

THE CONFORMATIONS AND VIBRATIONAL SPECTRA OF 2,2,5,5,6,6,9,9-OCTAMETHYL-3,7-DECADIYNE

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ABSTRACT

The IR spectra of the title compound as a solute in various solvents, as a melt and as a crystalline solid have been recorded. Raman spectra of the solutions, the melt and of the crystalline solid were obtained and semiquantitative polarization measurements carried out.

The data have been interpreted in terms of one conformer (*anti*) present in the crystal. In the melt and in solutions an additional conformer (*gauche*) was present in low abundance, probably between 5 and 10%, and ΔH° (*gauche* \rightarrow *anti*) was estimated to be -7.9 ± 2 kJ mol⁻¹. Spectral correlations with the related molecule, 1,5-hexadiyne are pointed out.

INTRODUCTION

The title compound 2,2,5,5,6,6,9,9-octamethyl-3,7-decadiyne (OMDD), $(\text{CH}_3)_3\text{CC}\equiv\text{CC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{C}\equiv\text{CC}(\text{CH}_3)_3$ (+ \equiv + \equiv + \equiv) can be considered a derivative of 1,5-hexadiyne (bipropargyl). Thus, like bipropargyl OMDD should have conformational alternatives due to a restricted rotation around the central C—C bond. It was concluded from the IR and Raman spectra of bipropargyl [1, 2] that this compound exists as an equilibrium mixture of *anti* and *gauche* conformations in the vapour phase, in the amorphous solid, in the liquid and in solution. In the crystalline solid, however, the molecules were all present in the *anti* conformation. In a later gaseous electron diffraction study [3] a preponderance of the *anti* conformer at ambient temperature was confirmed. Further spectroscopic studies, using an IR matrix isolation technique with the heated nozzle method [4] revealed an enthalpy difference of 3.1 ± 0.4 kJ mol⁻¹ in the vapour [5], the *anti* being the more stable form. Spectral studies of the two brominated bipropargyls 1,6-dibromo-1,5-hexadiyne [6] and 1-bromo-1,5-hexadiyne [7] gave similar results. The *anti* and *gauche* conformers were present in the vapour and liquid states, while both compounds crystallized in the *anti* conformer.

When a sample of OMDD was synthesized we found it interesting to carry out a spectral and conformational study of this compound. Due to the large size of this molecule (48 atoms) giving in principle rise to 138 fundamentals for each conformer, no detailed analysis of the IR and Raman spectra was attempted.

EXPERIMENTAL

Synthesis of OMDD

OMDD has previously been prepared by reductive dimerization of the propargylic chloride 2-chloro-2,5,5-trimethyl-3-hexyne [8]. We used the corresponding propargylic bromide, obtained by bromination with phosphorous tribromide of 2,5,5-trimethyl-3-hexyn-2-ol, which was obtained as previously described [9].

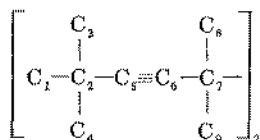
Preparation of 2-bromo-2,5,5-trimethyl-3-butyne

17.3 g (0.065 mol) PBr_3 in 50 ml diethylether were added to a solution of 20 g (0.162 mol) 2,5,5-trimethyl-3-hexyn-2-ol and 1 ml pyridine in 110 ml diethylether at 238 K under dry nitrogen. After stirring overnight the mixture was heated for 45 min to 323 K and then poured into 100 ml saturated aq. NaCl. Extraction with diethylether, drying over MgSO_4 and distillation under reduced pressure after removal of the ether yielded 13 g (42%) of 2-bromo-2,5,5-trimethyl-3-hexyne (b.p. 298 K at 5.3×10^{-4} bar). $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.2$ ppm (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.95 ppm (s, 6 H, $\text{C}(\text{Br})(\text{CH}_3)_3$). IR (film, KBr): 2980–2880 cm^{-1} (—C—H), 640 cm^{-1} (—C—Br). Ms (70 eV): $m/e = 202$ (4%, M^+), 187 (3%, $\text{M}-\text{CH}_3$), 123 (100%, $\text{M}-\text{Br}$), $\text{C}_9\text{H}_{15}\text{Br}$ (203.13), calcd. C 53.22%, H 7.44%, Br 39.34%; found C 53.36%, H 7.41%, Br 39.34%.

