Journal of Mathematical Chemistry 13(1993)53–57

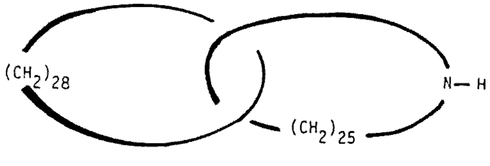
Real molecules as models for mathematical chemistry

II. Crystallographic data of the [2]-[azacyclohexacosane]-[cyclooctacosane]-catenane

Walter Littke and Enno Logemann
Chemisches Laboratorium der Universität Freiburg/Brsg., Albertstrasse 21, D-7800 Freiburg/Brsg., Germany

Well-shaped single crystals of the [2]-[azacyclohexacosane]-[cyclooctacosane]-catenane were crystallized from butyl acetate solution. Investigating monocrystals with X-rays, we have found a tetragonal symmetry: $a = b = 10.48$ Å, $c = 52.15$ Å; four molecules per unit cell; space lattice type $I4_1$. The scattering intensities of the crystals had been extremely weak at higher theta values. We tried to calculate the structure with only 253 reflections and therefore the refinements (full matrix) converged to $R = 0.15$.

Molecules with interlocking rings, named catenanes, can be obtained in preparative yields by directed synthesis or by synthesis according to statistical methods [1–3]. In 1972, we published the synthesis of the [2]-[azacyclohexacosane]-[cyclooctacosane]-catenane



and its acetyl derivative [4,5]. These compounds were the first catenanes to be obtained in crystalline form from solution. The structure has been proven by mass spectrometry [6], ^{1}H and ^{13}C NMR spectrometry [7–9]. In this paper, we report experiments carried out in order to verify the crystal structure of the catenane amine.

Single crystals with dimensions of about 1 × 1 × 0.2 mm were obtained by slow evaporation of butyl acetate solutions at room temperature. The crystals grew in an apparatus especially designed to allow observation of the growth process and at the same time optimizing the conditions for crystallization.

Rotating, oscillating and precession photographs with Cu K_α radiation resulted in the following data: tetragonal crystal symmetry with $a = b = 10.48$ Å and $c = 52.15$ Å, $V = 5727.7$ Å^3, space group $I4_1$. Based on the molecular weight of $M = 758.45$ for $C_{53}H_{107}N$ and four molecules per unit cell, the density is calculated as $\rho = 0.88$ g cm^{-3}. The density $\rho = 0.91$ g cm^{-3} experimentally obtained by the suspension method (methanol/water) is in good conformity with the expected value.

X-ray intensities were measured on an automatic Nonius CAD-4 diffractometer, with graphite-monochromated Mo K_α radiation and pulse height discrimination. According to usual criteria, only 253 structure amplitudes with $I \leq 2\sigma(I)$ have been processed as observed. As shown in fig. 1, the spot intensities break down abruptly near $\Theta = 10°$. This effect drastically reduces the number of structure amplitudes to be determined. Therefore, the accuracy of the final result implies uncertainties.

Fig. 1. Rotating crystal photograph; Cu K_α radiation. Note that the intensities of the reflexions abruptly break down at higher Θ values.

According to usual experience, one needs approximately five reflexions per one parameter to be refined (six anisotropic temperature factors U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{23} and three atomic coordinates x y, z for heavier atoms such as carbon and nitrogen, as well as one isotropic temperature factor B and three atomic coordinates x, y, z for the hydrogen atoms). In our case, 914 parameters ($54 \times 9 + 107 \times 4$) have to be refined, and therefore 4570 instead of 253 reflexions should be available in order to obtain a good reliability.

The phase problem could be solved by direct methods (Multan 74). Isotropic and anisotropic refinements of the carbon atomic coordinates resulted in an R-value of 0.164. The positions of hydrogen atoms were partially deduced by difference Fourier synthesis, but mainly generated by the numerical method. Further refinements of all atomic parameters converged to a final R-value of 0.151.

The molecular structure of the catenane is presented in fig. 2. For clarity, the hydrogen atoms are not plotted. Both rings approximately correspond to the cyclic geometry. The position of the nitrogen atom inside the smaller ring could not be definitely identified. The least-square planes of both rings are twisted against each

Table 1

Atom coordinates.

