Proton Magnetic Resonance Spectra of Benzene and Benzene-1-^{13}C in Isotropic and in Nematic Solution

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Th ^{1}H-NMR-spectra of benzene and benzene-1-^{13}C in the isotropic phase (CCl_4 solution) as well as in the nematic phase of a liquid crystal are analysed and the resulting direct and indirect couplings presented. The comparison of observed direct couplings with values calculated from known Raman structural data shows deviations of up to 9% relative to the $HH_{(\mathrm{ortho})}$-coupling. This corresponds to an apparent increase of the carbon-proton distance of 0.03 Å. Possible reasons are discussed such as anisotropy of the indirect couplings, solvent effects on indirect couplings and intramolecular vibrations. The conclusion is reached that the consideration of intramolecular vibrational motion perfectly explains the discrepancies.

1. Introduction

The NMR-spectrum of benzene dissolved in a nematic phase was the first complex spectrum of an oriented molecule which was recorded[1] and analysed[2]. Furtheron, it has become one of the best studied spectra in this special field of NMR[3]. The anisotropy of its chemical shift was measured[1] and the influence of molecular vibrations on the observed geometry was discussed recently[4, 5]. The spectrum of the oriented molecule C_6H_5D was used for a precise determination of the deuteron quadrupole coupling constant[6].

The spectrum of oriented C_6H_6 is not particularly rich in information as it depends only on the two distance ratios for the protons, $r_{\mathrm{meta}}/r_{\mathrm{ortho}}$ and $r_{\mathrm{para}}/r_{\mathrm{ortho}}$. It was found that the direct proton-proton couplings were in the expected ratio for a regular hexagon within the limits of error[2]. The substitution of one nucleus ^{12}C by ^{13}C greatly increases the available information in that the spectrum now depends also on the 4 different carbon-proton distances. However, the complexity of the spectrum increases considerably because, due to the limited enrichment in ^{13}C, the two spectra of benzene and benzene-1-^{13}C are observed as a superposition. As, on the other hand, the resolution and precision in the NMR-spectroscopy of oriented molecules has increased considerably in the last few years, an analysis of the complex spectrum seemed to be promising. It was performed, as described in the present paper, not only in order to derive the additional geometrical details, but also with the aim of gathering more information on the peculiar and up to now unsolved problem of the apparent increase in carbon-proton distance as determined by NMR with respect to results of various other spectroscopies[5, 7].

In this connection it seemed reasonable to us to redetermine first all the indirect couplings of benzene-1-^{13}C in isotropic (CCl_4) solution and to compare these values with the ones obtained from the analysis of the spectra in the nematic phase and with data published in literature.

2. Experimental

2.1. Compounds and Instrumentation

All spectra were recorded on a Varian HA 100 NMR spectrometer in frequency sweep mode at 28 ± 1 °C.

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[2] A. Saupe, Z. Naturforsch. **20 a**, 572 [1965].

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[4] W. Bovée, C. W. Hilbers, and C. MacLean, Mol. Phys. **17**, 75 [1969].

[5] S. Meiboom and L. C. Snyder, Accounts of Chemical Res. **4**, 81 [1971].

[6] P. Diehl and C. L. Khetrapal, Can. J. Phys. **47, 1411** [1969].

[7] L. C. Snyder and S. Meiboom, J. Chem. Phys. **47**, 1480 [1967] — S. Meiboom and L. C. Snyder, J. Amer. Chem. Soc. **89**, 1038 [1967]. — G. Englert and A. Saupe, Mol. Cryst. and Liquid Cryst. **8**, 233 [1969]. — A. D. Buckingham, E. E. Burnell, and C. A. de Lange, Mol. Phys. **16**, 299 [1969].

Before the spectra were recorded, the sample tubes were kept in the probe for several hours in order to achieve thermal equilibrium. Benzene-1-^{13}C with ca. 60% enrichment in ^{13}C was purchased from Merck, Sharp and Dohme, Canada. The nematic solvent was N-[p-ethoxybenzylidene]-p-n-butylaniline

$n\text{-}C_4H_9-C_6H_4-N=CH-C_6H_4-OCH_2CH_3$,

m. p. 38 °C, clearing point 80 °C.

Analysis of the spectra was performed with the aid of the iterative computer program LAOCOONOR[8]. Computations were done on an Univac 1108 or via Teleprocessing on an IBM 360/65 computer. Spectra were plotted on an IBM 1627 plotter linked to an IBM 1130 computer.

