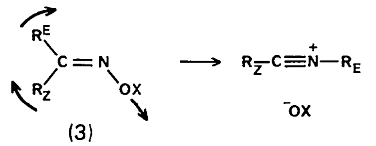
In these circumstances it is more useful to use the structure-correlation approach pioneered by Bürgi & Dunitz (1983). We use the N—O bond length as the reference parameter, and look for trends in the geometrical changes in the oxime group associated with the lengthening of the N—O bond. The data, summarized in Table 3, show that there are no significant trends in bond lengths C—C or C=N, or in bond angles C—N—O. But small changes are apparent in the bond angles at the oxime C centre, where very large changes of angle must take place during reaction. These changes are summarized in formula (3), and plotted in Fig. 2, which shows that as the N—O*X* bond lengthens, as a result of increasing electron-withdrawal in the group *X*, the *syn* substituted (R_Z) moves closer to linearity. The *anti* substituent moves in the same (clockwise) sense, also without change in the C—C bond length, with the result that the C atom of the group which will migrate in the Beckmann rearrangement (R_E) is brought closer to the migration terminus. [The N—C_E distance falls, as N—O lengthens, from 2·368 Å in the oxime ether to 2·334 Å in the 2-naphthalenesulfonate (1). In molecules 1 and 2 of (2) it is 2·344 (5) and 2·368 (5) Å.] The angle C—N—O is not expected to change significantly as the leaving group (*X*O⁻) departs, as it is already close [mean value 108·9 (1·1)° for the four molecules] to the Bürgi–Dunitz angle for addition of a nucleophile to a π system.



(3)

Thus as the O atom is made more electronegative in ketoximine derivatives (1→3), the N—O bond lengthens substantially, but further changes, primarily in the bond angles at the potential migration origin, are relatively minor. The trends can be interpreted in terms of progress along the reaction coordinate for the Beckmann rearrangement, but the effects on bond lengths in particular suggest that the positive charge induced by increasing polarization of the N—O*X* bond in the sense N^+ ^-OX, is largely localized on nitrogen. More substantial progress in the direction of reaction, which might reveal more details of the intriguing and extensive geometrical changes which must occur on rearrangement, is probably not to be expected from the study of ground-state structures, at least in this system.

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Structure of (8*S*)-8-Hydroxymethyl-6,9-diazaspiro[4.5]decane-7,10-dione, a Spirocyclic Dipeptide

By Jindřich Symerský and Karel Bláha

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 *Praha* 6, *Czechoslovakia*

and Vratislav Langer

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 02 *Praha* 6, *Czechoslovakia*

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Abstract. $C_9H_{14}N_2O_3$, $M_r = 198{\cdot}22$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}437\ (6)$, $b = 20{\cdot}187\ (15)$, $c = 6{\cdot}241\ (4)$ Å, $V = 937\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}40\ (1)$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 8{\cdot}44$ cm^{-1}, $F(000) = 424$, $T = 295$ K. Final $R = 0{\cdot}0831$ for 570 reflections. The 2,5-piperazinedione ring adopts a flat boat conformation with the axially substituted hydroxymethyl group twisted over the ring to which the

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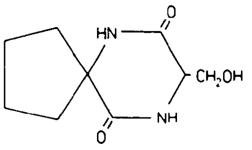
five-membered aliphatic ring is nearly perpendicular. There is dubious localization of the amide group H atoms.

Introduction. The project of peptide group investigation undertaken by Bláha *et al.* (1978), Bláha & Maloň (1980), Kálal, Bláha & Langer (1984), Symerský, Kálal, Bláha & Langer (1986), Bláha *et al.* (1984) and Tichý, Farag, Maloň, Kálal & Bláha (1984) by means of X-ray structure determination, IR, CD or NMR measurements includes at this stage the X-ray structure determination of the title spirocyclic dipeptide (I). No data have been found in the Cambridge Structural Database for this group of compounds. The influence of the ring size of the spiro substituent on the 2,5-piperazinedione ring geometry is the main aim of our investigation on this series of compounds.



(I)

