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Short Communication

Crystal Conformation of Cyclohexasarcosyl $2CH_3OH$ at −156°C

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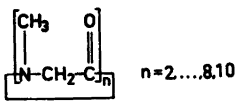
With exception for the case $n=6$, the crystal structures of cyclic oligopeptides of sarcosine with the general formula I are known.[1a-g]



(I)

For $n=2$, 3, 4, and 8 the conformations could be predicted on the basis of NMR-data.[2] For $n=5$, 6, 7, and 10 no conformational evidences are obtainable from NMR-spectroscopy. The crystal structure of cyclohexasarcosyl, $C_{18}H_{30}N_6O_6$, (crystallizing with two molecules of methanol per formula unit) is now reported.

The crystals belong to the orthorhombic system with space group $Pna2_1$ and cell dimensions $a=14.379(6)$ Å, $b=10.203(4)$ Å, $c=16.236(5)$ Å, and $Z=4$ ($D_m=1.35$ g cm^{-3}, $D_x=1.36$ g cm^{-3}).

With $2\theta_{max}=50°$ and Mo$K\alpha$-radiation 2165 independent reflections were measured on an automatic four-circle diffractometer. The crystals are unstable at room temperature and data were therefore collected at −156 °C. Using an observed − unobserved cutoff at $2.5\sigma(I)$, 1264 reflections were recorded as observed. No corrections for absorption or secondary extinction were applied (crystal size $0.3\times0.2\times0.3$ mm^3).

The structure was solved by direct methods [3] and refined by full-matrix least-squares technique.[4*] Hydrogen atom positions were partly calculated and partly localized in difference Fourier maps (except for those of the methanol molecules which remained undetermined). Anisotropic temperature factors were introduced for O, N and C atoms and weights in least-

* All programs used (except those for phase determination) are included in this reference.

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations. The expression for anisotropic vibration is $\exp[-2\pi^2(h^2a^{*2}U11+\cdots+2klb^*c^*U23)]$. Hmn is bonded to Cm, HMmn to CMm and HOm to Om.

ATOM	x	y	z	U11	U22	U33	U12	U13	U23
O1	.2194(3)	.8173(5)	.7773(8)	.0291(29)	.0429(32)	.0177(26)	.0045(28)	.0026(24)	-.0035(26)
O2	.0878(4)	.9082(5)	1.0045(3)	.0267(32)	.0486(39)	.0325(33)	-.0169(30)	-.0010(27)	-.0041(28)
O3	.3481(3)	1.0146(5)	1.0759(3)	.0262(30)	.0262(32)	.0258(30)	-.0012(26)	.0029(23)	-.0001(27)
N1	.3702(4)	.7744(6)	.8693(3)	.0127(31)	.0315(45)	.0159(29)	-.0018(31)	-.0054(25)	-.0059(29)
N2	.1788(4)	.9853(6)	.8588(3)	.0287(36)	.0304(37)	.0119(30)	.0098(35)	-.0025(29)	-.0013(31)
N3	.1597(4)	1.0609(6)	1.0821(3)	.0272(34)	.0325(37)	.0135(30)	-.0075(31)	.0009(30)	-.0012(32)
C1	.2775(5)	.8160(9)	.9158(5)	.0174(43)	.0298(58)	.0249(41)	.0045(42)	-.0016(36)	-.0072(41)
C2	.1828(7)	1.0671(10)	.9348(5)	.0245(55)	.0394(58)	.0175(45)	.0054(46)	-.0065(38)	-.0023(43)
C3	.2236(6)	1.1717(8)	1.0893(5)	.0267(45)	.0275(49)	.0169(39)	-.0018(39)	.0035(41)	-.0099(42)
CC1	.2211(5)	.8778(7)	.8446(4)	.0097(38)	.0325(46)	.0187(40)	-.0025(37)	.0007(32)	-.0002(37)
CC2	.1386(5)	1.0028(8)	1.0094(4)	.0176(42)	.0345(48)	.0266(42)	.0025(42)	.0048(35)	-.0001(40)
CC3	.3266(5)	1.1312(7)	1.0777(4)	.0382(48)	.0179(44)	.0017(38)	.0342(40)	-.0002(35)	-.0048(35)
CM1	.3896(8)	.6383(10)	.8763(7)	.0311(61)	.0295(60)	.0317(58)	-.0048(50)	-.0058(55)	-.0007(50)
CM2	.1146(7)	1.0367(11)	.7937(6)	.0172(47)	.0552(73)	.0222(48)	.0058(47)	-.0064(41)	-.0053(49)
CM3	.1265(7)	1.0028(11)	1.1684(5)	.0306(52)	.0424(65)	.0277(48)	-.0171(52)	.0002(42)	.0188(53)
O7	.4500(5)	1.2388(7)	.8254(4)	.0705(49)	.0516(43)	.0789(49)	-.0355(45)	.0165(36)	.0075(44)
C7	.3588(6)	1.2840(9)	.8399(5)	.0493(63)	.0672(82)	.0558(59)	.0212(55)	.0091(49)	.0186(54)