2.2. Samples

2.2.1. Isotropic Phase

The CCl_4-solution (ca. 0.4 ml) of 40 mg benzene-benzene-1-^{13}C was degassed by four freeze-pump-thaw cycles on a vacuum line and sealed in a 5 mm tube. Some TMS was added to serve as internal lock. Two scans of the low-field, central and high-field part of the spectrum were recorded on a sweep width of 50 Hz with 2500 or 5000 sec sweep time. The line frequencies were measured with respect to the lock signal (TMS = 0 Hz) by interpolation between intervals spaced approximately 5 Hz apart from each other. The average deviation of the lines from their mean was 0.05 Hz. The half-width of resolved lines was ca. 0.15 to 0.20 Hz. The frequency of the singlet of benzene was directly measured with a frequency counter.

2.2.2. Benzene in Nematic Solution

A sample of 31 mg was dissolved in ca. 500 mg of the liquid crystal (18 mole-%). Four consecutive frequency sweep recordings of 1000 Hz sweep width each with overlapping parts of several 100 Hz were recorded. Selected lines served as lock signals. The total spectral width was ca. 2600 Hz. Line frequencies were directly measured with a frequency counter and the shift offset between the different lock signals was carefully calibrated. The frequencies, which were then referred to the center of gravity of the spectrum, showed an average deviation of 0.5 Hz. The line width was between 2.5 and 3 Hz throughout the spectrum.

2.2.3. Benzene and Benzene-1-^{13}C in Nematic Solution

The concentration used was 38 mg in 540 mg of the liquid crystal (20 mole-%). Slightly more than one half of the symmetrical spectrum (total width ca. 3000 Hz) was recorded as two overlapping parts with 1000 Hz sweep width and 2500 sec sweep time. Most of the line frequencies were then directly measured with a frequency counter, the residual ones were obtained by interpolation in the spectra. The average line width was about 3 to 3.5 Hz. The accuracy of the line frequencies is estimated to be about 1 Hz or better.

3. Results

3.1. Analysis of the Spectra

3.1.1. Indirect Couplings in Benzene and Benzene-1-^{13}C

Usually in the analysis of spectra of oriented molecules the indirect electron-coupled spin-spin couplings are assumed to be the same as those in the isotropic phase measured at temperatures above the clearing point. Since the precision of such an analysis is generally inferior to that obtained from ordinary solutions we preferred first of all to measure and analyse the spectrum of benzene-1-^{13}C in CCl_4 solution and then to compare the results with data from literature and with those obtained from the spectra of oriented benzene.

The low-field and the central part of the approximately symmetrical spectrum of benzene-1-^{13}C in CCl_4 are shown in Fig. 1 together with a theoretically computed spectrum, the parameters of which were iteratively determined by LAOCOONOR upon assignment of 148 transitions. The parameters of the iterative fitting are given in column I of Table 1 together with their standard deviations. The final r.m.s.-deviation between calculated and experimental line positions was 0.07 Hz. Part of this error is due to the fact that in the central part more than 100 transitions are so closely spaced that they could not be sufficiently resolved experimentally and, therefore, only the most intense transitions could be used for the iteration. However, as is seen in Fig. 1 the fit between the experimental and the theoretical spectrum is found to be excellent even for the very weak outer lines of the central part of the spectrum. It was found that the singlet due to C_6H_6 appears slightly downfield from the center of gravity of the central part (ν_B). The latter also appears at slightly lower field than the center of gravity of the low- and high-field $^{13}C-H$-satellites (ν_A). This is caused by carbon-13 isotope effects[9, 10]. Therefore, the spectrum was treated as an $ABB'B''B'''B''''X$-type

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[8] P. Diehl, C. L. Khetrapal, and H. P. Kellerhals, Mol. Phys. **15**, 333 [1968].

[9] G. M. Ford, L. G. Robinson, and G. B. Savitsky, J. Mag. Res. **4**, 109 [1971].

[10] H. Batiz-Hernandez and R. A. Bernheim, Progress in NMR-Spectroscopy, Vol. 3 [1967], p. 63; J. W. Emsley, J. Feeney, and L. H. Sutcliffe Eds., Pergamon Press, London 1967.