Type of atom	x	y	z	Type of atom	x	y	z
C1	– 0.3199	0.5385	0.4910	C29	0.4553	0.4930	0.4225
C2	– 0.3030	0.4044	0.5028	C30	0.3469	0.5771	0.4326
C3	– 0.2630	0.3100	0.4816	C31	0.2784	0.4930	0.4526
C4	– 0.1991	0.1933	0.4941	C32	0.2357	0.5771	0.4753
C5	– 0.1142	0.1268	0.4740	C33	0.2212	0.4935	04993
C6	– 0.0120	0.0483	0.4881	C34	0.2313	0.5771	0.5234
C7	0.1024	0.0252	0.4698	C35	0.2757	0.4930	0.5460
C8	0.2211	– 0.0125	0.4856	C36	0.3452	0.5771	0.5659
C9	0.3388	0.0252	0.4698	C37	0.4347	0.4930	0.5820
C10	0.4541	0.0415	0.4878	C38	0.5439	0.5771	0.5924
C11	0.5525	0.1268	0.4740	C39	0.6609	0.4930	0.5983
C12	0.6412	0.1896	0.4939	C40	0.7815	0.5771	0.5980
C13	0.7056	0.3065	0.4814	C41	0.8985	0.4930	0.5932
C14	0.7374	0.4044	0.5028	C42	1.0052	0.5771	0.5820
C15	0.7588	0.5365	0.4909	C43	1.0952	0.4930	0.5659
C16	0.7450	0.6359	0.5123	C44	1.1637	0.5771	0.5464
C17	0.7262	0.7669	0.5004	C45	1.2063	0.4930	0.5233
C18	0.6411	0.8343	0.5205	C46	1.2236	0.5771	0.4993
C19	0.5565	0.9349	0.5074	C47	1.2050	0.4930	0.4753
C20	0.4663	0.9960	0.5272	C48	1.1621	0.5771	0.4526
C21	0.3524	1.0519	0.5122	C49	1.0939	0.4930	0.4327
C22	0.2326	1.0481	0.5293	C50	1.0038	0.5771	0.4167
C23	0.1137	1.0453	0.5119	C51	0.8970	0.4930	0.4054
C24	0.0001	0.9901	0.5269	C52	0.7809	0.5771	0.3996
C25	– 0.1049	0.9502	0.5080	C53	0.6626	0.4930	0.4047
C26	– 0.1874	0.8456	0.5205				
C27	– 0.2563	0.7669	0.5004	N1	0.5397	0.5615	0.4044
C28	– 0.2951	0.6381	0.5124				

Table 2

Bond length (Å).

C1/C2	1.5445	C19/C20	1.5397	C37/C38	1.5430
C2/C3	1.5420	C20/C21	1.5429	C38/C39	1.5411
C3/C4	1.5393	C21/C22	1.5407	C39/C40	1.5409
C4/C5	1.5417	C22/C23	1.5419	C40/C41	1.5307
C5/C6	1.5379	C23/C24	1.5377	C41/C42	1.5390
C6/C7	1.5516	C24/C25	1.5356	C42/C43	1.5401
C7/C8	1.5437	C25/C26	1.5409	C43/C44	1.5395
C8/C9	1.5353	C26/C27	1.5170	C44/C45	1.5423
C9/C10	1.5398	C27/C28	1.5425	C45/C46	1.5419
C10/C11	1.5430	C28/C1	1.5503	C46/C47	1.5435
C11/C12	1.5411	C29/C30	1.5315	C47/C48	1.5432
C12/C13	1.5433	C30/C31	1.5430	C48/C49	1.5380
C13/C14	1.5525	C31/C32	1.5426	C49/C50	1.5379
C14/C15	1.5337	C32/C33	1.5357	C50/C51	1.5418
C15/C16	1.5338	C33/C34	1.5361	C51/C52	1.5326
C16/C17	1.5196	C34/C35	1.5438	C52/C53	1.5442
C17/C18	1.5472	C35/C36	1.5444	C53/N1	1.4746
C18/C19	1.5377	C36/C37	1.5369	N1/C29	1.4797

Table 3

Bond angle (°).