Preparation of OMDD

7.1 g (0.037 mol) 2-bromo-2,5,5-trimethyl-3-hexyne were added under nitrogen to 20 ml dry diethylether and 0.9 g (0.037 mol) magnesium turnings. After refluxing for 2 h the mixture was poured into 20 ml saturated aq. NH_4Cl and extracted with ether. The ethereal solution was dried over MgSO_4 . During evaporation 3 g (66%) of OMDD crystallized out in colourless needles (subl. temp.: 342 K [8] m.p. 385.6 K). $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.17$ ppm (s, 18 H; $\text{C}(\text{CH}_3)_3$ [8] 1.19 ppm), 1.22 ppm (s, 12 H, $\text{C}(\text{CH}_3)_2$ [8] 1.21 ppm). $^{13}\text{C-NMR}^*$ (CDCl_3): $\delta = 26.1$ ppm (q, C-8, C-9), 27.33 ppm (s, C-7),

*Atomic numbering for ^{13}C NMR data



31.45 ppm (q, C-1, C-3, C-4), 37.88 ppm (s, C-2), 84.07 ppm (s, C-5), 89.64 ppm (s, C-6). MS (70 eV): $m/e = 246$ (17.6%, M^+), 231 (36%, $M-CH_3$), 189 (69%, M -tert-butyl), 123 (100%, $M/2$) (identical with [8].)

Instrumental

Infrared spectra were recorded with a Perkin-Elmer model 225 spectrometer ($4000-200\text{ cm}^{-1}$) and on a Bruker IFS-114 c Fourier transformer spectrometer ($800-50\text{ cm}^{-1}$). Spectra of OMDD were recorded as a capillary melt at ca. 380 K between KBr and CsI plates. The melt was subsequently crystallized under a temperature gradient and dichroic IR spectra recorded. Additional spectra of KBr and polyethylene pellets of the sample were recorded in the middle and far IR regions, respectively. IR spectra of OMDD were studied further as a solute in saturated solutions of CCl_4 and CS_2 (middle IR) and C_6H_6 and C_6H_{12} (far IR).

Raman spectra were recorded with a Dilor triple monochromator spectrometer interfaced with the Aspect 2000 computer of the Bruker spectrometer. A Spectra-Physics argon ion laser model 2000 was employed for excitation, using the 514.5 nm line in the 90° and 180° illumination geometries. Contained in a tube of ca. 3 mm inner diameter, the sample was recorded as a polycrystalline material at ambient temperature and at ca. 180 K cooled by cold nitrogen gas when enclosed in a Dewar [10]. Moreover, the tube was placed inside a 300 mm long furnace and heated to melting at ca. 385 K. Raman spectra and semiquantitative polarization measurements were obtained. The sample was very stable and after 20 h as a melt and subsequent crystallization, the Raman spectra had not changed significantly. Additional Raman spectra and polarization data of OMDD dissolved in CCl_4 and C_6H_6 were obtained.

RESULTS AND DISCUSSION

Conformation

A first quick glance at the IR and Raman spectra of OMDD in the solid state and in the melt indicated nearly identical features. The immediate conclusion would therefore be that this compound exists as one conformer in both states of aggregation. A closer inspection, however, revealed that additional weak bands appeared in the melt and in the solution spectra compared to those of the solid. Some of these spectra have been reproduced and the middle IR spectrum of a capillary melt between two KBr or CsI windows at ca. 370 K is shown in Fig. 1. When the melt was cooled with a temperature gradient a preferred orientation of the polycrystalline solid was achieved. The dichroic spectra of OMDD at ambient temperature are shown in Fig. 2. Raman spectra of the melt at ca. 385 K and of the crystalline solid at ambient temperature are given in Figs. 3 and 4, respectively. A number of additional