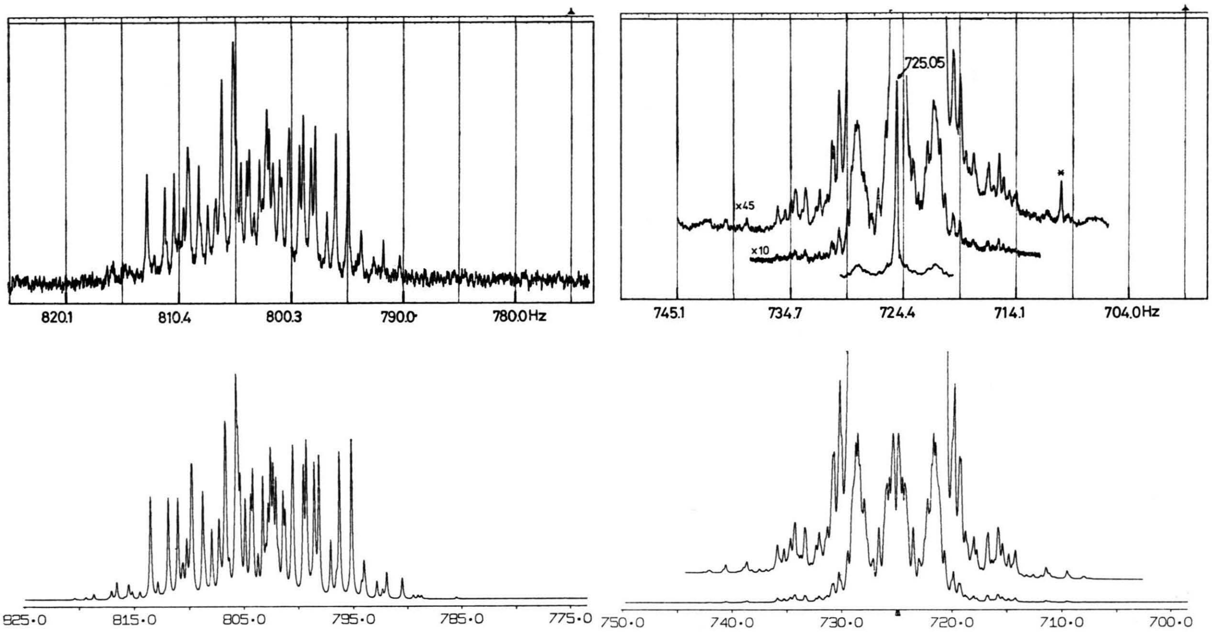

Fig. 1. *Top:* low-field ^{13}C-satellite and central part of the PMR-spectrum of benzene-benzene-1-^{13}C (100 MHz, ca. 29 °C, in CCl_4). *Bottom:* computer simulated spectrum calculated from the parameters given in column I of Table 1 (half-width 0.18 Hz). * Impurity.

Table 1. Indirect couplings and chemical shifts in Hz (100 MHz) for benzene and benzene-1-^{13}C.

Parameter	I benzene-1-^{13}C (CCl_4)	II benzene-1-^{13}C (neat[11])	III benzene-1-^{13}C (neat[12])	IV benzene (nematic phase)	V benzene (lyotropic phase[13])
J_{HH}(ortho)	7.54 ± 0.01	7.56 ± 0.04	(7.7)[a]	7.62 ± 0.02	7.53 ± 0.05
J_{HH}(meta)	1.38 ± 0.01	1.38 ± 0.04	(1.4)[a]	1.31 ± 0.03	1.38 ± 0.05
J_{HH}(para)	0.64 ± 0.02	0.68 ± 0.04	(0.6)[a]	0.64 ± 0.06	0.70 ± 0.05
$^1J_{CH}$	158.17 ± 0.02	158.34 ± 0.04	157.5		
$^2J_{CH}$	1.13 ± 0.03	$^3J - {}^2J = 6.22 \pm 0.18$	1.0		
$^3J_{CH}$	7.62 ± 0.04		7.4		
$^4J_{CH}$	-1.16 ± 0.05	$^4J - {}^2J = -2.14 \pm 0.18$	-1.1		
ν_A	724.82 ± 0.01				
ν_B	724.98 ± 0.01				
$\nu_{C_6H_6}$	725.05 ± 0.04				

[a] assumed.

spectrum ($X = {}^{13}C$). Since ^{13}C-isotope effects are expected to be much smaller than deuterium isotope effects [9], only shift differences between proton A, directly attached to carbon-13, and all other protons B (assumed to have the same shift) have been taken into account. Close inspection of the central part reveals that very small deviations from this spectral type do occur. However, they are thought to be too small and were thus neglected.

For comparison, Table 1 also contains data of Ref. [11] obtained from the analysis of the low- and high-field ^{13}C satellites only of neat benzene (column II). In this case, the long-range ^{13}C to H couplings were obtained only as differences, since the central part of the spectrum of benzene-1-^{13}C in natural abundance was not measured. As expected, it was found to be obscured under these conditions by the very strong line of ordinary benzene. The carbon-13 proton couplings of column III of Table 1

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[11] J. M. Read, Jr., R. E. Mayo, and J. H. Goldstein, J. Mol. Spect. **21**, 235 [1966].

were obtained by WEIGERT and ROBERTS [12] from an analysis of the ^{13}C spectrum of benzene (natural abundance). The proton-proton couplings of column IV are the weighted mean values of the anlyses of the sample of 18 mole % of benzene in the nematic phase (see Section 2.2.2) and of the 6-spin partial spectrum of benzene in the mixture with benzene-1-^{13}C (Section 2.2.3). The weighted errors quoted for the two measurements illustrate the good accuracy for the analysis of spectra of oriented molecules being achieved in favourable cases. As is shown in column V of Table 1, the results are in reasonable agreement with a previous analysis of the spectrum of benzene oriented in a lyotropic liquid crystal [13].

