NMR STUDIES ON DIMETHYL SELENIDE AND DIMETHYL TELLURIDE ORIENTED IN THE NEMATIC PHASE OF A LIQUID CRYSTAL

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Summary

^{1}H NMR spectra of dimethyl selenide with ^{13}C and ^{77}Se satellites and of dimethyl telluride with ^{13}C, ^{123}Te and ^{125}Te satellites have been investigated. The structural information has been derived and is found to be in good agreement with microwave results for dimethyl selenide. For dimethyl telluride our results disagree with earlier data obtained by extrapolation from similar molecules.

Introduction

The high sensitivity of the proton as an NMR probe has often been used to study nuclei with low sensitivity and low natural abundance by investigation of the satellite spectra. Several such experiments have in the past been performed on molecules oriented in the nematic phase of liquid crystals [1,2]. Most of these concentrated on the satellite spectra due to ^{13}C and only few results were reported on ^{29}Si, ^{77}Se, ^{111}Cd, ^{113}Cd, ^{117}Sn, ^{119}Sn, ^{183}W, ^{195}Pt and ^{199}Hg.

We have analysed the proton spectra of dimethyl selenide including the ^{13}C (natural abundance 1.11%) and ^{77}Se (natural abundance 7.50%) satellites and dimethyl telluride including the ^{13}C, ^{123}Te (natural abundance 0.89%) and ^{125}Te (natural abundace 7.06%) satellites in the nematic phase of a thermotropic liquid crystal. An earlier measurement on dimethyl selenide [2] had provided no structural information because only the proton—proton and proton—^{77}Se couplings could be observed. Studies on the analogous derivatives of mercury [3—5] and cadmium [6] have also been reported. Both are linear molecules and consequently the structural information may be derived even without the observation of couplings between protons and ^{13}C [3,6]. Dimethyl selenide and dimethyl telluride are known to be bent [7,8]. The motion of the methyl group in dimethyl selenide is hindered by a potential of 1.5 kcal/mol [7] in the gas

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TABLE 1

SPECTRAL PARAMETERS AND THE DIPOLAR COUPLINGS CORRECTED FOR HARMONIC VIBRATIONS FOR DIMETHYL SELENIDE AND DIMETHYL TELLURIDE DISSOLVED IN A NEMATIC PHASE

Indirect couplings	Dimethyl selenide (Hz)	Dimethyl telluride (Hz)	Direct couplings	Dimethyl selenide		Dimethyl telluride	
				Experimental (Hz)	Corrected for harmonic vibrations (Hz)	Experimental (Hz)	Corrected for harmonic vibration (Hz)
J_{12} [b]	a	a	D_{12}	362.46 ± 0.02	415.03 ± 0.02	226.39 ± 0.02	260.19 ± 0.02
J_{13} [b]	140.3	140.7	D_{13}	281.76 ± 0.05	316.86 ± 0.05	182.68 ± 0.06	207.31 ± 0.06
J_{14} [b]	10.5	−20.8	D_{14}	−37.54 ± 0.04	−39.14 ± 0.04	34.41 ± 0.03 [c]	35.66 ± 0.03
J_{15} [b]	4.0	3.1	D_{15}	−57.00 ± 0.05	−57.76 ± 0.05	−32.50 ± 0.05	−32.45 ± 0.05
J_{16}	0.12 ± 0.03	−0.03 ± 0.02	D_{16}	−188.10 ± 0.02	−185.14 ± 0.02	−108.03 ± 0.01	−108.40 ± 0.01

[a] Coupling does not affect spectrum. [b] Taken from the isotropic phase value [11,12]. [c] For ^{125}Te, for dimethyl telluride (^{123}Te) $|J + 2D|_{Te—H} = 39.88 \pm 0.11$ Hz.

TABLE 2

STRUCTURAL AND ORIENTATIONAL PARAMETERS FOR DIMETHYL SELENIDE FROM NMR AND MICROWAVE SPECTROSCOPY [7] AND FOR DIMETHYL TELLURIDE FROM NMR AND EXTRAPOLATION [8,9]

Parameter	Dimethyl selenide		Dimethyl telluride	
	NMR	Microwave	NMR	Extrapolated
r(C—H)	1.073 ± 0.006 Å	1.093 ± 0.04 Å	1.073 Å [a]	1.093 Å
r(C—metal)	1.943 Å [a]	1.943 ± 0.001 Å	2.158 ± 0.039 Å	2.141 Å
Angle C—Metal—C	95.70 ± 0.25°	96.10 ± 0.16°	93.11 ± 0.57°	93.55°
Angle 2θ	100.85 ± 0.22°	100.12 ± 0.33°	94.66 ± 0.25°	97.50°
Angle H—C—metal	106.22 ± 0.33°	106.70 ± 0.33°	107.34 ± 0.62°	107.49°
Angle H—C—H	110.142 ± 0.004°	110.30 ± 0.33°	110.709 ± 0.004°	108.47°
S_{xx}	−0.01876 ± 0.00072	—	−0.00770 ± 0.00079	—
S_{zz}	−0.05745 ± 0.00054	—	−0.04304 ± 0.00021	—

