Acta Chemica Scandinavica A 33 (1979) 199–201

The Crystal Conformations of Cyclotetraeicosane and Cyclohexaeicosane at —160 °C

P. GROTH

Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystals of $(CH_2)_{24}$ belong to the monoclinic system with cell dimensions $a=27.645(12)$ Å, $b=8.030(3)$ Å, $c=10.167(3)$ Å, $\beta=99.42(3)$°, space group *Cc* and $Z=4$. The $(CH_2)_{26}$ crystals are triclinic with cell dimensions (for Dirichlets reduced cell) $a=5.306(3)$ Å, $b=7.954(4)$ Å, $c=14.767(8)$ Å, $\alpha=101.82(4)$°, $\beta=95.96(4)$°, $\gamma=97.34(4)$°, space group $P\bar{1}$ and $Z=1$. The structures were solved by direct methods and refined by full-matrix least-squares to *R*-values of 7.2 % for $(CH_2)_{24}$ and 10.8 % for $(CH_2)_{26}$. Both rings have a compact conformation with the shape of two parallel straight chains bridged at both ends. The 24-membered ring has approximate C_2 symmetry, while $(CH_2)_{26}$ is centrosymmetric.

Cycloalkanes $(CH_2)_n$ with $n=8,9,...$ melt above 0 °C.[1] However, in the range $n=8,...,21$ many of the apparent melting points are not true melting points, inasmuch as the entropy of fusion is abnormally low. In compensation, there is at least one transition point at lower temperatures in the solid state, with a correspondingly high entropy of transition, so that the upper solid phase has to be regarded as already more than "half-melted".

Crystallographic conformational evidence on the phases stable just below the melting points is almost completely lacking. Cyclooctane has been studied,[2] but the cubic structure is highly disordered and no conclusions concerning the ring conformation could be drawn. Disordered structures seem likely also in the cases $n=9$ and 10.[3] Although the structure of cycloundecanone is determined,[4] the corresponding cycloalkane has hot been examined. In fact, the structures of cyclododecane[5] and cyclotetradecane[6] are the only two known in this group. All other crystallographic conformational studies have been based upon structure determinations of various derivatives.[7]

Preliminary investigations indicate disordered structures for $n=15$ and 19. In the case of cyclohexadecane the fall of intensities with increasing scattering angle is much smaller, but all crystals examined so far have been twins.

In the group $(CH_2)_{15}$ to $(CH_2)_{21}$ there are several possible conformations, one of which is a more or less "circular disk". Above $n=21$ the interior "hole" in such rings becomes too large, and the molecule collapses to the shape of two parallel straight chains bridged at both ends.[1] This is confirmed (for $n=34$) by the crystal structure determination of cyclotetratricontane.[8] In order to verify the postulate for smaller values of *n*, crystal structure investigations of cyclotetraeicosane ($C_{24}H_{48}$) and cyclohexaeicosane ($C_{26}H_{52}$) have been carried out by growing the crystals above 0 °C and then cooling them rapidly to *ca.* −160 °C.

The crystals of $(CH_2)_{24}$ belong to the monoclinic system with cell dimensions $a=27.645(12)$ Å, $b=8.030(3)$ Å, $c=10.167(3)$ Å, $\beta=99.42(3)$°, space group *Cc* and $Z=4$, ($D_x=1.00$ g cm^{-3}, $D_m=1.02$ g cm^{-3}. The $(CH_2)_{26}$ crystals are triclinic with cell dimensions (for Dirichlets reduced cell) $a=5.306(3)$ Å, $b=7.954(4)$ Å, $c=14.767(8)$ Å, $\alpha=101.82(4)$°, $\beta=95.96(4)$°, $\gamma=97.34(4)$°, space group $P\bar{1}$, and $Z=1$ ($D_x=1.01$ g cm^{-3}, $D_m=1.00$ g cm^{-3}). 828 (for $n=24$) and 1436 (for $n=26$) reflections were measured on an automatic four circle diffractometer (Mo*K*α-radiation). The structures were solved by direct methods[9] and refined by full-matrix least-squares technique.[10]* Anisotropic temperature factors were

---

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

0302-4377/79/030199-03$02.50

Table 1. Final fractional coordinates with estimated standard deviations for $(CH_2)_{24}$. Hmn is bonded to Cm.