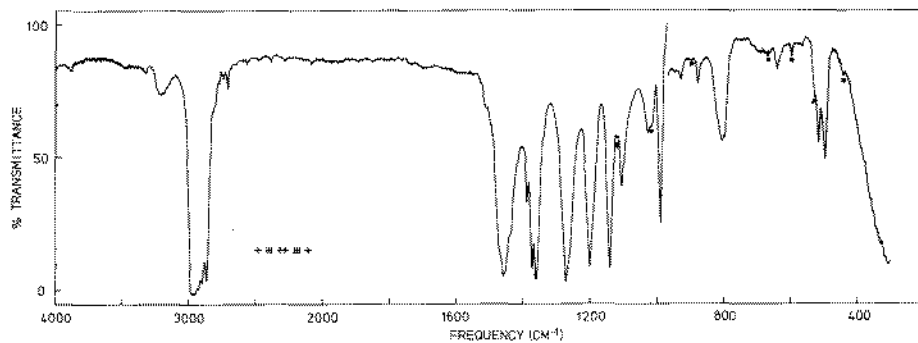


Fig. 1. Mid IR spectrum of 2,2,5,5,6,6,9,9-octamethyl-3,7-decadiyne (OMDD) as a capillary melt at ca. 385 K between KBr plates. Bands with asterisks vanish in the crystal spectra and are attributed to the *gauche* conformer.

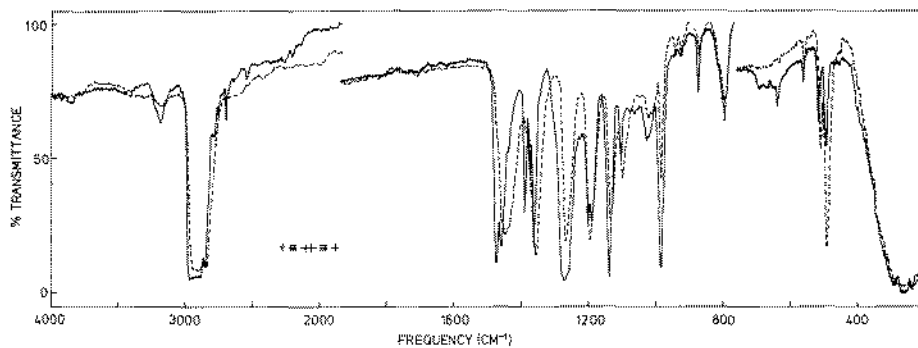


Fig. 2. Mid IR dichroic spectra of OMDD crystallized in a preferred direction.

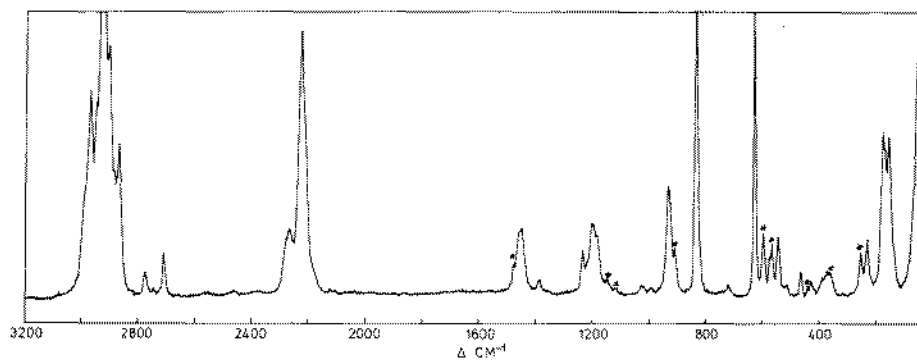


Fig. 3. The Raman spectrum of molten OMDD at ca. 385 K; the asterisks denote bands which vanish in the crystal spectrum.

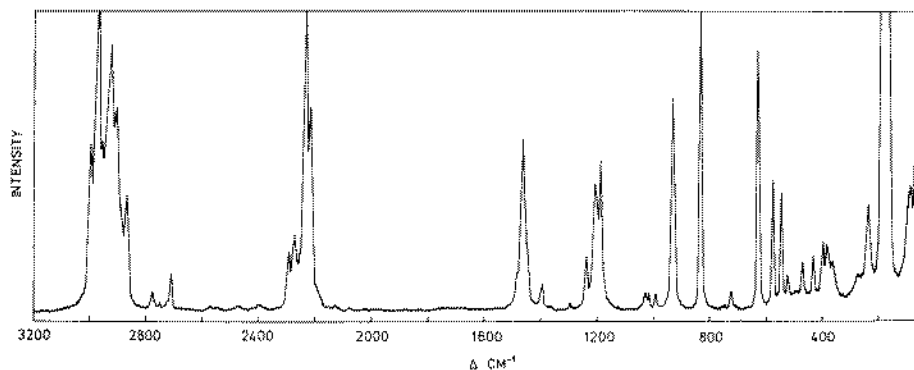


Fig. 4. The Raman spectrum of crystalline OMDD at ambient temperature.