However, as the average line width and hence the r.m.s.-deviation between experimental and theoretical line frequencies of the spectra of oriented molecules are considerably greater than for the isotropic case the results summarized in column I of Table 1 obtained from the spectra in the CCl_4 solvent are considered to be more reliable, and the following analyses of the spectra of the oriented molecules are therefore based on these values for the indirect coupling constants. The differences between the values of the couplings, obtained from the CCl_4 solution, the neat liquid, or from the spectra of molecules oriented in nematic or in a lyotropic mesophase are so small that it seems not worthwhile to interpret them in terms of possible solvent effects.

3.1.2. Direct Couplings in Benzene and Benzene-1-^{13}C

The analysis of the spectrum of oriented benzene (Section 2.2.2) was straightforward, since starting values for the different couplings wer obtained from the formulae given in Ref. [2]. After assignment of ca. 150 transitions, refinement of the starting parameters was achieved with the aid of the iterative program LAOCOONOR. The very small isotope effects were neglected in this analysis. The r.m.s.-deviation between calculated and experimental line frequencies was 0.27 Hz. The obtained values for the indirect proton-proton couplings have already been discussed. The calculated direct couplings and their standard deviations are:

$$D_{\mathrm{HH}}(\mathrm{ortho}) = -329.74 \pm 0.02\ \mathrm{Hz},$$
$$D_{\mathrm{HH}}(\mathrm{meta}) = -\ \ 63.24 \pm 0.02\ \mathrm{Hz},$$
$$D_{\mathrm{HH}}(\mathrm{para}) = -\ \ 40.90 \pm 0.02\ \mathrm{Hz}.$$

In the analysis of the spectrum of the mixture of benzene and benzene-1-^{13}C (Section 2.2.3) the first step was the identification of the transitions due to the 6-spin spectrum of the former. Most of the remaining lines were then assigned to about 190 transitions of the 7-spin molecules of ^{13}C enriched benzene and the spectral parameters again obtained by the iterative procedure with assumed values for the indirect proton-proton and proton-carbon-13 couplings (column I of Table 1). The r.m.s.-deviation of the fit was 0.96 Hz. As is seen from Fig. 2 the agreement between experimental and computer-simulated spectra obtained as the sum of the 6- and 7-spin partial spectra is excellent. The direct proton-proton couplings obtained from both spectra were used to calculate their weighted values and weighted standard deviations which are given together with the direct carbon-13-proton couplings in Table 2. The ratio of the proton-proton couplings was 1 : 0.1920 : 0.1250 as compared to 1 : 0.1924 : 0.1250 expected for a regular hexagon.

Table 2. Direct couplings (in Hz) in benzene-1-^{13}C.

$D_{\mathrm{HH}}(\mathrm{ortho})$	$= -283.39 \pm 0.05$
$D_{\mathrm{HH}}(\mathrm{meta})$	$= -\ 54.40 \pm 0.12$
$D_{\mathrm{HH}}(\mathrm{para})$	$= -\ 35.44 \pm 0.14$
$D_{^{13}\mathrm{CH}}$	$= -782.96 \pm 0.22$
$D_{^{13}\mathrm{C(C)H}}$	$= -107.27 \pm 0.16$
$D_{^{13}\mathrm{C(CC)H}}$	$= -\ 27.49 \pm 0.16$
$D_{^{13}\mathrm{C(CCC)H}}$	$= -\ 19.15 \pm 0.22$

3.2. Information from the Direct Couplings

A possible check of our results can be obtained from a comparison of the experimentally obtained direct couplings with those calculated on the basis of the known molecular geometry of benzene. Unfortunately, the r_e-structure seems not to be published and we therefore used the r_0-structure as determined by Raman spectroscopy [14] (see Table 3). The couplings were evaluated via the dependence upon the inverse cube of the internuclear distances (neglect of vibrational effects) assuming equal HH(ortho) values, leading to an orientational parameter $S_{C_6} = -0.0721 \pm 0.0004$. In Table 3 the calculated couplings, their deviation from the observed ones in Hz and percent are given.

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[12] F. J. WEIGERT and J. P. ROBERTS, J Amer. Chem. Soc. **89**, 2967 [1967].

[13] P. J. BLACK, K. D. LAWSON, and T. J. FLAUTT, J. Chem. Phys. **50**, 542 [1969].