ATOM	x	y	z	B	ATOM	x	y	z	B
H11	.279(4)	.882(6)	.958(4)	2.8	H12	.248(3)	.734(6)	.937(3)	2.8
H21	.159(5)	1.145(7)	.923(4)	2.8	H22	.240(5)	1.071(7)	.947(4)	2.8
H31	.225(5)	1.238(8)	1.136(4)	2.8	H32	.211(4)	1.256(7)	1.053(3)	2.8
HM11	.440(6)	.626(8)	.857(5)	2.8	HM12	.342(9)	.682(14)	.838(8)	2.8
HM13	.385(8)	.592(13)	.930(7)	2.8	HM21	.071(8)	.975(10)	.768(6)	2.8
HM22	.157(13)	1.078(18)	.758(12)	2.8	HM23	.078(9)	1.111(13)	.817(8)	2.8
HM31	.071(10)	1.053(13)	1.180(8)	2.8	HM32	.177(4)	1.089(5)	1.282(3)	2.8
HM33	.112(6)	.926(10)	1.154(6)	2.8	H07	.439(12)	1.153(17)	.858(11)	2.8

squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as

$$\sigma(I) = [C_T + (0.02\ C_N)^2]^{\frac{1}{2}}$$

where C_T is the total number of counts and C_N the net count. The form factors used were those of Hanson *et al.*[5] except for hydrogen.[6] The molecule has a pseudo centre of symmetry at $X_0 = 0.3789$, $Y_0 = 1.0012$, $Z_0 = 0.9774$. This fact was indeed reflected in large correlation coefficients between corresponding positional as well as thermal parameters. The refinement converged at $R_w = 8.5$ % ($R = 9.1$ %) and some of the bond distances thus obtained were unreasonable. By introducing the extra symmetry in the least-squares refinement, the final R_w-value was 8.0 % ($R = 8.9$ %) for 1264 observed reflections, and the bond distances and angles (given in Table 2) do not deviate significantly from normal values.[1f] Final fractional coordinates (for half the molecule) together with thermal parameters are listed in Table 1. Positional parameters for the pseudo centrosymmetrically related atoms are given by $X' = 2X_0 - X$, $Y' = 2Y_0 - Y$, $Z' = 2Z_0 - Z$. A Fourier synthesis with $Pna2_1$ symmetry and phases corresponding to the parameters of Table 1 (and their pseudo-equivalents) were calculated. By averaging the mean values of pseudo-related peak coordinates no significant shifts in X_0, Y_0, Z_0 were obtained.

Table 2. Bond distances, bond angles and dihedral angles with estimated standard deviations.

