{-1})	0.63	0.63
Range of		
h	0 6	18 18
k	0 19	0 6
l	0 21	0 23
ΔI for standard reflections (%)	2.5	3.2
No. of reflections		
measured	1411	1945
unique ($F_o \geq 5\sigma(F_o)$)	1276	993
R_{int}		0.042
Programs used*		
for structure solution	*MULTAN*	*SHELX*86
for refinement	*SHELX*76	*SHELX*76
No. of parameters refined	226	225
R for $(F_o) \geq 5\sigma(F_o)$	0.044	0.056
wR for $(F_o) \geq 5\sigma(F_o)$	0.048	0.050
w	$1/[\sigma^2(F_o) + 0.009644(F_o)^2]$	$1/[\sigma^2(F_o)]$
Goodness of fit, S	0.610	1.530
$(\Delta/\rho)_{max}$	0.069	0.143
$\Delta\rho_{max}$ (e Å^{-3})	0.21	0.28
$\Delta\rho_{min}$ (e Å^{-3})	0.18	−0.32

* *MULTAN*84 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1984); *SHELX*86 (Sheldrick, 1986); *SHELX*76 (Sheldrick, 1976).

* Lists of structure factors, anisotropic temperature parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54907 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0537]

Table 2. *Final atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$B_{eq} = (8\pi^2)(U_{11} + U_{22} + U_{33})/3$

	x	y	z	B_{eq}(Å^2)
L-Glutamic acid complex				
N(1)	−0.0952 (9)	0.2174 (2)	0.5916 (2)	1.82 (10)
O(2)	0.4910 (7)	0.1550 (2)	0.6729 (2)	2.38 (9)
O(1)	0.0903 (8)	0.1084 (2)	0.6742 (2)	3.29 (10)
C(1)	0.2530 (11)	0.1567 (3)	0.6568 (2)	1.87 (11)
C(2)	0.1766 (10)	0.2286 (3)	0.6147 (2)	1.83 (11)
C(3)	0.2097 (11)	0.3062 (3)	0.6525 (2)	1.91 (12)
C(4)	0.0650 (12)	0.3096 (3)	0.7187 (3)	2.10 (12)
C(5)	0.1299 (11)	0.3825 (3)	0.7597 (2)	2.02 (12)
O(6)	0.0119 (8)	0.3910 (2)	0.8139 (2)	2.92 (11)
O(7)	0.2963 (10)	0.4288 (2)	0.7400 (2)	4.22 (14)
N(11)	0.5101 (9)	0.0741 (2)	0.7961 (2)	1.93 (10)
O(11)	0.2969 (8)	0.1932 (2)	0.8641 (2)	3.98 (12)
O(12)	−0.0746 (8)	0.1325 (2)	0.8805 (2)	2.87 (10)
C(11)	0.1546 (10)	0.1358 (3)	0.8588 (2)	2.00 (12)
