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The Conformations of Cyclotetradeca-1,8-diyne

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A conformational change takes place in the solid at 30° for cyclotetradeca-1,8-diyne. The high-temperature solid phase conformation is indistinguishable by IR- and Raman-spectroscopy from the solution conformation, which is identified by dynamic ^1H and ^{13}C NMR-spectroscopy. Conformational interconversion mechanisms are discussed.

When cyclotetradeca-1,8-diyne was first synthesized,[1] its high melting point and ease of formation were rationalized on the basis of a single strain-free chair-like conformation (A, Fig. 1) although the closely related boat-like conformation B could not be excluded. There are also other possible ways of constructing a ring conformation with staggered pentamethylene chains (C and D), but these contain a larger number of *gauche* bonds and were therefore disregarded. Nevertheless, the crystal conformation, as determined by King [2] using X-ray methods, turned out to be C and not A or B. This result remained unexplained, and conformation C had to be assumed also for the solution, since very similar IR-spectra were observed for the solid, the melt and the solutions (Fig. 2 c,b,a).

We have now found by calorimetry that there is a solid-solid transition point at 30° with relatively small enthalpy and entropy changes ($\Delta H_{tr} = 1.06$ kcal/mol; $\Delta S_{tr} = 3.5$ e.u.) compared with the changes at the melting point (98°; $\Delta H_m = 5.07$ kcal/mol; $\Delta S_m = 13.7$ e.u.). Since there is a considerable heating of the sample by the beam during the IR-measurement, it is clear that our earlier solid spectrum (Fig. 2c) referred to the high-temperature crystal phase, whereas the crystal structure was determined on the low-temperature phase. In fact, the IR-spectrum of a cooled sample (Fig. 2d) is markedly different, and it may be significant that the bands are more numerous and each individual band is no sharper than in the high-temperature solid. It therefore seemed possible that the upper crystal phase and the solution might after all contain the conformation A, and that by cooling the solid there is a change to the more compact conformation C (see Fig. 1). The latter has a lower symmetry in

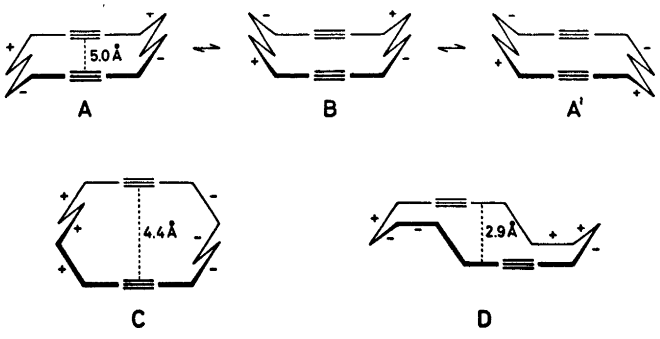

Fig. 1. Possible conformations of cyclotetradeca-1,8-diyne having staggered CH_2-CH_2 bonds. Right- and left-handed *gauche* bonds are indicated by + and − signs.

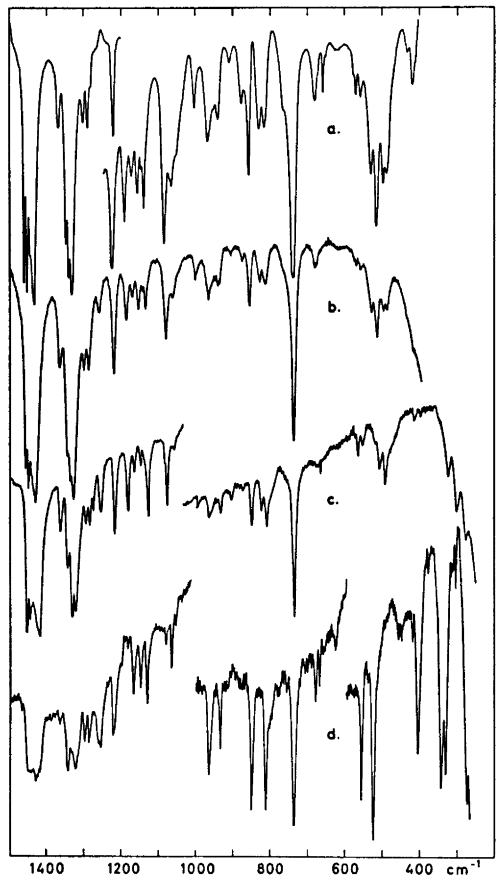

Fig. 2. Infrared spectra of cyclotetradeca-1,8-diyne (a) in solution in CCl_4 (left curve) and in CS_2 (right curve); (b) in liquid film at 110°; (c) in solid film at 40°; and (d) in solid film at −70°.

the pentamethylene chain and must give rise to a greater number of infrared active vibrations.