DISTANCE	(Å)	DISTANCE	(Å)
CC1 - O1	1.25(1)	CC2 - O2	1.21(1)
CC3 - O3	1.23(1)	N1 - CM1	1.43(1)
N2 - CM2	1.43(1)	N3 - CM3	1.48(1)
N1 - CC3′	1.34(1)	N2 - CC1	1.34(1)
N3 - CC2	1.36(1)	N1 - C1	1.46(1)
N2 - C2	1.50(1)	N3 - C3	1.46(1)
C1 - CC1	1.54(1)	C2 - CC2	1.51(1)
C3 - CC3	1.55(1)	C7 - O7	1.42(1)
O7 - O3	2.76(1)		

ANGLE	(°)	ANGLE	(°)
O1 - CC1 - C1	117.9(6)	O2 - CC2 - C2	122.8(7)
O3 - CC3 - C3	120.2(7)	O1 - CC1 - N2	122.7(7)
O2 - CC2 - N3	122.6(7)	O3 - CC3 - N1′	123.1(7)
CM1 - N1 - CC3′	124.6(7)	CM2 - N2 - CC1	118.7(7)
CM3 - N3 - CC2	120.1(6)	CM1 - N1 - C1	120.1(7)
CM2 - N2 - C2	117.7(7)	CM3 - N3 - C3	116.3(6)
CC3′ - N1 - C1	115.2(6)	CC1 - N2 - C2	122.9(6)
CC2 - N3 - C3	123.2(6)	N1 - C1 - CC1	112.0(6)
N2 - C2 - CC2	112.0(7)	N3 - C3 - CC3	112.7(8)
C1 - CC1 - N2	119.2(7)	C2 - CC2 - N3	114.6(7)
C3 - CC3 - N1′	116.6(6)	C7 - O7 - O3	93.3(5)
O7 - O3 - CC3	146.5(5)		

DIHEDRAL ANGLE	(°)
C3′ - CC3′ - N1 - C1	168.5(6)
CC3′ - N1 - C1 - CC1	74.9(8)
N1 - C1 - CC1 - N2	-137.6(7)
C1 - CC1 - N2 - C2	13.5(10)
CC1 - N2 - C2 - CC2	-75.1(9)
N2 - C2 - CC2 - N3	169.5(6)
C2 - CC2 - N3 - C3	-3.6(10)
CC2 - N3 - C3 - CC3	-73.5(9)
N3 - C3 - CC3 - N1′	166.5(6)

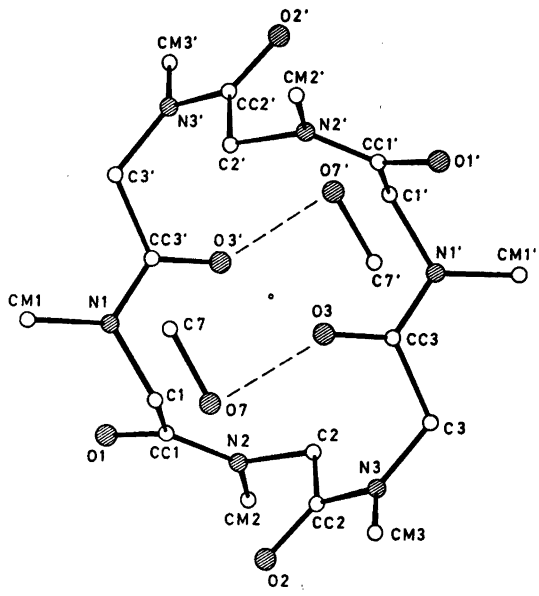


Fig. 1. Schematic drawing of the molecule.

The principal axes of the thermal vibration ellipsoids for oxygen, nitrogen, and carbon atoms were calculated from the temperature parameters of Table 1. Maximum r.m.s. amplitudes for the atoms of the cyclohexasarcosyl molecule range from 0.17 to 0.24 Å, while those of C7 and O7 are 0.30 Å.

Fig. 1 is a schematic drawing of the molecule where the pseudo centre of symmetry, the two methanol molecules, and the numbering of atoms is indicated. It may also be seen that the configuration of the six *N*-methyl amide groups has the sequence, *cis*, *cis*, *trans*, *cis*, *cis*, *trans*. Corresponding sequences for other cyclic peptides of sarcosine are given in Ref. 1g. It should be pointed out that no conformation with more *trans*- than *cis*-configurations has been observed. Another striking feature is the general occurrence of sequences of only *cis*- or only *trans*-amide configuration. The torsion angles ϕ(C−N) and ψ(C−CC) of these compounds will be discussed elsewhere.[7]

A list of observed and calculated structure factors is available from the author.

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