freiheitsgraden. Dieser wurde damals zusätzlich auf ähnliche Weise eingeführt wie in dieser Arbeit. Im Hochtemperaturverhalten sind die Unterschiede gering, da hier die scheinbare Aktivierungsenergie nicht sehr stark von den Einzelheiten der Summation von $1/\tau$ über die erlaubten Übergänge abhängt.

Zum Schluß sei noch kurz die Frage diskutiert, weshalb bisher bei der Beschreibung von Kernresonanzexperimenten in Stoffen mit behinderter Rotation keine Quanteneffekte berücksichtigt wurden. Dies dürfte vor allem daran liegen, daß wenig Messungen bei tiefen Temperaturen durchgeführt wurden, und die Behinderungspotentiale durchweg größer waren. In diesem Falle sind die Torsionsaufspaltungen zu klein, und der hier eingeführte Relaxationsmechanismus ist bei tiefen Temperaturen nicht mehr bestimmend. Bei genauer Inspektion älterer Messungen (z. B. Abb. 6 und 7 von Anm. [9]) kann man jedoch erkennen, daß bei Potentialschwellen in der Größenordnung von 2 kcal/Mol bereits gewisse Abweichungen vom klassischen Verhalten auftreten, die jedoch nicht berücksichtigt wurden. Erst bei so niedrigen Behinderungspotentialen wie bei Toluol treten die Quanteneffekte in aller Deutlichkeit zu Tage.

Herrn Dr. R. F. GLODEN von der Computer-Abteilung CETIS des Gemeinsamen Forschungszentrums danken wir für die Berechnung der Eigenwerte mit Hilfe der verallgemeinerten Mathieu-Gleichung.

Proton Magnetic Resonance Study of Mercury Dimethyl in a Nematic Liquid Crystal

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The P.M.R.-spectrum of mercury dimethyl partially oriented in a nematic liquid crystal has been studied. From the ratio of the direct magnetic dipole-dipole interactions of the protons the ratio ξ_0/ϱ is calculated, ξ_0 being the distance of the two parallel planes containing the methyl protons, and ϱ being the distance of the methyl protons from the molecular symmetry axis. From this ratio the splitting due to the direct coupling of the protons with ^{199}Hg of spin 1/2, present in about 17% natural abundance, is calculated and compared with the experimentally observed one. Exact agreement is obtained under the assumption that the methyl groups are rapidly rotating and that the direct and indirect ^{199}Hg—H-couplings have like signs. Since the preferred orientation of the long axis of mercury dimethyl is probably parallel to the direction of the magnetic field, the absolute sign of $J_{^{199}\mathrm{Hg,H}}$ is found to be negative. Correspondingly it is shown that the sign of $J_{\mathrm{CH_3,CH_3}}$ is positive. No evidence is found for a possible contribution of the anisotropic part of the indirect couplings.

The discoveries that molecules dissolved in nematic liquid crystals are partially oriented and that their proton magnetic resonance (P.M.R.) spectra show highly resolved line splittings due to direct magnetic dipole-dipole interactions [1], have stimulated an increasing number of investigations. Thus, information has been obtained on the absolute signs of indirect spin couplings, on the anisotropy of chemical shifts and on the intermolecular forces causing specific average orientations of solute molecules of various chemical structure.

The most important application, however, has been the determination of bond angles and ratios of internuclear distances from the measured direct dipole-dipole couplings which are proportional to the inverse cube of the internuclear distance. To obtain the couplings from the observed splittings, one generally assumes that the anisotropic part of the indirect coupling can be neglected. This assumption seemed, in general, to be justified because for molecules containing only ^{1}H, ^{13}C and ^{15}N as magnetic nuclei the bond angles or ratios of internuclear dis-

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tances were found to be in excellent agreement with those obtained by other techniques, e. g. microwave spectroscopy, x-ray and electron diffraction. Small deviations have been attributed to minor changes of the molecular geometry in the liquid phase or to the influence of molecular vibrations.

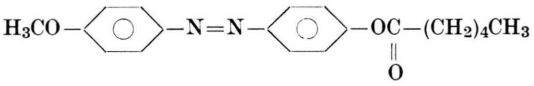
With molecules containing ^{19}F, however, neglection of the anisotropic part of the indirect coupling might lead to unreasonable geometrical data since anisotropic contributions of considerable magnitude have been reported in several cases [2–4]. The question whether other magnetic nuclei might also give rise to an anisotropic part of the indirect coupling seemed therefore to us to be of general theoretical interest.