NMR-SPECTROSCOPY

The 251 MHz ^1H and 63.1 MHz ^{13}C NMR-spectra strongly suggest that A (or B) is in fact the solution conformation. In the compressed ^1H spectrum (Fig. 3) the three bands due to the α-, β-, and γ-protons on cooling broaden at −150° and each then splits up into two bands at −165° ($T_c \sim -160°$ (α-protons)); $\Delta G^{\ddagger} = 5.0 \pm 0.2$ kcal/mol. Only one process is observed. The ^{13}C spectrum on the other hand remains

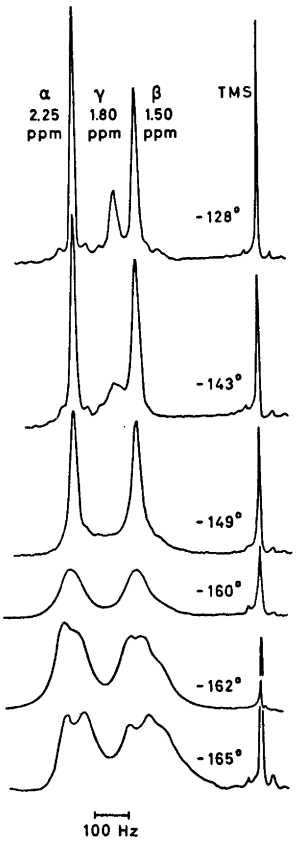

Fig. 3. 251 MHz ^1H spectra at various temperatures of a 1 % solution of cyclotetradeca-1,8-diyne in $CHCl_2F/CHClF_2$ (4:1).

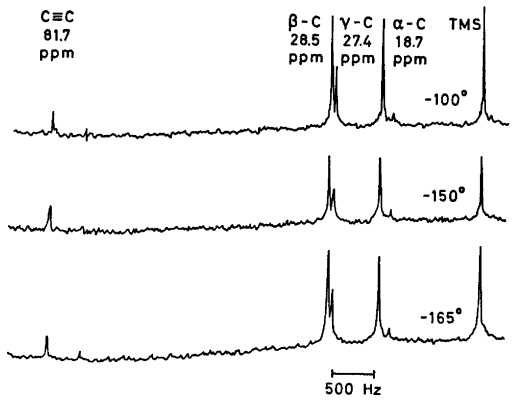

Fig. 4. Proton-decoupled 63.1 MHz ^{13}C Fourier transform spectra (500 transients) at various temperatures of a 4 % solution of cyclotetradeca-1,8-diyne in $CHCl_2F/CHClF_2$ (4:1).

unchanged on cooling through this temperature range (Fig. 4), so that there can be only one type each of all four constitutionally different carbon atoms. The most simple and immediate interpretation is of course that the solution contains the chair-like conformation, and that the geminally non-equivalent hydrogen atoms of each CH_2 become equivalent by direct flipping to the boat-like conformation B and further on to the inverted "chair" A′ (Fig. 1). However, this is an energetically expensive mechanism, since each step must involve a more or less concerted *syn*-eclipsing of two CC-bonds. Also, one cannot *a priori* exclude that the low-temperature spectrum only reflects the apparent symmetry of a rapidly exchanging species of still lower symmetry, such as C or D. We have therefore analysed the situation on the basis of a multistep conformational interconversion scheme constructed on the same principles as earlier [3] for cycloalkanes (Fig. 5).

CONFORMATIONAL INTERCONVERSION PATHS

Assuming that A is the lowest-energy conformation of cyclotetradeca-1,8-diyne, it can be converted over a series of barriers, each involving the full eclipsing of only one CC-bond, to the inverted conformation A′, and this can occur along two different paths (Fig. 5). One path goes through three intermediate conformational minima to B and then through three equivalent minima in the reversed order to A′. The other path goes through nine minima among which are both C and D and their equivalents D′ and C′. Each path, as well as a mixture of both paths in equal or unequal amounts, would satisfy the observed spectra revealing a single process, but it is difficult to estimate which of the several barriers on each is highest and therefore decisive kinetically, and it is equally difficult to guess which of the two paths is actually preferred.