C(12)	0.2500 (10)	0.0601 (3)	0.8240 (2)	1.75 (11)
C(13)	0.2457 (12)	−0.0128 (3)	0.8676 (2)	1.98 (11)
C(14)	0.4212 (13)	−0.0092 (3)	0.9272 (3)	2.38 (14)
C(15)	0.4335 (12)	−0.0848 (3)	0.9680 (2)	2.21 (13)
O(16)	0.5963 (11)	−0.0854 (2)	1.0138 (2)	3.89 (12)
O(17)	0.2958 (10)	−0.1410 (2)	0.9555 (2)	3.61 (11)
N(21)	−0.2728 (11)	0.2854 (3)	0.8831 (3)	2.63 (11)
C(22)	−0.3288 (13)	0.3256 (3)	0.9469 (3)	2.75 (15)
C(23)	−0.5409 (12)	0.3865 (3)	0.9398 (3)	2.57 (14)
C(24)	−0.4660 (11)	0.4574 (3)	0.8975 (3)	2.51 (13)
N(25)	−0.6956 (9)	0.5067 (3)	0.8821 (2)	2.14 (10)
DL-Glutamic acid complex				
N(1)	0.6094 (4)	0.5836 (17)	0.3765	2.67 (21)
O(2)	0.5784 (5)	0.7683 (11)	0.4912 (5)	2.17 (18)
O(1)	0.5889 (5)	1.1719 (16)	0.4599 (5)	3.75 (20)
C(1)	0.5843 (5)	0.9270 (22)	0.4521 (5)	2.20 (24)
C(2)	0.5785 (6)	0.8611 (26)	0.3854 (5)	3.42 (31)
C(3)	0.4807 (5)	0.8803 (22)	0.3635 (5)	3.05 (26)
C(4)	0.4205 (8)	0.6920 (22)	0.3930 (6)	3.85 (31)
C(5)	0.3215 (7)	0.7759 (19)	0.3900 (6)	2.59 (29)
O(6)	0.2948 (4)	0.8760 (19)	0.3427 (4)	4.57 (24)
O(7)	0.2767 (5)	0.7284 (14)	0.4332 (5)	3.75 (24)
N(11)	0.1434 (5)	0.5955 (19)	0.7371 (3)	2.44 (20)
O(11)	0.1731 (7)	0.7783 (15)	0.6247 (5)	4.45 (29)
O(12)	0.1699 (5)	1.1837 (14)	0.6574 (4)	3.17 (20)
C(11)	0.1735 (5)	0.9451 (22)	0.6652 (5)	2.58 (26)
C(12)	0.1820 (5)	0.8497 (21)	0.7297 (4)	1.89 (23)
C(13)	0.2789 (7)	0.8556 (20)	0.7482 (5)	3.07 (27)
C(14)	0.3368 (5)	0.6530 (19)	0.7181 (5)	2.06 (22)
C(15)	0.4302 (7)	0.7022 (20)	0.7321 (6)	2.30 (26)
O(16)	0.4652 (4)	0.6261 (17)	0.7776 (4)	4.05 (21)
O(17)	0.4745 (5)	0.8329 (21)	0.6955 (5)	6.36 (31)
N(21)	0.2244 (4)	1.0683 (16)	0.5227 (4)	2.27 (17)
C(22)	0.2998 (9)	1.2420 (18)	0.5383 (6)	3.07 (36)
C(23)	0.3794 (7)	1.0813 (15)	0.5567 (6)	2.81 (19)
C(24)	0.4565 (8)	1.2447 (19)	0.5746 (6)	3.04 (37)
N(25)	0.5312 (5)	1.0777 (16)	0.5914 (4)	2.67 (19)