IR and Raman spectra were recorded when OMDD was dissolved in various solvents, as KBr and polyethylene pellets and as a crystalline solid at various temperatures. These spectra have not been reproduced for the sake of brevity. The IR spectral data obtained are listed in Table 1 whereas the Raman data are listed in Table 2.

A careful comparison between Figs. 1 and 2 and between Figs. 3 and 4 reveal a number of weaker bands present in the melts (marked with asterisks) which are absent in the crystal. The conclusion to be drawn is that the conformer present in the crystalline solid is present in large abundance in the melt (and in solution). However, a second conformer is also present in the last two phases. Since the two conformers expected for OMDD have unlike symmetries with different selection rules it should be possible to decide which of them is present in the crystal. Assuming a favourable staggered orientation of the ten methyl groups, the *anti* conformer should possess C_{2h} symmetry while the *gauche* conformer will belong to point group C_2 . Therefore, all the vibrational modes of the *gauche* should be IR and Raman active. The *anti* conformer, on the other hand should as a molecule with a centre of symmetry have mutual exclusion between the IR and Raman bands. It can be seen from Figs. 2 and 4 and from Tables 1 and 2 that more than half of the bands in IR and Raman have no counterparts in the other spectrum. Accordingly, with a great deal of confidence the stable conformer can be assigned as *anti*. The coincidences which do occur in the crystal spectra can be explained as accidental degeneracies between the Raman active a_g (in phase) and IR active b_u (out-of-phase) modes as well as between the b_g and a_u modes. The typical CH_3 group frequencies (CH_3 asymmetric and symmetric stretch and bending and to a lesser extent rocking and wagging) from the ten methyl groups of OMDD are expected to coincide in the appropriate regions. In recent vibrational studies of tert-butyl (tert-butylimino)-borane $(CH_3)_3CB=NC(CH_3)_3$ and di-tert-butylethyne $(CH_3)_3CC=CC(CH_3)_3$ [11] the spectral observations and the normal coordinate analyses revealed extensive coincidences between the methyl group frequencies.

TABLE 1

IR spectral data^a for OMDD (+==+==+)

Melt	Solution		Solid ^b 295 K	Approx. motion	Conformer ^c
	CCl ₄	CS ₂ ^d			
3322 vw ^e	3320 w				
3210 w	3220 m		3240 w, sh 3220 w 3195 w 3190 w		
	2980 s, sh	2980 s, sh			
	2969 vs	2970 vs	2970 vs	} CH ₃ asym str	
2960 s	2948 s	2964 s			
2928 s	2926 vs		2920 vs	} CH ₃ sym str	
2904 vs	2900 vs				
		2987 s			
2870 s	2866 s	2864 s	2863 s	} C=C str?	
	2285 w		2280 vw		
	2230 w				
1475 s	1475 s		1476 s	} CH ₃ asym def	
			1473 vs		
1460 s	1463 s		1460 vs	}	
	1457 s		1454 s		
	1439 w, sh		1438 m, sh		
1390 m	1390 s		1390 s	} CH ₃ sym	
	1375 s	1376 w, sh	1364 m, sh		
		1362 m, sh			
1362 vs	1362 vs	1360 vs	1362 vs	} def	
			1339 vw, sh		
1273 vs	1273 vs	1272 vs	1272 vs	}	
	1262 m	1260 m			
1202 s	1204 s	1203 s	1203 s	} C—C str	
	1192 w, sh		1192 s		
1141 s	1143 s	1141 s	1141 s	}	<i>gauche</i>
1118 w	1117 w	1116 w	—		
1105 m	1108 s	1106 w	1106 m	}	<i>gauche</i>
	1069 w		—		
1028 m	1030 w	1028 w	1028 w	}	<i>gauche</i>
1019 w, sh		1012 w	—		
1015 m, sh		1016 w, sh	1017 w, sh	}	
988 s	988 s	989 m	987 vs		
	944 vw	943 vw	943 vw	} CH ₃ rock	
925 w	926 w	927 vw	927 vw		
	896 vw				
890 vw			—?	}	
	876 w	876 m	875 m		
818 m, sh		818 w, sh		}	
803 m		806 w			
797 m, sh		797 w, sh	796 m	}	
	656 vw?		—		
	636 w, sh		—		<i>gauche</i> <i>gauche</i>