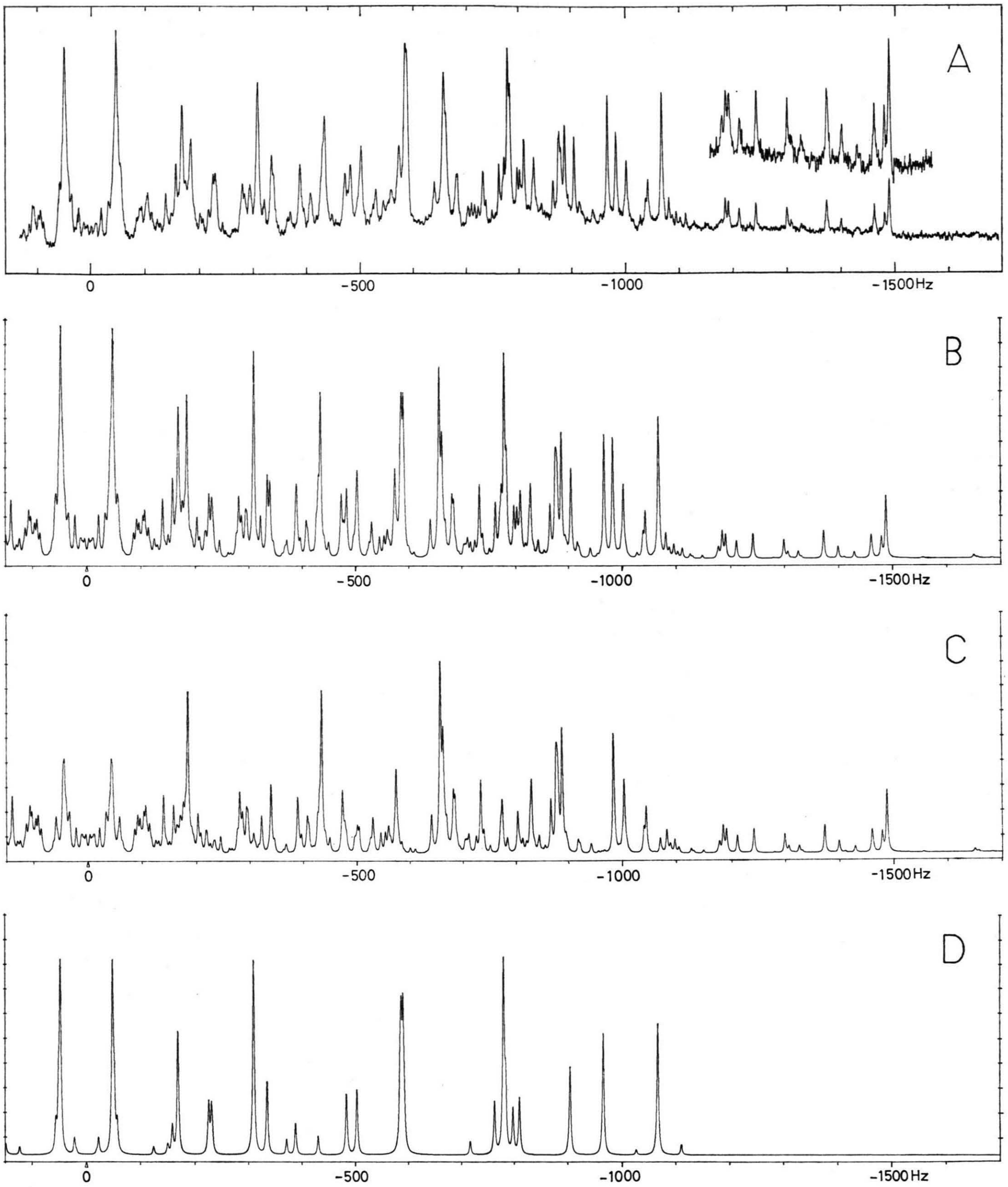

Fig. 2. A: high-field half of the symmetrical 100 MHz PMR-spectrum of benzene-benzene-1-^{13}C, oriented in a nematic liquid crystal at ca. 28 °C. B: superposition of the computer simulated 7- and 6-spin partial spectra of benzene-1-^{13}C (C) and benzene (D). The parameters used are given in column I of Table 1 and in Table 2. Half-width 3.5 Hz.