squares was $\sum w(|F_o| - |F_c|)^2$. Scattering-factor values for all atoms were as contained in the program *SHELX*76 (Sheldrick, 1976). The structures are shown in Fig. 1.

Results and discussion

The asymmetric unit of each of these complexes consists of two glutamic acid and one propanediamine molecules. The program *PARST* (Nardelli, 1983) was used to determine all molecular parameters. The bond lengths and bond angles in these molecules (Table 3) are in close agreement with the corresponding values observed in other structures. The torsion angles of the four glutamic acid molecules of the two structures are recorded in Table 4. In order to compare the glutamic acid conformations, the structures were superposed following the procedure of Kearsley (1989). The glutamic acid conformations are similar to that of the protonated form of the same molecule (Sequeira, Rajagopal & Chidambaram, 1972). However, the orientation of the carboxyl groups shows differences.

On the other hand, the propanediamines in the two structures have strikingly different conformations. In the L complex, propanediamine has a *trans–gauche* conformation in contrast to the fully extended *trans* conformation found in the DL complex. There are notable differences in the molecular packing in the two structures (Figs. 2 and 3). All amino groups of the L and DL complexes each form three hydrogen bonds. The packing coefficient as

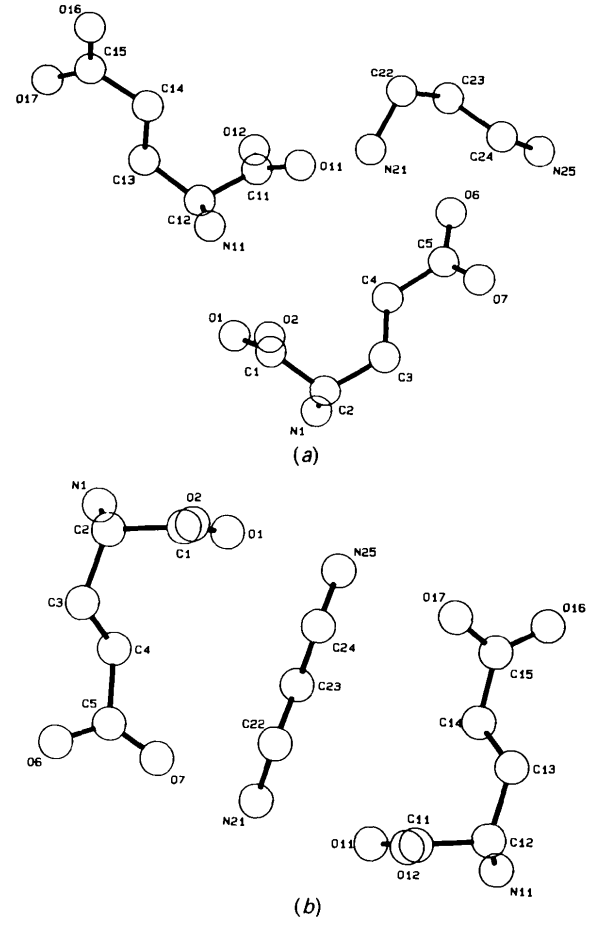

Fig. 1. (*a*) Schematic diagram of propanediamine–L-glutamic acid complex showing the numbering scheme. (*b*) Schematic diagram of propandiamine–DL-glutamic acid complex showing the numbering scheme.

Table 3. *Bond distances* (Å) *and angles* (°) *for non-*H *atoms with e.s.d.'s in parentheses*

Glutamic acid	L Complex		DL Complex	
	Glu (I)	Glu (II)	Glu (I)	Glu (II)
N(1)—C(2)	1.499 (6)	1.482 (6)	1.52 (1)	1.44 (1)
O(2)—C(1)	1.279 (6)	1.269 (6)	1.20 (1)	1.25 (1)
O(1)—C(1)	1.224 (6)	1.221 (6)	1.27 (1)	1.24 (1)
C(1)—C(2)	1.528 (6)	1.535 (6)	1.53 (1)	1.53 (1)
C(2)—C(3)	1.520 (6)	1.507 (6)	1.57 (1)	1.53 (1)
C(3)—C(4)	1.528 (7)	1.505 (8)	1.49 (1)	1.52 (1)
C(4)—C(5)	1.515 (7)	1.514 (7)	1.56 (1)	1.47 (1)
C(5)—O(6)	1.257 (6)	1.249 (7)	1.24 (1)	1.21 (1)
C(5)—O(7)	1.229 (6)	1.212 (6)	1.21 (1)	1.25 (1)
O(2)—C(1)—O(1)	125.5 (4)	124.9 (4)	125.2 (10)	125.3 (10)
O(1)—C(1)—C(2)	120.2 (4)	120.0 (4)	110.8 (10)	117.6 (9)
O(2)—C(1)—C(2)	114.1 (4)	115.0 (4)	123.6 (10)	116.9 (9)
N(1)—C(2)—C(1)	108.4 (4)	109.5 (3)	108.5 (8)	111.4 (7)
C(1)—C(2)—C(3)	112.0 (3)	113.9 (3)	110.1 (8)	109.2 (7)
N(1)—C(2)—C(3)	111.6 (4)	111.2 (4)	108.1 (8)	112.1 (8)
C(2)—C(3)—C(4)	114.2 (4)	114.8 (4)	113.6 (8)	114.9 (8)
C(3)—C(4)—C(5)	113.1 (4)	114.9 (4)	112.9 (9)	110.0 (8)
C(4)—C(5)—O(7)	119.6 (4)	121.2 (4)	116.7 (10)	117.9 (10)
C(4)—C(5)—O(6)	116.9 (4)	115.6 (4)	117.5 (9)	122.9 (9)
O(6)—C(5)—O(7)	123.3 (4)	123.0 (4)	125.5 (10)	119.1 (10)
Propanediamine				
N(21)—C(22)	1.477 (8)		1.49 (1)	
C(22)—C(23)	1.512 (8)		1.52 (1)	
C(23)—C(24)	1.515 (7)		1.50 (1)	
C(24)—N(25)	1.486 (7)		1.47 (1)	
N(21)—C(22)—C(23)	111.8 (4)		110.1 (7)	
C(22)—C(23)—C(24)	113.5 (4)		112.7 (7)	
C(23)—C(24)—N(25)	110.4 (4)		109.9 (8)	

Table 4. *Torsion angles* (°) *of glutamic acid molecules and propanediamine in the two complexes*