TABLE I (continued)

Melt 380 K	Solution		Solid ^b 295 K	Approx. motion	Conformer ^c	
	CCl ₄	CS ₂ ^d				
637 m	630 m		635 m	} skel def		
	609 vw					
595 vw	594 w	592 w	—			<i>gauche</i>
	584 vw					
568 w	572 w, sh	567 w	—			<i>gauche</i>
	562 w	564 w ^c	562 m ^b			<i>gauche</i>
523 w, sh	520 w	519 vw	—			
515 m	513 s	514 s	515 s			
496 m	493 s	495 s	492 s			
485 vvw	483 vw	473 vw	—			<i>gauche</i>
440 w	442 w	442 w	—			<i>gauche</i>
	414 w					
		394 m	399 m			} CH ₃ tors
		389 w	386 w, br			
		373 w	371 w			
		361 w	—	<i>gauche</i>		
		347 s	347 s			
		301 w	301 w			
		260 m	264 m			
		254 w	—	<i>gauche</i>		
		224 w	—	<i>gauche</i>		
		207 w	—	<i>gauche</i>		
		167 w	—	<i>gauche</i>		
		151 m	154 m			
		136 vw?	—?	<i>gauche</i>		
		102 s	109 s			
		75 m				
		64 m	67 m			
		52 w				

^aBands outside the fundamental regions 4000–3300, 2800–2150 and 2100–1500 cm⁻¹ are omitted. ^bCapillary crystalline film above 550 cm⁻¹, polyethylene pellet below 550 cm⁻¹. ^cNo entry indicates *anti* or overlapping *anti* and *gauche* bands. ^dCS₂ solution above 550 cm⁻¹, C₆H₆ solution below 550 cm⁻¹. ^eAbbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

The bands appearing in the melt and in solution, belonging to a less stable conformer should have vibrational bands of symmetry species *a* and *b* active both in IR and in Raman. Since most of the IR and Raman bands in question are very weak, the number of coincidences is uncertain. However, the bands at 440, 568 and 594 cm⁻¹ appearing in the melt were definitely present in both spectra while those at 170, 1069 and 1120 cm⁻¹ were more uncertain. The scant spectral data are therefore in agreement with a *gauche* conformer. Very uncertain estimates, based upon the IR and Raman intensities of the available bands indicate less than 10% of the *gauche* conformer.

TABLE 2

Raman spectral data^a for OMDD (++++)

Melt	Solution		Solid	Approx. motion	Conformer ^b
	CCl ₄	C ₆ H ₆			
2989 w, sh, D ^c		2989 w, sh	2997 m	CH ₃ asym str	
2970 s, D	2970 m	2969 m	2971 vs		
2947 w, sh, D	2949 m	2949 vs	2953 m		
		2934 s, sh		CH ₃ sym str	
2927 vs, P	2926 vs	2925 vs	2925 vs		
2906 s, P	2903 s	2903 vs	2902 s		
2868 s, D	2865 m	2865 m	2865 m		
2278 w, sh	2282 w			C=C str	
2266 m, P	2268 m	2265 m	2265 m		
2225 vs, P	2230 vs	2230 vs	2228 vs		
2214 w, sh, P?	2215 s	2214 s, sh	2211 s		
	2192 w, sh	2189 w, sh	2187 w, sh	CH ₃ sym asym def.	
2127 vw, P?	2128 vw	2122 vw	2123 vw		
1474 w, P?	1476 vw	1477 w, sh			
	1458 m	1458 m, sh	1459 m	CH ₃ sym asym def.	
1448 m, D	1445 m	1447 m	1439 w, sh		
1358 w, D	1390 vw	1387 vw	1358 w		
	1385 vw			C-C str.	
	1363 vvw	1362 w			
		1308 vvw			
1233 m, P	1291 vw	1288 vvw	1284 vw	C-C str.	
1201 m, D	1234 w	1234 w	1239 w		
	1203 m	1203 m, sh?	1203 m		
			1199 w, sh	gauche	
1186 w, sh, D	1186 m		1185 m		
1148 w, D	1153 w		—		
1122 vvw	1118 vvw		—	gauche	
1070 vvw		1069 vw	—	gauche	
1030 w, D	1028 w		1031 w	CH ₃ rock	
	1017 vw, sh		1019 vw		
993 w, D	994 w		993 vw		
931 m, D	934 m, sh	933 m	933 m	gauche	
	928 m	930 m			
910 m, P	911 w	911 w	—		
832 vs, P	833 vs		831 vs	gauche	
724 w, P	730 w	722 w	724 vw		
628 vs, P	626 vs	625 vs	629 m		
597 m, P	595 w		—	gauche	
572 w	573 w	574 w	570 m		
566 w, D	565 w	566 w, sh	—		
544 m, P?	543 w	543 m	541 w	skel. def.	
513 vw, D	516 w	517 vw	515 vw		
		497 vvw	488 w, sh		
465 w, P		465 w	465 w	gauche	
441 vw, P		441 vw	—		
429 w, D		429 w	428 w		