An analogous scheme can be constructed on the assumption that B is the lowest-energy conformation; conformation A then plays the role of an intermediate on one path, and C and D are replaced by similar conformations on the other path. The NMR-spectra can make no distinction between A and B, and it is even possible that the chemical shifts are too close to

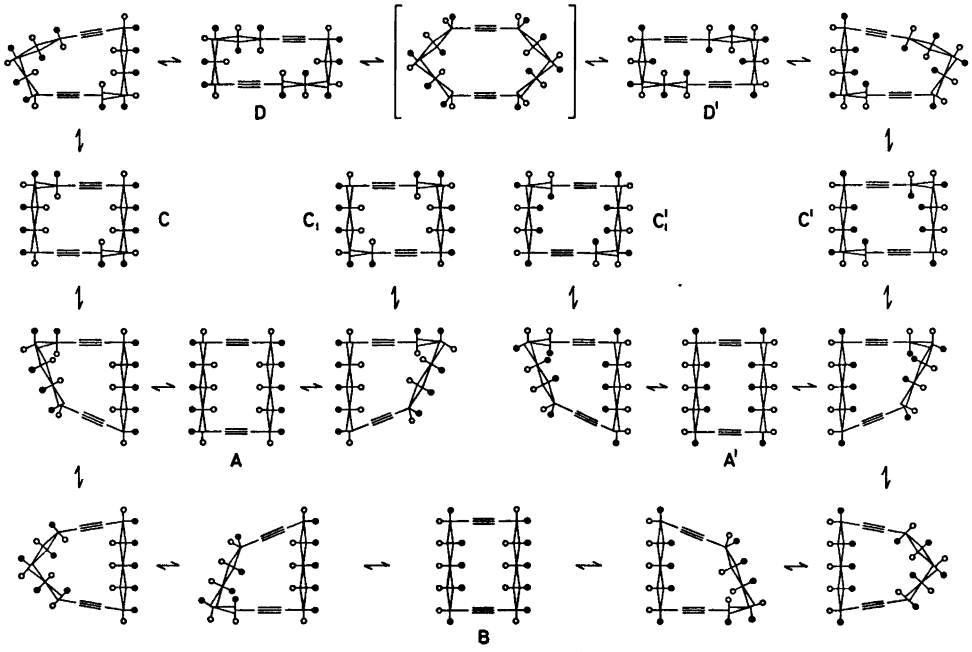

Fig. 5. Conformational interconversion paths for cyclotetradeca-1,8-diyne.

allow detection of a mixture of the two. Also the gas-phase electron-diffraction data, which have been discussed [4] on the basis of the chair-like conformation A of large vibrational amplitudes, would hardly allow a distinction to be made between A and B.

If one of the less symmetric conformations, C or D, had been of lowest energy, two separate processes should have been observed in dynamic NMR-spectroscopy. Thus, the interconversion scheme in Fig. 5 shows that C can either be converted to C′ along the path CDD′C′, whereby unequal α- and β-carbon atoms are fully exchanged, but not their geminally different hydrogen atoms, or it can be converted to C_1 along the path CAC_1, whereby again the carbon atoms but not the hydrogen atoms are exchanged. Only when both processes can occur, will complete exchange of all geminal hydrogen atoms take place, for example by going from C to C_1′ *via* DD′C′A′ or from C′ to C_1 *via* D′DCA. Since the decisive barrier on path CDD′C′ is different from that on path CAC_1, one should expect to observe the high-temperature process only by ^1H spectroscopy and the low-temperature process both by ^1H and ^{13}C spectroscopy. The possibility that the latter has such a low barrier that the coalescence temperature is below −165° seems unlikely. The observed value of 5 kcal/mol is already quite low, considering that full eclipsing of a CC-bond is involved in the barrier and that the conformational minima have completely staggered polymethylene chains and so must be very low in energy.

Thus, also the observation of one, and not two, dynamic processes in NMR-spectroscopy suggests that A (or B) is the solution conformer of cyclotetradeca-1,8-diyne.

CHAIR OR BOAT?

The chair conformation (A) and the boat conformation (B) are expected to have similar energies for the isolated molecule and in solution, since the two pentamethylene chains are too far apart to interact directly, and since there is hardly any rotational barrier for the methyl groups in dimethylacetylene and similar compounds.[5] On the other hand, the crystal lattice may well favour the centro-symmetric chair, as observed for the related molecules 1,6-dioxacyclodeca-3,8-diyne [6] and cyclotetradeca-1,3,8,10-tetryne.[7]

Not only the NMR-spectra are unsuited for settling this question. Also, the IR-spectra are expected to be very similar for the two conformations. The mechanical coupling between the pentamethylene chains being very weak, the hydrogen vibrations, which dominate the IR-spectrum, must obey the local symmetry, which is the same in both conformations. It is therefore dangerous to draw any conclusion from the observation (Fig. 2) that the IR-spectra of the upper solid phase, the melt and the solutions are very nearly identical. On the other hand, the Raman spectra should be dominated by the more strongly coupled skeletal vibrations, and by the C≡C stretching. Thus, if the upper solid contains conformation A, only the symmetric C≡C stretching mode should appear strongly in the Raman spectrum, while a mixture of A and B should show two additional bands due to both C≡C stretching modes of B.