Glutamic acid	L Complex		DL Complex	
	Glu (I)	Glu (II)	Glu (I)	Glu (II)
O(1)—C(1)—C(2)—N(1)	10.3 (6)	5.0 (6)	157.6 (8)	30.2 (12)
O(2)—C(1)—C(2)—N(1)	172.2 (4)	175.1 (4)	27.5 (14)	151.5 (8)
O(1)—C(1)—C(2)—C(3)	113.3 (5)	120.2 (5)	84.0 (11)	94.2 (11)
O(2)—C(1)—C(2)—C(3)	64.1 (5)	59.4 (5)	90.6 (12)	83.9 (11)
C(1)—C(2)—C(3)—C(4)	55.6 (5)	63.5 (5)	62.9 (11)	70.3 (10)
N(1)—C(2)—C(3)—C(4)	66.2 (5)	60.9 (5)	55.6 (11)	53.7 (11)
C(2)—C(3)—C(4)—C(5)	172.0 (4)	175.3 (4)	158.4 (9)	171.3 (8)
C(3)—C(4)—C(5)—O(6)	177.6 (4)	173.4 (4)	39.6 (14)	83.8 (13)
C(3)—C(4)—C(5)—O(7)	4.1 (7)	5.3 (7)	143.1 (10)	94.7 (12)
Propanediamine				
N(21)—C(22)—C(23)—C(24)	67.5 (6)		178.3 (9)	
C(22)—C(23)—C(24)—N(25)	169.3 (4)		179.5 (9)	

evaluated by the program *OPEC* (Gavezzotti, 1983) is 0.733 for the DL complex while it is 0.717 for the L complex. In the DL complex, a diamine molecule is sandwiched between glutamic acid molecules of the same chirality which are in a nearly antiparallel orientation. This organization helps formation of hydrogen bonds between propanediamine amino groups and the carboxyl groups of the two glutamic acid molecules. Extensive van der Waals interactions are also formed between the backbone non-polar atoms of the polyamine and glutamic acid. The crystal structure is made up of juxtaposed molecular aggregates of opposite chirality related by glide planes perpendicular to the *b* axis resulting in efficient packing along the *a* axis. Similar chains parallel to the *a* axis are packed such that the glutamic acid molecules form hydrogen bonds, mainly between main-chain and side-chain amino and carboxyl groups respectively.

The extensive stabilizing interactions between the sandwiched polyamine and the two glutamic acid molecules in the DL complex suggests that this complex might also exist in solution. The two glutamic acid molecules interacting with the polyamine are of the same chirality. Hence, occurrence of such a complex is, in principle, also possible in the structure of the L complex. However, examination of the molecular packing of the L complex (Fig. 2) shows the absence of such a cluster. Molecular packing in the L complex appears to be dominated by close interactions between the antiparallel glutamic acid molecules. The pair of glutamic acid molecules are held together by hydrogen bonding as well as van der Waals interactions. This will result in partial neutral-

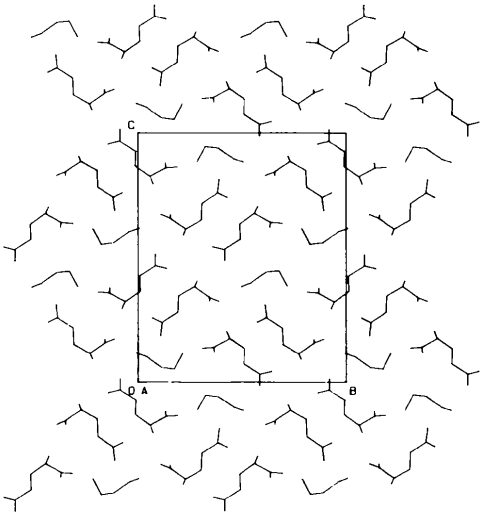

Fig. 2. Packing diagram of propanediamine–L-glutamic acid complex.

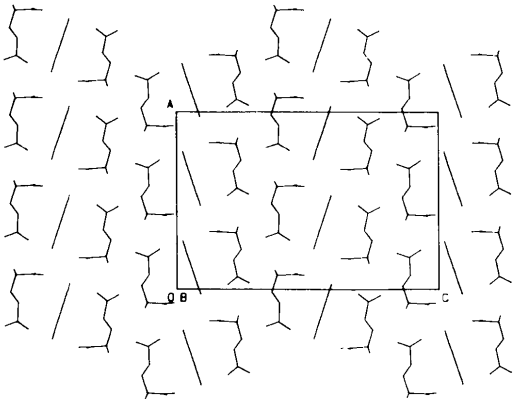

Fig. 3. Packing diagram of propanediamine–DL-glutamic acid complex.

ization of the glutamic acid amino group and side-chain carboxyl groups and leave the charged main-chain carboxyl groups jutting out of the tight dimer. Polyamines dispersed between such dimers effectively neutralize the carboxyl groups. However, the nature of the packing forces drives the polyamine backbone to adopt a less favourable *trans–gauche* conformation. This adaptability combined with their ability for electrostatic, hydrogen bonding and van der Waals interactions are important for their ubiquitous role as biological cations.