TABLE 2 (continued)

Melt	Solution		Solid 90 K	Approx. motion	Conformer ^b
	CCl ₄	C ₆ H ₆			
380 K					
	403 w, sh	403 w, sh	—	} CH ₃ tors.	<i>gauche</i>
393 vw, D	395 m	395 m	392 w		
371 w, D	374 w	375 w, sh	380 w		
362 w			—		
	354 w	356 w, sh	358 vw		
254 m, P		255 w	—		
230 m, P		232 m	232 m		
			186 s		
172 s, D	175 s		—		
151 s, P?	155 s		159 s		
138 w, sh, D			—	} lattice	<i>gauche</i>
			91 w		
			75 m		
			36 s		

^aBands outside the fundamental regions 4000—3300, 2800—2150 and 2100—1500 cm⁻¹ are omitted. ^bNo entry indicates *anti* or overlapping *anti* or *gauche* bands. ^cAbbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; P, polarized; D, depolarized.

A comparison between the *gauche* band intensities in the melt at ca. 370 K with those in CCl₄, CS₂ and C₆H₆ solution at ca. 300 K clearly show higher intensities in the former. The Raman intensities of the bands at 597 (*gauche*)/441 (*anti*) and 572 (*gauche*)/566 (*anti*) cm⁻¹ were employed to estimate the enthalpy difference ΔH° between the two conformers. Thus, the CCl₄ solution value at 295 K and the melt values at 385 K were used in the van't Hoff equation $\ln [K(385)/K(295)] = -\Delta H^\circ [1/T(385) - 1/T(295)]/R$. The band peak intensities were employed rather than integrated intensities, and we assumed that the molar band intensities did not vary with temperature. More uncertain is the assumption that the CCl₄ solution data at 295 K can be combined with the melt values at 385 K. The melt might slightly favour the more polar *gauche* conformer compared to the unpolar CCl₄ solution. The ΔH° (*gauche*—*anti*) values obtained, 7.4 and 8.3 kJ mol⁻¹ for the two band pairs, respectively, might therefore be considered as upper limits. Using the simple Boltzmann equation $K = 2e^{-\Delta H^\circ/RT}$ (the factor 2 is the statistical weight of the *gauche* conformer) we obtain $K = [gauche]/[anti]$ equal to 0.098 and 0.068, giving 10.9 and 7.3% of *gauche* at 295 K. These values seem in good agreement with the estimated abundance made from band intensities.

In comparison, the electron diffraction [3] and the spectral data [1, 2] indicate ca. 25% abundance of *gauche* at 293 K in the vapour phase of bipropargyl. From IR matrix isolation measurements with the hot nozzle method [4], a ΔH° value between 3.2 and 5.9 kJ mol⁻¹ was obtained [5].

Thus, the steric and electron donating properties of the 10 methyl groups in OMDD result in an increased stabilization of the *anti* conformer compared to that of bipropargyl.