The recorded Raman-spectra (Table 1), however, only confirmed what the IR-spectra had already shown, that the lower solid phase is different from the upper solid phase. Only very marginal differences exist between solution and upper solid phase spectra even at the lowest frequencies. The strongest band in all three phases is at 2230 cm^{-1} and there is no indication of its splitting in solution. The additional band at 2280 cm^{-1} is too far away compared with the very modest splitting expected for so weakly coupled triple bonds, and is probably due to an overtone in Fermi resonance, as observed for other acetylenes.[5] Thus, it can only be concluded that the solution and the upper solid phase contains either of the conformations A or B or an identical mixture of the two.

The possibility that the upper solid phase contains a mixture of A and B is rendered unlikely by the normal magnitude of the entropy of melting. Only expanded crystal lattices displaying a very low entropy of melting, are generally capable of accepting different molecules. Hence, also the solution contains only one conformation.

It remains to make a choice between the chair and the boat, of which only the former has a center of symmetry. This is of course in principle possible by a comparison of IR and Raman spectra, but in such large molecules numerous

Table 1. Raman spectral data (300 – 2400 cm^{-1}) for cyclotetradeca-1,8-diyne.

Solid Lower phase cm^{-1}	Upper phase cm^{-1}	Solution CCl_4 cm^{-1}
	327 vw	325 sh [b,c]
	353 vw	352 sh
367 s[a]		
	383 s	381 s
		415 w
433 m	432 w	428 w [b]
483 m	~500 w	~490 w [b]
	556 m	554 vw
583 m	576 w	574 w
~680 w	679 w	677 w
		737 vw [b]
764 m	~765 w	765 sh [b]
820 m	816 sh	818 sh
828 sh	830 m	830 sh
880 m	880 m	879 w
908 w	908 w	907 vw
950 m	~949 w	~951 w
1002 m	1001 m	1002 w
1049 m	1052 m	1051 w
1072 m	1068 m	1068 m
1080 sh	1082 m	1084 m
1102 w		
1136 m	1128 m	1129 w
~1160 w		1158 vw
		1190 vw
1224 m	1226 s	1224 m
1268 s	1267 s	1266 s
1301 sh	1300 s	1296 sh
1309 m		1304 m
1327 s	1327 vs	1330 vs
1337 sh		
1374 w	1370 w	1372 w
~1404 w		
1430 vs	1435 vs	1437 vs
1450 vs	1462 sh	1464 sh
2113 w		
2180 w		2178 sh
2232 vs	2226 vs	2232 vs
2269 sh	2259 w	2259 w
2281 vs	2281 vs	2286 vs
2331 m	2334 w	

[a] Abbreviations: s, m, w = strong, medium, weak; v = very; sh = shoulder. [b] Frequencies from CS_2 solution. [c] Additional low-frequency bands observed in solution: 311 w[b], 287 m[b] and ~180 w.

accidental coincidences must occur. It seems most likely, however, that the high-temperature solid contains the chair, and we have then to conclude that the chair is also alone in solution and in the melt. Such a conformational preference can only be attributed to a preference for staggering across the triple bond, as observed for simple acetylenes,[5] but the effect seems surprisingly strong in view of the very low barriers to methyl rotation in simple acetylenes.[5]

EXPERIMENTAL

Calorimetric data. A Perkin-Elmer Differential Scanning Calorimeter 1 B was used down to a temperature of −90°.

Infrared spectra. These were recorded with a Perkin-Elmer model 225 spectrometer. Saturated solutions in CS_2 and CCl_4 were measured using 0.5 mm KBr cells. The low temperature spectrum was obtained with a VLT-2 cell from RIIC, cooled with dry ice. The sample was contained between two pressed KBr discs. A heated cell from Perkin-Elmer equipped with KBr optics was used for studying the melt.

Raman spectra. These were measured with a Cary model 81 spectrometer equipped with a CRL 52G argon ion laser (5145 Å). Concentrated solutions in CS_2 and CCl_4 and the upper solid phase were studied using the 180° illumination technique and capillary cells. The low temperature spectrum was obtained under 90° illumination employing a cryostat with a copper tip cooled with liquid nitrogen.

NMR spectra. The spectra of $CHCl_2F/CHClF_2$ solutions were obtained on Prof. Anet's superconducting solenoid NMR spectrometer operating at 251 MHz for protons and at 63.1 MHz for ^{13}C. Acquisition and Fourier transform of free induction spectra were carried out with a Data General Nova computer.

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