Experimental. Colorless, long, prismatic, poor single crystals grown by slow evaporation from solution in methanol. The compound was prepared by Vanžura, Kasafírek, Krejčí & Rojček (1985), density measurement was not performed owing to the insufficient amount of material. The weak scattering power of the crystals had to be compensated by long exposure with Cu $K\alpha$ radiation when Weissenberg photographs were taken from which the preliminary cell dimensions and space group were determined. Final cell dimensions were refined on 25 diffractometer reflections with $12{\cdot}6 < 2\theta < 39{\cdot}6°$. Crystal $0{\cdot}05 \times 0{\cdot}30 \times 0{\cdot}1$ mm, Syntex $P2_1$ automated diffractometer with graphite monochromator, Cu $K\alpha$ radiation, $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}6095$ Å^{-1}, θ–2θ scan technique, no background measurement, intensities and their respective e.s.d.'s were calculated using a combined method of profile analysis (Lehmann & Larsen, 1974) and mask procedure (Sjölin & Wlodawer, 1981). $0 \le h \le 9$, $0 \le k \le 24$, $0 \le l \le 7$; in the range up to $2\theta = 140°$, 1050 unique reflections were measured, only 570 considered observed with $I > 1{\cdot}96\sigma_I$. Check reflections (021, 110, 120) showed decreasing intensity throughout data collection (to 87, 85, 86% of initial value, respectively). The measurements were reduced to the same scale with the program *INTER* (Langer, 1973). Corrections were made for Lorentz and polarization factors, not for absorption. The phase problem was solved using direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Two subsequent weighted Fourier syntheses revealed all non-H atoms. Refinement was performed on $|F|$ by full-matrix LS method with the program *SHELX*76 (Sheldrick, 1976). The $\Delta\rho$ map showed no peaks corresponding to H atoms and they were therefore calculated in theoretical positions and a planar bond arrangement at the N atoms was assigned. We tried to localize the H(11), alcoholic H atom, in the following way. Using the program *TLSSMOL* (Petříček, 1985) we kept the distance O(1)—H(11) = 0·96 Å and the angle C(2)—O(1)—H(11) = 110° (Cotrait & Ptak, 1978) to find the minimum of the function $R(\varphi)$, where R is the common residual factor and φ is the rotation angle of the C(2)—O(1)—H(11) fragment around the link C(2)—O(1). A unique minimum was found and the corresponding coordinates of H(11) were kept fixed in the final stage of refinement as for all H atoms with exception of H(41) and H(121), for which bond-length constraints were applied. $U_{\rm iso} = 0{\cdot}15$ Å^2 was assigned to the two latter H atoms, $U_{\rm iso} = 0{\cdot}1$ Å^2 for the other H atoms. An empirical correction was made for secondary extinction as $F_c^{\rm corr} = F_c(1 - gF_c^2/\sin\theta)$, where $g = 0{\cdot}5\,(1) \times 10^{-5}$. Refinement stopped when $(\Delta/\sigma)_{\max} = 0{\cdot}036$; total number of parameters refined was 132. Final $R = 0{\cdot}0831$, $wR = 0{\cdot}0819$ for 570 reflections, $w = 0{\cdot}3790/[\sigma_F^2 + (0{\cdot}0425F)^2]$; σ_F is taken from counting statistics. Final $\Delta\rho$ on all reflections did not show significant residual electron density, maximum 0·56 and minimum −0·57 e Å^{-3}. The enantiomorph change had no influence on final R. The rather high final R value is due to the poor quality of the crystal. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Geometrical interpretations of the structure were calculated with the program *PARST*83 (Nardelli, 1983).

Discussion. A view of the molecule with the numbering scheme is shown in Fig. 1. Fractional atomic coordinates and $B_{\rm eq}$ values are given in Table 1, selected bond lengths and angles in Table 2.* The crystal packing and hydrogen bonds are shown in Fig. 2. The parameters of the hydrogen bonds are: N(12)—H(121) = 1·0 (1), N(12)···O(6$^{\rm i}$) = 2·92 (1), H(121)···O(6$^{\rm i}$) = 2·1 (1) Å, and N(12)—H(121)···O(6$^{\rm i}$) = 142 (12)°; N(4)—H(41) = 1·0 (1), N(4)···O(14$^{\rm ii}$) = 2·96 (1), H(41)···O(14$^{\rm ii}$) = 1·97 (8) Å and N(4)—H(41)···O(14$^{\rm ii}$) = 165 (12)°; O(1)—H(11) = 0·98, O(1)···O(14$^{\rm iii}$) = 2·68 (1), H(11)···O(14$^{\rm iii}$) = 1·96 Å and O(1)—H(11)···O(14$^{\rm iii}$) = 128 (1)°. There are two hydrogen bonds for each molecule connecting the 2,5-piperazinedione rings in ribbons parallel to the c axes. Moreover we can consider the third weak hydrogen contact connecting

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* Lists of structure factors, anisotropic thermal parameters, and H-atom coordinates and thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43376 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the molecules in helices perpendicular to the ribbons along the *a* axis.