C2 /C1 /C28	107.8	C19/C20/C21	107.0	C36/C37/C38	108.5
C3 /C2 /C1	109.2	C20/C21/C22	109.1	C37/C38/C39	109.5
C2 /C3 /C4	108.9	C21/C22/C23	108.6	C38/C39/C40	108.9
C3 /C4 /C5	108.8	C22/C23/C24	109.5	C39/C40/C41	109.2
C5 /C6 /C7	109.1	C23/C24/C25	109.3	C41/C42/C43	108.9
C6 /C7 /C8	109.5	C24/C25/C26	108.9	C42/C43/C44	109.0
C7 /C8 /C9	107.2	C25/C26/C27	111.2	C43/C44/C45	109.0
C8 /C9 /C10	109.4	C26/C27/C28	108.7	C44/C45/C46	109.3
C9 /C10/C11	107.7	C1 /C28/C27	109.9	C45/C46/C47	108.5
C10/C11/C12	109.6	C30/C29/N1	112.6	C46/C47/C48	109.5
C11/C12/C13	108.6	C31/C30/C29	104.4	C47/C48/C49	109.0
C12/C13/C14	108.3	C30/C31/C32	109.1	C48/C49/C50	108.9
C13/C14/C15	109.7	C31/C32/C33	109.2	C49/C50/C51	109.0
C14/C15/C16	107.7	C32/C33/C34	109.6	C50/C51/C52	108.8
C15/C16/C17	109.2	C33/C34/C35	108.7	C51/C52/C53	106.0
C16/C17/C18	102.1	C36/C35/C34	109.3	N1 /C53/C52	114.9
C17/C18/C19	110.1	C35/C36/C37	109.1	C53/N1 /C29	106.2
C18/C19/C20	109.9				

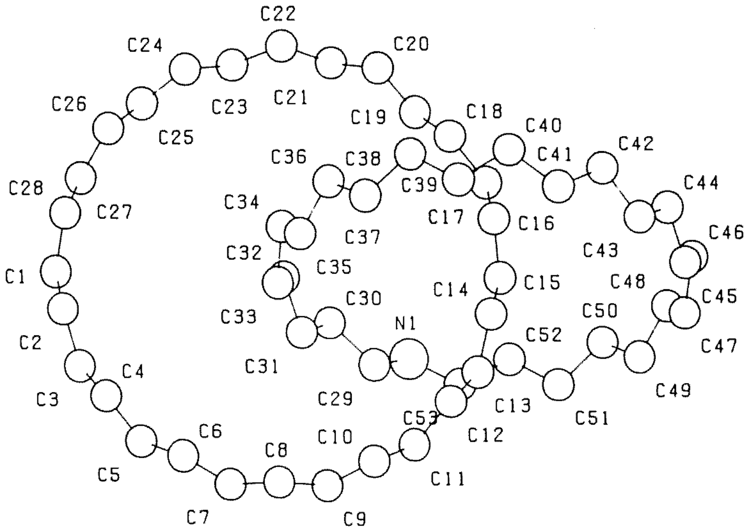


Fig. 2. Molecular geometry of the [2]-[azacyclohexacosane]-[cyclooctacosane]-catenane. Program PLUTO. The hydrogen atoms are not plotted.

other by 78.8°, i.e. these rings are nearly rectangular against each other. Compared with the values to be expected, bond lengths as well as bond angles do not show remarkable deviations. In tables 1–3, bond lengths, bond angles and atom coordinates are listed.

Due to this experience, we will attempt to collect high-energy neutron scattering data. This should provide a chance for further improvements of the structure.

References

[1] G. Schill, Catenanes, rotaxanes and knots, in: *Organic Chemistry*, A Series of Monographs, Vol. 22, ed. A.T. Blomquist (Academic Press, New York, 1971).
[2] G. Schill, E. Logemann and W. Littke, Chemie in uns. Zeit 18(1984)130.
[3] C.O. Dietrich-Buchecker and J.P. Sauvage, Chem. Rev. 87(1987)795.
[4] G. Schill, E. Logemann and W. Vetter, Angew. Chem. Int. Ed. 11(1972)1089.
[5] E. Logemann, G. Schill and W. Vetter, Chem. Ber. 111(1978)2615.
[6] W. Vetter, E. Logemann and G. Schill, Org. Mass Spectr. 12(1977)351.
[7] H. Fritz, E. Logemann, G. Schill and T. Winkler, Chem. Ber. 109(1976)1258.
[8] H. Fritz, P. Hug, H. Sauter, T. Winkler and E. Logemann, Org. Magn. Reson. 9(1977)108.
[9] H. Fritz, P. Hug, H. Sauter and E. Logemann, J. Magn. Reson. 21(1976)373.