4. Discussion

As may be seen from Table 3, there are no significant deviations between NMR and Raman data for the proton-proton couplings, i. e. they closely correspond to the geometry of a regular hexagon. There are, however, significant differences for the carbon-13-proton couplings, especially for the ^{13}CH-coupling. The observed ^{13}CH-coupling is different from the value calculated on the basis of the Raman data by as much as 71 Hz. As was pointed out in the introduction, such discrepancies have already been observed earlier [5, 7]. In principle they may have several different origins: intramolecular vibrations and solvent effects on the indirect couplings as well as the anisotropy of the indirect couplings. If all these are neglected the observed discrepancy reflects an increase of the $C-H$ bond length, in terms of the HH-ortho distance, of approximately 3% or 0.03 Å, corresponding to an increase of the carbon-proton bond length from 1.084 to 1.116 Å.

4.1. Anisotropy of the Carbon-proton Indirect Coupling Constants

The difference in the direct carbon-proton couplings as determined by NMR and calculated from the r_0-structure may, in principle, be attributed to the anisotropy of the indirect couplings. This effect was already found for $^{19}F-{}^{19}F$ couplings; however, no definite proof for anisotropic contribution seems to have been established for proton-proton and carbon-13-proton couplings. No evidence for the existence of an anisotropic contribution to $J_{^{199}\mathrm{Hg},\,\mathrm{H}}$ in mercury dimethyl has been found experimentally [15].

As may be seen from Table 3, anisotropic contributions of the different indirect ^{13}CH-couplings would have to be of the order of 9%, 1.5%, 0.6% and 2.5% of the corresponding direct couplings in the ^{13}CH, ^{13}C(C)H, ^{13}C(CC)H and ^{13}C(CCC)H-cases, respectively. Several theoretical papers, however, predict that such contributions should be less than 1% [16] or even much smaller [17]. It can be deduced from the degree of orientation that the anisotropy of the $C-H$ indirect coupling $J_{\parallel}-J_{\perp}$ would have to be as large as -2950 ± 500 Hz in order to explain the observed discrepancy in bond-length ($\parallel$, $\perp$ means parallel and perpendicular, respectively, to the CH-bond axis). It is obvious that such an anisotropy is extremely unlikely.

4.2. Solvent Effects

Indirect coupling constants J_{CH} have been found to be solvent dependent in certain cases. Variations of up to 3% were detected, e. g., with $CHCl_3$ in several solvents [18]. Also a relationship between $C-H$ bondlength and J_{CH} has been suggested [19]. From such results it is evident that J_{CH} in benzene is not very sensitive to solvents. In fact, the values for the CCl_4 solution presented in Table 1 agree reasonably well with data obtained from neat benzene. It seems safe to asume that for these couplings contributions from solvent effects do not exceed 0.5 Hz and are therefore too small to explain the discrepancies in internuclear distances. Unfortunately the spectrum of oriented benzene-1-^{13}C does not allow a separate determination of the proton-carbon indirect couplings. The observed proton-spectrum is, due to the weak coupling with the carbon nucleus, effectively a superposition of two abb′b″b‴b⁗ subspectra with effective Larmor-frequencies

$$\nu_{\mathrm{i}} = \nu \pm \left(\tfrac{1}{2}\,{}^{\mathrm{i}}J_{\mathrm{CH}} + {}^{\mathrm{i}}D_{\mathrm{CH}}\right),$$

where ν is the Larmor frequency of oriented benzene and ${}^{\mathrm{i}}J_{\mathrm{CH}}$ and ${}^{\mathrm{i}}D_{\mathrm{CH}}$, respectively, are the various carbon-proton indirect and direct couplings. Consequently, only the sums $({}^{\mathrm{i}}J_{\mathrm{CH}} + 2\,{}^{\mathrm{i}}D_{\mathrm{CH}})$ affect

Table 3. Benzene-1-^{13}C: direct couplings D computed from Raman data in comparison with observed values (without vibrational correction).

	Raman distance[14] [in Å]	D_{RAMAN} [in Hz]	$D_{\mathrm{RAMAN}} - D_{\mathrm{NMR}}$ [in Hz]	$\frac{D'_{\mathrm{RAMAN}} - D_{\mathrm{NMR}}}{D_{\mathrm{NMR}}}$ [in %]
HH(ortho)	2.481 ± 0.005	-283.4 ± 1.7	$0^{a} \pm 1.7$	$0^{a} \pm 0.6$
HH(meta)	4.297 ± 0.006	-54.6 ± 0.3	-0.2 ± 0.3	-0.4 ± 0.6
HH(para)	4.962 ± 0.007	-35.4 ± 0.2	0 ± 0.2	0 ± 0.6
^{13}CH	1.084 ± 0.005	-854.3 ± 12	-71 ± 12	-9.1 ± 1.5
^{13}C(C)H	2.154 ± 0.005	-108.8 ± 0.8	-1.6 ± 0.8	-1.5 ± 0.7
^{13}C(CC)H	3.402 ± 0.006	-27.6 ± 0.2	-0.2 ± 0.2	-0.6 ± 0.7
^{13}C(CCC)H	3.878 ± 0.005	-18.7 ± 0.1	$+0.5 \pm 0.2$	$+2.5 \pm 1.0$

[a] assumed.