ATOM	X	Y	Z
C1	.5855(0)	.1123(20)	.9017(0)
C2	.6184(9)	.0846(30)	.7952(26)
C3	.6722(10)	.0888(27)	.8458(27)
C4	.7105(9)	.0925(26)	.7444(25)
C5	.7605(8)	.0817(17)	.7973(22)
C6	.7917(12)	.0978(31)	.6854(30)
C7	.8502(9)	.0677(27)	.7451(25)
C8	.8774(9)	.1068(29)	.6290(26)
C9	.9332(9)	.0700(23)	.6885(22)
C10	.9678(5)	.0940(31)	.5830(14)
C11	.9657(10)	.2750(30)	.5213(27)
C12	.9826(9)	.4173(25)	.6265(24)
C13	.9660(9)	.5984(24)	.5730(24)
C14	.9137(11)	.6248(29)	.5525(29)
C15	.8856(9)	.5898(21)	.6656(23)
C16	.8317(11)	.6151(30)	.6339(26)
C17	.8058(11)	.6003(28)	.7563(28)
C18	.7502(10)	.5956(29)	.7220(25)
C19	.7228(9)	.6058(26)	.8421(22)
C20	.6655(12)	.6104(34)	.8036(29)
C21	.6421(9)	.6210(28)	.9355(29)
C22	.5834(12)	.5885(36)	.9002(29)
C23	.5687(10)	.4221(25)	.8627(26)
C24	.5911(8)	.2868(22)	.9566(24)
H11	.551	.090	.858
H12	.594	.023	.974
H21	.612	.178	.730
H22	.612	-.023	.752
H31	.680	-.007	.907
H32	.679	.196	.901
H41	.702	.191	.688
H42	.700	-.012	.686
H51	.768	-.030	.844
H52	.770	.172	.863
H61	.789	.209	.646
H62	.784	.009	.617
H71	.856	-.045	.780
H72	.860	.152	.819
H81	.874	.219	.602
H82	.867	.024	.558
H91	.938	-.048	.719
H92	.944	.146	.765
H101	.957	.021	.510
H102	1.001	.075	.629
H111	.932	.304	.486
H112	.988	.278	.457
H121	1.021	.417	.646
H122	.971	.346	.713
H131	.979	.616	.491
H132	.981	.679	.644
H141	.900	.543	.478
H142	.907	.738	.522
H151	.899	.673	.737
H152	.895	.475	.700
H161	.821	.512	.574
H162	.825	.714	.589
H171	.815	.698	.814
H172	.814	.494	.807
H181	.741	.498	.670
H182	.741	.701	.666
H191	.732	.713	.894
H192	.734	.510	.904
H201	.659	.490	.763
H202	.657	.691	.741
H211	.650	.735	.970
H212	.657	.536	1.001
H221	.571	.676	.830
H222	.571	.626	.985
H231	.580	.403	.774
H232	.533	.419	.852
H241	.575	.285	1.040
H242	.625	.303	.988

introduced for carbon atoms. Hydrogen atoms, the positions of which were calculated, were included in the structure factor calculations, but not refined. Weights for least-squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as

Table 2. Final fractional coordinates with estimated standard deviations for $(CH_2)_{26}$. Hmn is bonded to Cm.

ATOM	X	Y	Z
C1	-1.2408(9)	.0472(6)	-.3887(3)
C2	-1.1993(9)	.0676(6)	-.2844(3)
C3	-.9215(9)	.1270(6)	-.2385(3)
C4	-.8948(9)	.1571(6)	-.1325(3)
C5	-.6219(9)	.2100(6)	-.0830(2)
C6	-.6026(9)	.2431(6)	.0232(2)
C7	-.3297(9)	.2913(6)	.0741(2)
C8	-.3155(9)	.3164(6)	.1800(3)
C9	-.0448(9)	.3696(6)	.2332(3)
C10	-.0401(9)	.3856(6)	.3379(3)
C11	.2219(9)	.4584(6)	.3960(2)
C12	.3352(9)	.6409(6)	.3876(2)
C13	.1680(9)	.7773(6)	.4199(3)
H11	-1.145	-.042	-.420
H12	-1.434	.006	-.413
H21	-1.264	-.048	-.269
H22	-1.309	.155	-.255
H31	-.852	.239	-.254
H32	-.813	.037	-.261
H41	-.970	.046	-.116
H42	-.998	.250	-.109
H51	-.544	.319	-.101
H52	-.519	.115	-.105
H61	-.687	.134	.041
H62	-.704	.340	.046
H71	-.249	.403	.060
H72	-.228	.198	.051
H81	-.394	.204	.194
H82	-.424	.409	.202

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

where C_T is the total number of counts and C_N the net count. The final R-values are $R = 7.2\,\%$ ($R_w = 5.3\,\%$) for $(CH_2)_{24}$ and $R = 10.8\,\%$ ($R_w = 11.8\,\%$) for $(CH_2)_{26}$. Poor quality of the crystals must take the main responsibility for these high values.