In this connection we have studied the P.M.R.-spectrum of partially oriented mercury dimethyl which is especially well suited for several reasons: The special 6-spin spectrum of this highly symmetrical molecule is easily analysed [5]. If the anisotropic part of the indirect H,H-couplings is neglected, the ratio of the two distances ξ_0/ϱ can be obtained, ξ_0 being the distance of the two parallel planes containing the methyl protons, and ϱ being the distance of the latter from the molecular symmetry axis. Because of the presence of about 17% of the molecules containing ^{199}Hg of spin 1/2, additional splittings are observed in the spectrum due to the direct and indirect couplings of the protons with this nucleus. The high molecular symmetry [6] makes it possible to calculate this splitting from the observed proton-proton couplings if contributions of the anisotropic part of the indirect couplings are neglected. As will be seen, the predicted splitting is in excellent agreement with the experimental one and it is concluded therefore that anisotropic contribuitons of the different indirect couplings are in this case actually negligible.

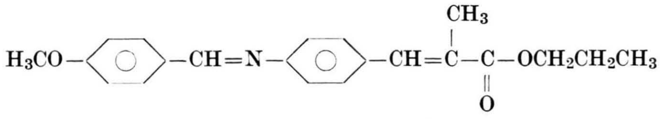
1. Experimental

All spectra were recorded on a Varian HA 100 N.M.R.-spectrometer (HR-mode). The experimental details were the same as previously given [5, 7]. A sample of pure mercury dimethyl $H_3C-Hg-CH_3$ was kindly provided by Dr. H. LINDE, Basle. The computer programs for the computation and graphical representation of the theoretical control spectra have already been briefly described elsewhere [5].

As solvent a 1 : 1 mixture (by weight) of the following two compounds was used [7]:



m. p. 70.5 °C, cl. p. 108.5 °C.



m. p. 54 °C, cl. p. 91 °C.

The measurements have been done at 27 °C, the probe temperature of the HA 100 spectrometer. Before recording the spectra, the sample was kept in the probe for several hours in order to achieve a good temperature equilibrium.

2. Results

The P.M.R.-spectrum at 27 °C of 110 mg of mercury dimethyl in 500 mg of a 1 : 1 mixture (by weight) of the two liquid crystalline compounds mentioned is shown in Fig. 1 (upper part). The spectrum is symmetrical with respect to the center of gravity (0 Hz) and therefore only the central and the high-field part are presented, recorded with different sweep speeds. In the high-field part additional lines with negative intensities are seen which correspond to the modulation side bands at 6003 Hz of the central part of the spectrum.

In ref. [5] the transition frequencies and intensities have been calculated for this special 6-spin system