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[14] A. Langseth and B. P. Stoicheff, Canad. J. Phys. **34**, 350 [1956].

[15] G. Englert, Z. Naturforsch. **24 a**, 1074 [1969].

[16] A. D. Buckingham and F. Love, J. Mag. Res. **2**, 338 [1970].

[17] M. Barfield, Chem. Phys. Letters **4**, 518 [1970].

[18] D. F. Evans, J. Chem. Soc. 5575 [1963].

[19] N. Muller and D. E. Pritchard, J. Chem. Phys. **31**, 768 [1959].

the spectrum, and for the analysis known values for $^1J_{\mathrm{CH}}$ have to be taken from the spectrum in the isotropic phase.

As may be seen by inspection of Table 3 the differences in the direct couplings are very likely too large to be attributed to solvent effects for the couplings ^{13}C(C)H and ^{13}C(CCC)H; they are entirely out of range for the coupling ^{13}CH. For the coupling ^{13}C(CC)H the deviation is too small to be significant.

4.3. The Influence of Vibrational Motions on the Internuclear Distances

It is well known that, due to the dependence of the direct coupling upon the inverse cube of the internuclear distance, the influence of vibrational motions has to be considered if NMR results are to be compared with geometrical data obtained by different methods [20].

A simple model in which the direct coupling is expanded in a Taylor series about the equilibrium geometry has recently been suggested [5]. In order to compute the changes in the direct couplings due to vibrational motions several simplifying assumptions are made. First of all, only motions of the hydrogens are taken into account (infinite mass of carbon atoms). The coordinates used are δr, $\delta \alpha_{\|}$ and $\delta \alpha_{\perp}$, corresponding to the three types of vibrational motions, namely the CH-stretching, in-plane and out-of-plane deformations. These motions are assumed to be independent of each other. If higher than quadratic terms are neglected one obtaines for the direct coupling (e = equilibrium value):

$$D_{\mathrm{NMR}} = D^{\mathrm{e}} + \left(\frac{\partial D}{\partial r}\right)^{\mathrm{e}} \cdot \langle \delta r \rangle + \frac{1}{2}\left(\frac{\partial^2 D}{\partial r^2}\right)^{\mathrm{e}} \cdot \langle \delta r^2 \rangle$$

$$+ \frac{1}{2} r_{\mathrm{e}}^2 \left(\frac{\partial^2 D}{\partial (r_{\mathrm{e}}\, \alpha_{\|})^2}\right)^{\mathrm{e}} \langle \delta \alpha_{\|}{}^2 \rangle + \frac{1}{2} r_{\mathrm{e}}^2 \left(\frac{\partial^2 D}{\partial (r_{\mathrm{e}}\, \alpha_{\perp})^2}\right)^{\mathrm{e}} \langle \delta \alpha_{\perp}{}^2 \rangle .$$

Linear terms in α are not included since the corresponding potential energy is symmetrical with respect to the CH-bond ($\alpha_{\|}$) and to the molecular plane ($\alpha_{\perp}$). Results for the mean square amplitudes could be located in the literature [21, 22]:

$$\langle \delta r^2 \rangle = 0.0059\ \text{Å}^2,$$
$$r_{\mathrm{e}}^2 \langle \delta \alpha_{\|}{}^2 \rangle = 0.0141\ \text{Å}^2,$$
$$r_{\mathrm{e}}^2 \langle \delta \alpha_{\perp}{}^2 \rangle = 0.0236\ \text{Å}^2.$$

In contrast, values of $\langle \delta r \rangle$ for benzene are not known. However, it has been pointed out [23] that the anharmonicity of the C – H stretching in benzene is similar to the one of an isolated diatomic CH-vibrator. An approximate value may consequently be derived from a theory of the change in bondlength of diatomic molecules due to anharmonic effects [24]. The result is:

$$\langle \delta r \rangle = +0.019\ \text{Å}.$$

The derivatives of the direct couplings with respect to the coordinates are computed and with the above given figures for the harmonic and anharmonic terms the relative corrections for the different HH- and CH-couplings are obtained as presented in Table 4.

Table 4. Vibrational corrections for observed direct couplings in percent.

coupling	Anharmonic correction	Harmonic correction	Total correction	adapted experimental correction
HH (ortho)	– 2.3	– 1.6	– 3.9	– 3.9[a] ± 0.6
HH (meta)	– 2.3	– 0.9	– 3.2	– 4.3 ± 0.6
HH (para)	– 2.3	– 0.7	– 3.0	– 3.9 ± 0.6
^{13}CH	– 5.2	– 7.8	–13.0	–13.0 ± 1.5
^{13}C(C)H	– 2.2	– 1.5	– 3.7	– 5.4 ± 0.7
^{13}C(CC)H	– 1.6	– 0.7	– 2.3	– 4.5 ± 0.7
^{13}C(CCC)H	– 1.5	– 0.6	– 2.1	– 1.4 ± 1.0

[a] assumed.