The first amide group [C(7), N(12), C(13), C(3), O(14), H(121)] deviates less significantly from planarity than the second one [C(3), N(4), C(5), C(7), O(6), H(41)]. The χ^2 values for the weighted mean planes are 29·6 and 111·7, respectively. Non-planarity parameters [following Winkler & Dunitz (1971) and Warshel, Levitt & Lifson (1970)] for the first amide group are: $\tau' = 27\ (9)^\circ$ (describes the torsion around amide bond), $\chi_C = 0(2)^\circ$ (pyramidicity on the carbonyl C atom), $\chi_N = 37\ (9)^\circ$ (pyramidicity on the amide N atom). The parameters for the second amide group are: $\tau' = 0\ (9)$, $\chi_C = -3\ (2)$, $\chi_N = 23\ (9)^\circ$. In consequence of the large e.s.d.'s we can only assume that the pyramidal bond arrangement at N is a main contribution to the non-planarity of both amide groups.

The six-membered 2,5-piperazinedione ring (DKP) has a slight twist-boat conformation, C(3) having the largest deviation from the weighted mean plane, the χ^2 value being 166·3. Relevant torsional angles of the DKP ring are given in Table 3.

The five-membered aliphatic ring has an envelope conformation, with the spiro C atom out of the plane, and is nearly perpendicular to the DKP ring.

The hydroxymethyl group [C(2)–O(1)–H(11)] is an axial substituent of the DKP twisted above it.

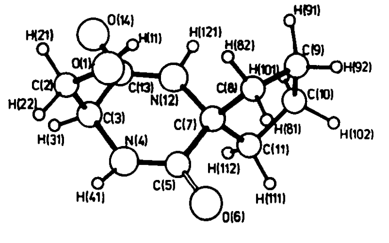

Fig. 1. Projection of the structure with numbering scheme.

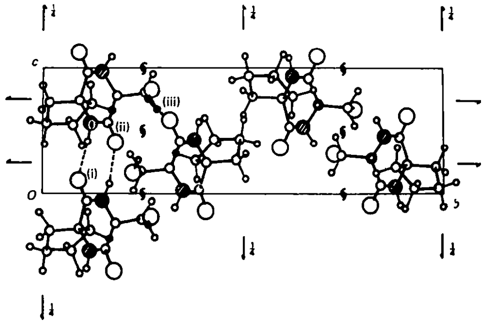

Fig. 2. Crystal packing in the projection along the *a* axis. N atoms are shaded. Hydrogen bonds are shown. Symmetry codes: (i) *x*, *y*, *z* + 1; (ii) *x*, *y*, *z* − 1; (iii) *x* − $\frac{1}{2}$, −*y* + $\frac{1}{2}$, 1 − *z*.

The most similar cyclo dipeptide so far studied as regards the X-ray geometry is *cyclo*(-Gly-L-Tyr-) (Lin & Webb, 1973). Comparison of torsional angles shows only non-significant differences in the geometry of the DKP ring.

The authors thank Dr K. Huml, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, for useful suggestions, Dr J. Vanžura, Faculty of Pharmacy, Charles University,

Table 1. *Fractional atomic coordinates* (×10⁴) *and* B_{eq} (Å²) *values with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O(6)	−9123 (12)	−4079 (4)	−6244 (10)	3·1
O(14)	−5931 (13)	−3180 (5)	836 (11)	5·0
C(7)	−9187 (18)	−4056 (6)	−2440 (16)	2·8
C(13)	−6667 (20)	−3381 (7)	−787 (20)	4·2
C(3)	−6013 (20)	−3159 (6)	−2906 (14)	3·1
C(5)	−8389 (18)	−3871 (5)	−4629 (17)	2·7
N(12)	−8023 (16)	−3793 (5)	−648 (12)	3·2
C(2)	−6386 (17)	−2413 (6)	−3149 (20)	3·8
C(11)	−9406 (19)	−4806 (5)	−2240 (19)	3·7
C(9)	−11983 (20)	−4251 (5)	−584 (18)	3·8
C(8)	−11153 (15)	−3801 (5)	−2243 (17)	2·8
N(4)	−6865 (16)	−3513 (4)	−4674 (13)	3·3
O(1)	−8248 (14)	−2261 (5)	−3320 (13)	5·0
C(10)	−10917 (20)	−4880 (6)	−519 (19)	5·2