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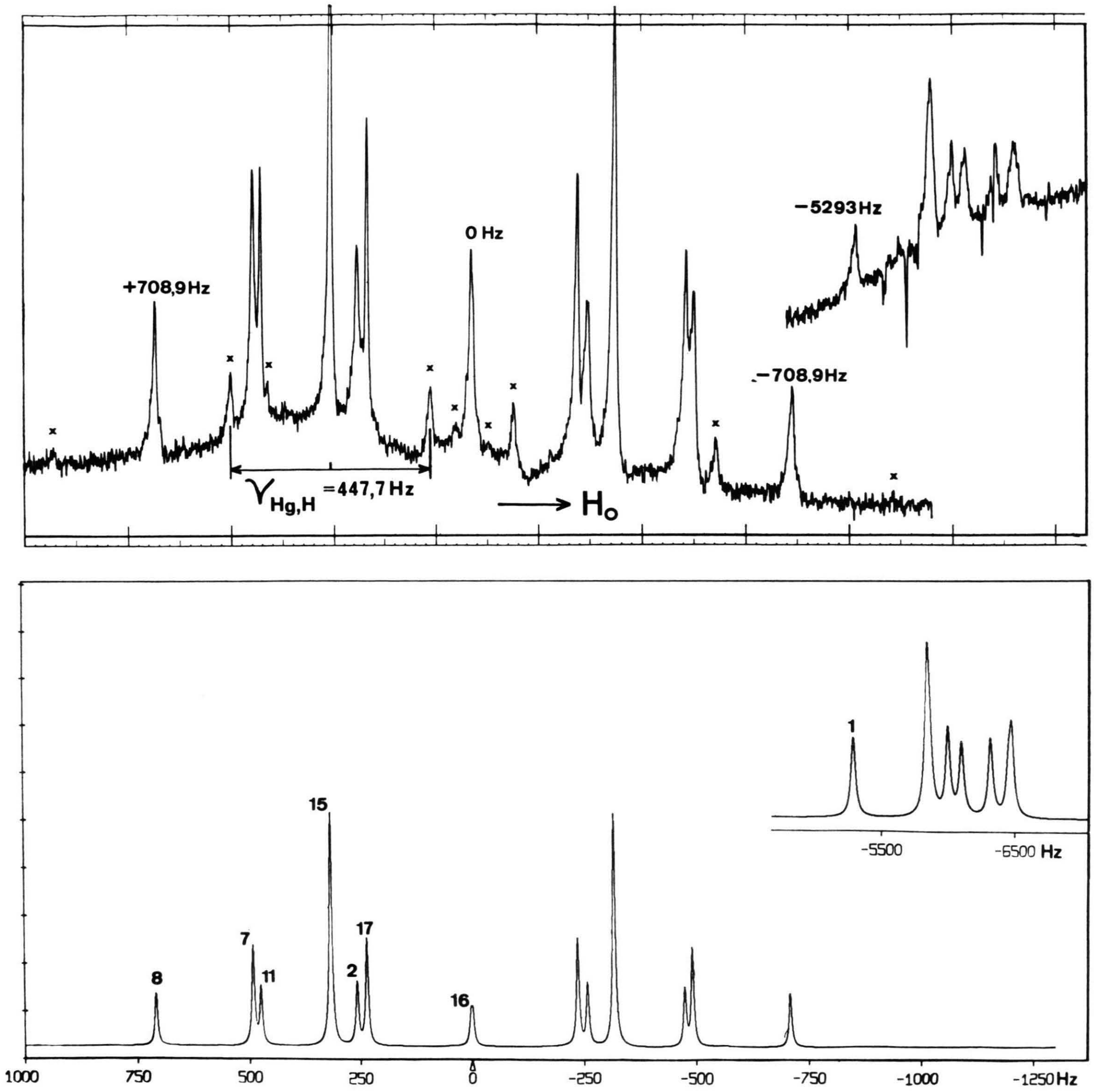

Fig. 1. *Upper part:* Experimental P.M.R.-spectrum of mercury dimethyl partially oriented in a nematic liquid crystal at 27 °C. Starred lines are due to the presence o about 17% of ^{199}Hg of spin 1/2. — *Lower part:* Theoretical spectrum calculated with $A=-157.53$ Hz, $B=+2000.5$ Hz, and $J_{CH_3,CH_3}=+0.45$ Hz. The central part has been plotted with an assumed half-width of the lines of 7 Hz. In the up-field part a half-width of 40 Hz was used in order to achieve agreement with the experimental line widths.

as a function of the following parameters:

$A_{CH_3,CH_3} \equiv A$: direct dipole-dipole coupling between protons of the two methyl groups,

$B_{CH_3} \equiv B$: direct coupling of the protons within a methyl group,

$J_{CH_3,CH_3} = J$: indirect coupling between the protons of the two methyl groups.

The value of A is directly calculated from lines (8) and (17), and B is obtained from line (1) (see Table 3 of Ref. [5]). The fact that (1) is the innermost line of the outer part immediately proves that A and B must have opposite signs.

From 8 spectra we obtained the following values:

$$A/B = -157.5/2000.5 = 0.07875 \pm 0.0001$$

(standard deviation).

A theoretical spectrum calculated with A negative, B positive and $J = +0.45$ Hz [8] is in excellent agreement with the experimental one (see lower part of Fig. 1). For an opposite (relative) sign of J the agreement is worse, since the distances between the pairs of lines (7) and (11), (2) and (17), and (16), (16) are wrong up to 3 Hz. If a parallel orientation of the long molecular axis with respect to the direction of the magnetic field is assumed, as has been proven for similar elongated molecules [5], the absolute signs of A and B are negative and positive, respectively, and therefore $J_{\mathrm{CH_3,CH_3}}$ should be positive. This is in agreement with expectation because extensive double resonance [8, 9] studies of the isotropic liquid have revealed the relative signs of all indirect couplings in mercury dimethyl and a positive sign of $J_{\mathrm{CH_3,CH_3}}$ was predicted under the generally accepted assumption that the one-bond coupling $J_{^{13}\mathrm{C,H}}$ is positive.