[a] Assumed.

phase and of 2.4 kcal/mol [9] in the solid state. The corresponding solid state value for dimethyl telluride is 2.27 kcal/mol [9], and no gas or liquid phase value has been reported. The symmetry axes of the methyl groups are non-coincident with the metal carbon bond for dimethyl selenide. For dimethyl telluride the geometrical parameters reported in the literature were obtained by extrapolation of the values for similar molecules [7,8]. Our results are presented in the following sections.

Experimental

^{1}H NMR spectra of commercially available dimethyl selenide as a 14.6 mole percent solution and of dimethyl telluride as a 16.1 mole percent solution in Merck phase IV were studied at 27°C on a Bruker WH 90-DS spectrometer. Heavy water in the coaxial outer cell of a double walled tube was used as the lock substance. About 4000 scans were accumulated and transformed on an ASPECT 2000 computer using pulse widths of 3.5 μs and delay times of 0.3 s. The average linewidth was less than 3 Hz.

Analysis of the spectra

For both the spectra satellites due to the less abundant species were observed, and analysed on a UNIVAC 1108 computer using the program LEQUOR [10]. Indirect spin—spin coupling constants were taken from the literature on the isotropic phase [11,12]. The spectral parameters are reported in Table 1 (for the numbering see Fig. 1). In dimethyl telluride only few satellites due to ^{123}Te could be resolved, because they appeared as shoulders on the much stronger lines due to ^{125}Te. In the structure determination these couplings were not considered. The splitting $|J + 2D|^{123}$Te—^{1}H = 39.88 ± 0.11 Hz was found to be consistent with the reported gyromagnetic ratios of the two tellurium isotopes. In the
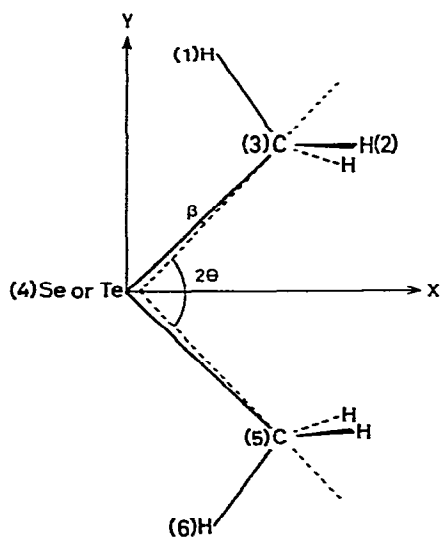

Fig. 1. Structure, numbering and coordinate system in dimethyl selenide and dimethyl telluride.

proton spectra iteration of the inter-methyl indirect couplings gave values of 0.12 ± 0.03 Hz and -0.03 ± 0.02 Hz for dimethyl selenide and dimethyl telluride, respectively, which agree well with the isotropic phase value of 0.15 ± 0.05 Hz and 0.0 ± 0.1 Hz [11,12].

The direct couplings were corrected for vibrational, as well as torsional harmonic motion by use of a computer program VIBR. For this purpose the available symmetry force constants [13] had to be transformed into internal force constants. The corrected dipolar couplings were further analysed by use of the program SHAPE [14] which calculated distance ratios, angles and components of the order matrix S.

Results and discussion

For dimethyl selenide the calculations were carried out with a fixed distance $r(C-Se) = 1.943$ Å [7]. For dimethyl telluride, on the other hand $r(C-H)$ was kept fixed and equal to the value derived for dimethyl selenide, because $r(C-Te)$ is not known. The results are summarised in Table 2.

The data show that for dimethyl selenide there is, except for the C—H bond lengths, very close agreement between the microwave structure and our r_α structure. For dimethyl telluride there are no microwave data available and only approximate structural data have been reported as extrapolated results [8,9]. Our r_α structure for this molecule disagrees substantially from the extrapolation in that the H—C—H bond angle is found larger than tetrahedral (and also larger than in dimethyl selenide). Also the angle, β, between the methyl group symmetry axis and the carbon—tellurium bond is much smaller ($0.78 \pm 0.62°$) than extrapolated ($1.98°$) and also smaller than in dimethyl selenide ($2.57 \pm 0.33°$).

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