We thank CSIR for financial assistance. SR is an UGC SRF. Thanks are due to B. S. Neela for the molecular superposition program.

References

FREDERICK, A. C., WILLIAMS, D. L., UGHETTO, G., VAN DER MAREL, A. G., VAN BOOM, J. H., RICH, A. & WANG, J. H. A. (1990). *Biochemistry*, **29**, 2538–2549.
GAVEZZOTTI, A. (1983). *J. Am. Chem. Soc.* **105**, 5220–5225.
GIGLIO, E., LIQUORI, A. M. & PULITI, R. (1966). *Acta Cryst.* **20**, 683–688.
GUISEPPE, S. & FERIOLI, M. E. (1990). *Adv. Cancer Res.* **36**, 1–20.
KEARSLEY, S. K. (1989). *Acta Cryst.* A**45**, 208–210.
KUEHN, G. D., GARAY, B. R., BAGGA, S. & PHILLIPS, G. C. (1990). *Plant Physiol.* **94**, 855–857.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1984). *MULTAN*84. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
PATTABI, V. & CHANDRASEKAR, K. (1982). *Conformation in Biology*, edited by R. SRINIVASAN & R. H. SARMA, pp. 291–298. New York: Adenine Press.
RAMASWAMY, S. & MURTHY, M. R. N. (1990). *Curr. Sci.* **59**, 379–382.
RAMASWAMY, S. & MURTHY, M. R. N. (1991). *Curr. Sci.* **60**, 173–176.
RAMASWAMY, S., NETHAJI, M. & MURTHY, M. R. N. (1989). *Curr. Sci.* **58**, 1160–1163.
SEQUEIRA, A., RAJAGOPAL, H. & CHIDAMBARAM, R. (1972). *Acta Cryst.* B**28**, 2514–2519.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). *SHELX*86. Program for crystal structure determination. Univ. of Göttingen, Germany.
SLOCUM, R. D., SWAHNEY, R. K. & GALSTON, A. W. (1984). *Arch. Biochem. Biophys.* **235**, 283–303.
SMITH, T. A. (1985). *Annu. Rev. Plant. Physiol.* **36**, 117–143.
TABOR, C. W. & TABOR, H. (1984). *Annu. Rev. Biochem.* **53**, 749–790.

Acta Cryst. (1992). B**48**, 492–498

Positive Identification of Two Orthorhombic Polymorphs of Sulfamerazine ($C_{11}H_{12}N_4O_2S$), their Thermal Analyses and Structural Comparison

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(*Received* 15 *October* 1991; *accepted* 20 *January* 1992)

Abstract

The independent existence of at least two polymorphs [designated (I) and (II)] of sulfamerazine [4-amino-*N*-(4-methyl-2-pyrimidinyl)benzenesulfonamide] has been demonstrated by thermal analysis, X-ray crystallographic and spectroscopic methods. The single-crystal X-ray analysis of polymorph (I) is reported. Crystal data are: (I), $C_{11}H_{12}N_4O_2S$, $M_r = 264.3$, orthorhombic, $Pn2_1a$, $a = 14.474$ (2), $b = 21.953$ (2), $c = 8.203$ (1) Å, $V = 2606.5$ (5) Å^3, $Z = 8$, $D_m = 1.34$ (1), $D_x = 1.347$ Mg m^{-3}, m.p. = 509–511 K, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.237$ mm^{-1}, $F(000) = 1104$, $T = 294$ K, final $R = 0.047$ for 1886 independent reflections. The structure of polymorph (II) (space group *Pbca*) was reported earlier [Acharya, Kuchela & Kartha (1982). *J. Crystallogr. Spectrosc. Res.* **12**, 369–376]. In both polymorphs, the repeating motif is a dimer [pseudocentrosymmetric in (I), centrosymmetric in (II)] formed *via* two N(amide)—H···N(pyrimidinyl) hydrogen bonds. Distinct differences in the X-ray powder patterns, infrared spectra and behaviour on heating for (I) and (II) allow their rapid identification. A phase transition from (II) to (I) occurring at 422–423 K has been detected. Experimental conditions for obtaining the individual polymorphs are described. The JCPDS File No. for sulfamerazine is 43-2000.

Introduction

Owing to a variety of possible hydrogen-bonding arrangements and ring-stacking modes, sulfonamides are predisposed to polymorphism (Yang & Guillory, 1972; Byrn, 1982). Numerous studies aimed at the isolation and characterization of individual

0108-7681/92/040492-07$06.00