It is seen that the total vibrational correction for the three proton-proton couplings are approximately of the same magnitude. This means that the vibrational motions do not affect the ratio of these couplings retaining the hexagonal symmetry as is experimentally observed.

In order to be able to compare the calculated vibrational corrections with the experimental values given in the last column of Table 3 which are based on the HH(ortho) distance of 2.481 Å, an adapted experimental correction may be calculated (last col-

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[20] L. C. Snyder and S. Meiboom, J. Chem. Phys. **47,** 1480 [1967].

[21] S. Y. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Elsevier Publishing Company, Amsterdam 1968, p. 245.

[22] W. V. F. Brooks, S. Y. Cyvin, and P. C. Krande, J. Phys. Chem. **69,** 1489 [1965].

[23] T. E. Martin and A. H. Kalantar, J. Chem. Phys. **49,** 235 [1968].

[24] M. Toyama, T. Oka, and Y. Morino, J. Mol. Spect. **13,** 193 [1964].

umn of Table 4) by assuming the HH-ortho correction to be -3.9. With this adaptation the experimental vibrational corrections for the different couplings are in good agreement with the calculated ones. It may be seen, therefore, that the simple model used can satisfactorily explain changes of the direct couplings due to intramolecular vibrations. Our results for benzene-1-^{13}C are in qualitative agreement with values recently obtained for this compound containing carbon-13 in natural abundance[5].

5. Conclusions

Summarizing the discussion of the various possible explanations for the observed discrepancies between NMR- and Raman data, we come to the conclusion that at least for the direct coupling $^{13}C-H$, solvent effects as well as the anisotropy of the indirect coupling are entirely out of question. The calculation of the influence of vibrational motions based on a simple model, however, satisfactorily explains the deviation observed between the two methods.

Paramagnetische Strahlungsdefekte in Fluoren- und Carbazolkristallen *

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Paramagnetic Radiation Defects in Fluorene and Carbazole Single Crystals

Two complementary radicals in fluorene and carbazole single crystals, irradiated by UV-, γ- or X-rays, have been identified by investigation of the hyperfine structure of ESR-spectra. Species I is formed by dissociation of a hydrogen atom from position 9, whereas species II results from addition of a hydrogen atom to one of the benzene rings. In carbazole there is evidence of a third radical. The annealing kinetics of all these radicals have been proved to be of second order, requiring activation energies between 1 and 2.1 eV.

1. Einleitung

In vielen organischen Einkristallen können durch Bestrahlung orientierte Radikale erzeugt werden[1]. Die ESR-Spektren solcher Radikale lassen sich in guter Näherung durch einen Spin-Hamilton-Operator der Form[2, 3]

$$H = g\,\mu_B\,H_0\,S + \sum_i S\,T_i\,I_i$$

beschreiben. Der erste Term gibt die Zeeman-Energie des ungepaarten Elektrons an, der zweite beschreibt seine Hyperfeinwechselwirkung mit den paramagnetischen Kernen, die sich aus der anisotropen Dipol-Dipol-Wechselwirkung $S\,T'\,I$ und der isotropen Fermi-Kontaktwechselwirkung $a\,s\,I$ zusammensetzt.

Einkristalle von Fluoren und Carbazol verfärben sich unter der Einwirkung von UV-, γ- oder Röntgen-Strahlen: Fluoren gelbbraun, Carbazol grün. In beiden Kristallsystemen wurden neben den optischen Absorptionszentren durch ESR-Messungen auch jeweils zwei verschiedene paramagnetische Defekte gefunden, die als komplementäre Radikale interpretiert wurden[4]. Je eines dieser Radikale entsteht durch Dissoziation eines H-Atoms, das andere durch Anlagerung eines H-Atoms. Diese Interpretation soll hier näher erläutert werden an Hand einer Analyse der Hyperfeinstruktur (HFS), insbesondere ihres anisotropen Anteils. In weiteren ESR-Messungen wird der Einfluß von verschiedenartigen Bestrahlungen, die Abhängigkeit von der Bestrahlungsdosis sowie die thermische Stabilität der Radikale untersucht.

2. Experimentelles

Einkristalle von Fluoren und Carbazol wurden nach dem Bridgeman-Stockbarger-Verfahren aus der Schmelze gezogen. Die Ausgangssubstanzen, die in technisch rei-

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