Final fractional coordinates with estimated standard deviations are given in Tables 1 and 2 (the thermal parameters are available from the author). Figs. 1 and 2 show the molecular conformations, the numbering of atoms, and the dihedral angles. Considerations based upon modified space-filling molecular models[1] show that the series with $n = 14, 18, 22, 26, \ldots$ have strain-free compact conformations, whereas those of the series with $n = 16, 20, 24, \ldots$ must either form an inner hole to become strain-free, or be strained to become compact. Fig. 1 shows that the 24-membered ring has a compact conformation with approximate C_2 symmetry. It may be seen that the strain to a small extent is reflected in the *trans* torsion angles which deviate slightly more from 180° than those of the centrosymmetric 26-membered ring illustrated in Fig. 2. However, the average C−C−C bond angles of 113.2(4) and 113.9(1)°, which are typical values for hydrocarbones, necessitate deviations from ideal torsion angles in the case of cyclic com-

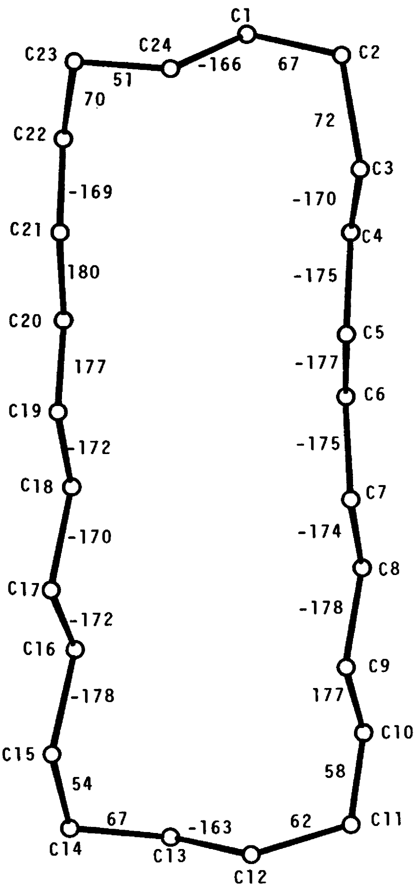

Fig. 1. Schematic drawing showing the conformation of $(CH_2)_{24}$. Estimated standard deviations in dihedral angles are about 2°.

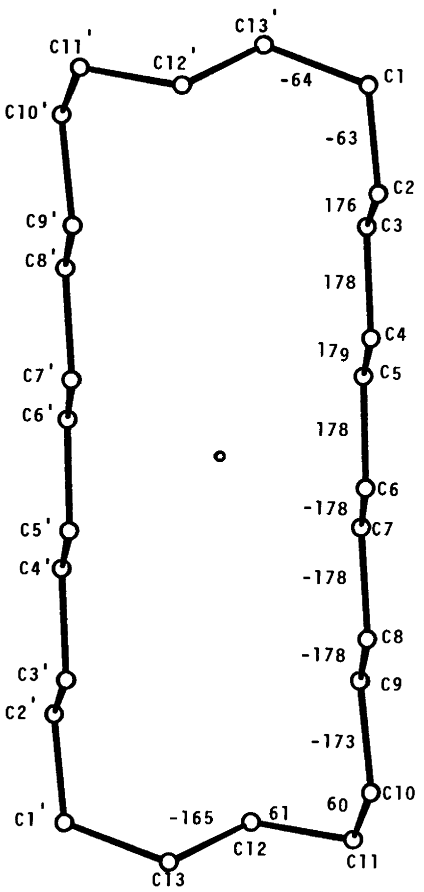

Fig. 2. Schematic drawing showing the conformation of $(CH_2)_{26}$. Estimated standard deviations in dihedral angles are about 0.5°.

pounds. It should be noted that the largest deviations occur at the chain bridges: 17 and 14° for $(CH_2)_{24}$, and 15° for $(CH_2)_{26}$. Average values for the rest of the *trans* dihedral angles are 5.3 and 2.7°, respectively. This effect was observed also for cyclotetradecane (9.9 and 3.7°).[6] The strain in the 24-ring as compared to that of the 26-ring is somewhat more pronounced in the divergence from 60° of the *gauche* torsion angles; in average 6.9 and 2.0°, respectively. Average C–C bond distances for $(CH_2)_{24}$ and $(CH_2)_{26}$, respectively, are 1.539(6) and 1.528(2) Å.

Acknowledgement. The author would like to thank Dr. G. Borgen for supplying the compounds.

REFERENCES

1. Dale, J. *J. Chem. Soc. 85* (1963) 93.
2. Sands, D. and Day, V. *Acta Crystallogr. 19* (1965) 278.
3. Dunitz, J. D. and Prelog, V. *Angew. Chem. 72* (1960) 896.
4. Groth, P. *Acta Chem. Scand. A 28* (1974) 294.
5. Dunitz, J. D. and Shearer, H. M. M. *Helv. Chim. Acta 43* (1960) 18.
6. Groth, P. *Acta Chem. Scand. A 30* (1976) 155.
7. Dunitz, J. D. *Perspectives in Structural Chemistry 2* (1968) 1.
8. Kay, H. F. and Newman, B. A. *Acta Crystallogr. B 24* (1968) 615.
9. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A 27* (1971) 368.
10. Groth, P. *Acta Chem. Scand. 27* (1973) 1837.

Received September 11, 1978.