With the above given ratio of A and B, the ratio of the two distances ξ_0 and ϱ has been calculated by numerical integration of Eq. (10) of Ref. [5]:

$$\xi_0/\varrho = 4.6943 \pm 0.0023\,.$$

If β denotes the angle betwteen the internuclear vector $r_{\mathrm{Hg,H}}$ and the molecular symmetry axis, it follows:

$$\operatorname{tg}\beta = 2\varrho/\xi_0 \quad \text{and} \quad \beta = 23^\circ\, 5'.$$

The direct coupling $B_{\mathrm{Hg,H}}$ is calculated from [10]

$$B_{\mathrm{Hg},H} = -3\sqrt{3}\,\frac{\gamma_{\mathrm{Hg}}}{\gamma_{\mathrm{P}}}\cdot B\cdot\sin^3\beta\,(2-\sin^2\beta)\,.$$

With $\gamma_{\mathrm{Hg}}/\gamma_{\mathrm{P}} = 0.17911$ and $|B| = 2000.5$ Hz we have

$$|B_{\mathrm{Hg,H}}| = 172.6 \text{ Hz}\,.$$

The splitting of all lines due to ^{199}Hg of spin $1/2$ in symmetrical doublets is seen in Fig. 1 (starred lines). The splitting $\nu_{\mathrm{Hg,H}}$ was best observed with the strongest lines (15). We obtained:

$$\nu_{\mathrm{Hg,H}} = |2\,B_{\mathrm{Hg,H}} + J_{\mathrm{Hg,H}}| = 447.7 \pm 0.5 \text{ Hz}.$$

Here $J_{\mathrm{Hg,H}}$ denotes the indirect spin coupling constant between ^{199}Hg and ^{1}H. Only the assumption of like signs of $B_{\mathrm{Hg,H}}$ and $J_{\mathrm{Hg,H}}$ leads to a reasonable values for the latter, namely

$$|J_{\mathrm{Hg,H}}| = 102.5 \text{ Hz}\,.$$

Exactly the same value of this coupling we measured in CDCl$_3$-solution in good agreement with the values reported in the literature (101.4 to 102.0 Hz [8, 9]) *. With parallel orientation of the long molecular axis of mercury dimethyl to the magnetic field direction it follows that the absolute sign of the indirect coupling $J_{^{199}\mathrm{Hg,H}}$ is negative as expected [8, 10].

The above-given ratio ξ_0/ϱ has been calculated under the assumption that the methyl protons are freely rotating, i. e. that all angles of rotation are equally probable. If three equally populated staggered or eclipsed conformation are assumed, only small changes in the ratio A/B of ± 0.0001 and of ξ_0/ϱ of ± 0.0023 are to be expected compared to the case of freely rotating methyl groups. These differences are of the same magnitude as the limits of error stated above. Therefore, hindered or free internal motion cannot be distinguished unequivocally. A different situation has been reported with ethane [4]. Here the smaller value of ξ_0/ϱ causes larger differences between the ratio A/B of the three possibilities and a better fit between experimental and theoretical data was obtained for staggered conformation.

3. Conclusions

From the P.M.R.-study of mercury dimethyl oriented in a nematic liquid crystal the following conclusions can be drawn:

The results are in agreement with the known linear and highly symmetrical structure. Although it cannot be distinguished experimentally between the cases of freely rotating methyl groups, rapid rotation between the three staggered or the three eclipsed conformations, the data indicate that a possible contribution of the anisotropic part of the indirect coupling between ^{199}Hg and H is negligeable. If a parallel orientation of the long molecular axis is assumed with respect to the magnetic field, the absolute signs of the scalar couplings $J_{^{199}\mathrm{Hg,H}}$ and $J_{\mathrm{CH_3,CH_3}}$ must be negative and positive, respectively.

Acknowledgement

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* Note added in proof: In the meantime, a value $J_{\mathrm{Hg,H}} = 102.4 \pm 0.2$ Hz was measured in the isotropic phase at 78 °C.