Spectral interpretations

With 48 atoms in the molecule it is a futile task to attempt a detailed spectral analysis of this molecule. In principle we expect 138 fundamentals for each conformer. However, as apparent from Figs. 1–4 and from Tables 1 and 2, the spectra are not very complex. There are three obvious reasons why the spectra are simpler than predicted. First, since the *anti* conformer has C_{2h} symmetry, roughly half of the bands are IR (a_u , b_u) and half are Raman active (a_g , b_g). Secondly, ca. 15 *gauche* bands were detected in the melt and in solution. With the low abundance of the *gauche* conformer, only strong bands were detected and the majority of the *gauche* bands probably coincide with *anti* bands. Third, as discussed above, the methyl modes from the 10 methyl groups appear as group frequencies in narrow regions: 20 asymmetric stretches for each conformer in the 2970–2990 cm^{-1} range whereas the 10 symmetric stretches are found around 2870 cm^{-1} . The bands at 1475–1448 cm^{-1} are due to the 20 asymmetric CH_3 deformations while the bands around 1362 cm^{-1} are caused by the 10 symmetric CH_3 deformations. Moreover, we expect 20 CH_3 rocks which are probably highly mixed with C–C stretches [11] and scattered around 950 cm^{-1} . Finally, the 10 CH_3 torsions expected below 200 cm^{-1} are probably too weak in the IR and in Raman regions to be detected.

The remaining number of normal vibrations (ca. 50) should be correlated with the skeletal stretching and bending motions. Of these, the C≡C stretch is a typical group frequency observed as a very intense, polarized Raman band at 2230 cm^{-1} . This is obviously the a_g mode of the *anti* (and *gauche*) conformer, whereas the corresponding b_u mode expected at the same frequency [1, 2] could barely be detected in the IR spectra. In the symmetric molecules bipropargyl [1, 2], 1,6-dideuterobipropargyl [2] and 1,4-dibromobipropargyl [6] these a_g and b_u modes have invariably coincided, and in all but the present compound the b_u mode had a significant intensity in the IR.

The bands interpreted as *gauche* modes generally fall below 1200 cm^{-1} in agreement with the results for bipropargyl [1, 2], dideuterobipropargyl [2] and dibromobipropargyl [6]. Force constant calculations [1, 2] also supported the suggestion that the C–C stretch and CCC and C≡C–C bend are the modes most likely to appear as separate bands in the *anti* and *gauche* conformers.

Finally, the IR spectra of Fig. 2 reveal that the crystallized melt was at least partly oriented. However, since the crystal structure of OMDD has not been determined the dichroic data which can be extracted do not contribute significantly to the spectral interpretations.

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REFERENCES

- 1 D. L. Powell, P. Klæboe, A. Pongsatha, B. N. Cyvin, S. J. Cyvin and H. Hopf, *J. Mol. Struct.*, 41 (1977) 203.
- 2 G. O. Braathen, C. J. Nielsen, P. Klæboe and H. Hopf, *J. Mol. Struct.*, 74 (1981) 233.
- 3 M. Traetteberg, P. Bakken, R. Seip, S. J. Cyvin, B. N. Cyvin and H. Hopf, *J. Mol. Struct.*, 51 (1979) 77.
- 4 Hs. H. Günthard, *J. Mol. Struct.*, 80 (1982) 87 and references therein.
- 5 G. O. Braathen, *Spectrochim. Acta, Part A*, 41 (1985) 933.
- 6 D. L. Powell, P. Klæboe, B. N. Cyvin and H. Hopf, *J. Mol. Struct.*, 41 (1977) 215.
- 7 D. L. Powell, P. Klæboe, B. N. Cyvin and H. Hopf, *J. Mol. Struct.*, 43 (1978) 193.
- 8 R. S. Macomber, *J. Org. Chem.*, 38 (1973) 816.
- 9 G. F. Hennion and T. F. Banigan, *J. Am. Chem. Soc.*, 68 (1946) 1202.
- 10 F. A. Miller and B. M. Harney, *Appl. Spectrosc.*, 24 (1970) 291.
- 11 P. Klæboe, D. Bougeard, B. Schrader, P. Paetzold and C. von Plötho, *Spectrochim. Acta, Part A*, 41 (1985) 53.