Table 2. *Bond lengths* (Å) *and angles* (°) *for the title molecule*

O(6)–C(5)	1·22 (1)	C(3)–C(2)	1·54 (2)
O(14)–C(13)	1·22 (2)	C(3)–N(4)	1·46 (1)
C(7)–C(5)	1·54 (2)	C(5)–N(4)	1·34 (2)
C(7)–N(12)	1·51 (2)	C(2)–O(1)	1·42 (2)
C(7)–C(11)	1·53 (2)	C(11)–C(10)	1·56 (2)
C(7)–C(8)	1·56 (2)	C(9)–C(8)	1·51 (2)
C(13)–C(3)	1·48 (2)	C(9)–C(10)	1·50 (2)
C(13)–N(12)	1·31 (2)		
C(11)–C(7)–C(8)	103 (1)	O(6)–C(5)–C(7)	119 (1)
N(12)–C(7)–C(8)	111 (1)	C(7)–C(5)–N(4)	118 (1)
N(12)–C(7)–C(11)	110 (1)	O(6)–C(5)–N(4)	123 (1)
C(5)–C(7)–C(8)	111 (1)	C(7)–N(12)–C(13)	128 (1)
C(5)–C(7)–C(11)	111 (1)	C(3)–C(2)–O(1)	113 (1)
C(5)–C(7)–N(12)	111 (1)	C(7)–C(11)–C(10)	103 (1)
O(14)–C(13)–N(12)	120 (1)	C(8)–C(9)–C(10)	108 (1)
C(3)–C(13)–N(12)	120 (1)	C(7)–C(8)–C(9)	104 (1)
C(13)–C(3)–N(4)	113 (1)	C(3)–N(4)–C(5)	128 (1)
C(13)–C(3)–C(2)	109 (1)	C(11)–C(10)–C(9)	106 (1)
C(2)–C(3)–N(4)	109 (1)	O(14)–C(13)–C(3)	120 (1)

Table 3. *Relevant torsional angles of the DKP ring* (°)

φ_1[C(13)–C(3)–N(4)–C(5)]	18 (2)
ψ_1[N(12)–C(13)–C(3)–N(4)]	−8 (2)
ω_1[C(3)–C(13)–N(12)–C(7)]	−5 (2)
φ_2[C(5)–C(7)–N(12)–C(13)]	10 (2)
ψ_2[N(4)–C(5)–C(7)–N(12)]	−1 (1)
ω_2[C(3)–N(4)–C(5)–C(7)]	−13 (2)

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4,17-Diacetyl-3α,8,12α,18β-tetramethyl-4,5,7,14,16,17-hexaazapentacyclo[10.6.2.$0^{2,11}$.$0^{3,8}$.$0^{13,18}$]icosa-5,7,9,13,15,19-hexaene (I*a*) 0·5-Methanol Solvate and Trimethyl 2α,8β-Dimethyl-3,4,6-triazatricyclo[6.2.2.$0^{2,7}$]dodeca-4,6,9,11-tetraene-3,9,10-tricarboxylate (II*b*)

BY GIUSEPPE FILIPPINI AND TULLIO PILATI

Centro del CNR per lo Studio delle Relazioni tra Struttura e Reattività Chimica, c/o Dipartimento di Chimica Fisica ed Elettrochimica dell'Università, via Golgi 19, *I*-20133 *Milano, Italy*

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Abstract. (I*a*): $C_{22}H_{26}N_6O_2.\frac{1}{2}CH_4O$, $M_r = 422{\cdot}5$, triclinic, $P\bar{1}$, $a = 10{\cdot}307$ (2), $b = 10{\cdot}378$ (2), $c = 11{\cdot}959$ (2) Å, $\alpha = 69{\cdot}28$ (2), $\beta = 69{\cdot}07$ (1), $\gamma = 69{\cdot}57$ (1)°, $V = 1080{\cdot}6$ (4) Å^3, $Z = 2$, $D_m = 1{\cdot}28$, $D_x = 1{\cdot}298$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu =$ 0·08 mm^{-1}, $F(000) = 450$, room temperature, $R =$ 0·047, $wR = 0{\cdot}046$ for 3235 observed reflections with $I > \sigma(I)$. (II*b*): $C_{17}H_{19}N_3O_6$, $M_r = 361{\cdot}4$, orthorhombic, *Pbca*, $a = 8{\cdot}313$ (2), $b = 16{\cdot}156$ (7), $c =$ 26·094 (9) Å, $V = 3505$ (2) Å^3, $Z = 8$, density not measured, $D_x = 1{\cdot}370$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}10$ mm^{-1}, $F(000) = 1520$, room temperature, $R = 0{\cdot}083$, $wR = 0{\cdot}062$ for 1321 observed reflections with $I > \sigma(I)$. The two structures demonstrate the existence of 1,8a-dihydro-1,2-benzodiazines, which cannot be isolated in the oxidation reaction of N^2-alkylamino-N^1-(2,6-dimethylphenyl)formamidines with MnO_2 in CH_2Cl_2. In fact, the reaction either continues to form the dimer (I) or, in the presence of an excess of dimethyl acetylendicarbonate, gives (II). The dienophilic attack occurs in the *endo* position. The 'common' part of both molecules shows no substantial differences in geometrical terms.

Introduction. Within a framework of research on triazadienes of the type (IV), as precursors of 1,2,4-benzotriazines or 1,2,4-benzotriazepines, Garanti (1986) oxidized the azoketimine (III) with MnO_2 in CH_2Cl_2. The reaction product was a dimer of (IV), to which the structure (I) was tentatively attributed on the basis of NMR and mass spectroscopy. The hypothetical intermediate (V) was not isolated and its

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