metry, whereas in the polycrystalline solid they follow those for S_6.

Cubane may be regarded as six C_4 rings locked together to form a cube. It is a surprising and curious coincidence that the breathing mode of the (nonplanar) cyclobutane ring, 1004.5 cm^{-1},[10] is only 3 cm^{-1} different from the breathing mode of cubane (1002 cm^{-1}).

It was our expectation that the spectra would have some unusual features because of the severely strained bond angles at the cube corners. To our surprise there is no obvious evidence of this. The modes of d_0 come about where one would expect by analogy with unstrained, saturated hydrocarbons, and its spectrum seems to be quite normal. For example, the frequency of a C–H stretch usually rises as the C–C–C bond angle of the saturated carbon becomes smaller. Thus the highest C–H stretch in cyclohexane is 2963 cm^{-1},[11] in cyclopentane is 2966 cm^{-1},[12] in cyclobutane is 2987 cm^{-1},[10] and in cyclopropane the four modes range between 3025 and 3102 cm^{-1}.[13] Many other examples could be cited, but this is enough to show the trend. We had expected to find at least some of the C–H stretches in cubane above 3000 cm^{-1}, but the highest is 2995 cm^{-1}. This is only a little higher than the highest in cyclobutane. A fairer comparison is to use the average of all the C–H stretches weighted for degeneracy. This average is 2916 cm^{-1} for cyclohexane, 2926 cm^{-1} for cyclopentane (averaged over the eight known stretches), 2939 cm^{-1} for cyclobutane, 2977 cm^{-1} for cubane, and 3059 cm^{-1} for cyclopropane. This does reflect the strain in cubane.

It may be that the force field will show the influence of bond strain more clearly. One of us (E.F.M.) expects to publish a normal-coordinate calculation for cubane. We hope that this will give quantitative information on how normal the bonds are. For now the most we can say is that the spectrum of cubane seems remarkably similar to that of the other saturated hydrocarbons.

There is one interesting point of difference, however. Cubane has no low molecular modes; its lowest fundamental is 617 cm^{-1}. The C_8 cube is a "tight" system because it is bonded three dimensionally, and it is therefore not easy to deform even if all the bonds are single ones. By contrast, benzene, although having much stronger C–C bonds, is considerably more floppy and has an out-of-plane bending mode at 404 cm^{-1}.

References and Notes

(1) (a) The Flinders University of South Australia. (b) University of Pittsburgh. (c) A portion of this paper is from a thesis to be submitted by Gerald L. Jones in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pittsburgh.

(2) The *Chemical Abstracts* name for cubane is pentacyclo[$4.2.0.0^{2,5}.0^{3,8}.0^{4,7}$]octane. It is *Chemical Abstracts* compound 277-10-1.

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^1H, ^2H, and ^{13}C ENDOR Studies of Phenalenyl Radicals in Nematic and Smectic Mesophases of Liquid Crystals

B. Kirste, H. Kurreck,* H.-J. Fey, Ch. Hass, and G. Schlomp

Contribution from the Institut fur Organische Chemie, Freie Universitat Berlin, Takustr. 3, 1000 Berlin 33, West Germany.

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Abstract: ESR, ^1H, ^2H, and ^{13}C ENDOR and TRIPLE experiments have been performed on labeled chloro- and methylphenalenyls ("perinaphthenyls") in isotropic, nematic, and smectic phases of liquid crystals. Hyperfine coupling constant shifts were measured and the assignment to molecular positions is discussed. The results suggest that the substituents cause additional alignment effects of the radicals. Smectic A phases have proved to be advantageous as compared to nematic phases in these studies. The first successful detection of ^{13}C ENDOR lines in a nematic mesophase is reported. Quadrupole splittings were observed for all of the ^2H ENDOR lines, and the complete quadrupole coupling tensor of the ring deuterons ($e^2qQ/h = (174 \pm 10)$ kHz, $\eta = 0.08 \pm 0.04$) and the quadrupole coupling of the methyl deuterons ($e^2qQ/h \sim 130$ kHz) could be determined.

Introduction

Information about the anisotropic hyperfine or **g**-tensor contributions can in principle be obtained from ESR spectra of organic radicals imbedded in amorphous or polycrystalline solid matrices. However, these spectra usually are very complex and poorly resolved. In isotropic fluid solution, on the other hand, the angular-dependent contributions are averaged out by the Brownian motion resulting in well-resolved ESR spectra, but only the isotropic contact hyperfine interactions and the isotropic g factor can be observed and all information about the anisotropic interactions is lost.

Previously it could be shown in a variety of papers that this lack can be overcome by using liquid crystals as solvents.[1] The long axes of the solvent molecules within the nematic liquid crystals tend to be parallel, and they are macroscopically aligned by applying a magnetic field (~0.3 T). Consequently, the molecular motion of dissolved nonspherical molecules is no longer isotropic, and the ordering of the solute will more or less reflect the ordering of the solvent. This alignment of the radical under study constitutes nonvanishing contributions from the anisotropic hyperfine tensors resulting in quite different hyperfine coupling constants as compared to the isotropic splittings. Unambiguous evaluation of the shifts caused by the anisotropic motion of the molecules calls for the proper determination of the respective isotropic hyperfine coupling constants under the same experimental conditions. A more approximate measurement of the isotropic couplings is

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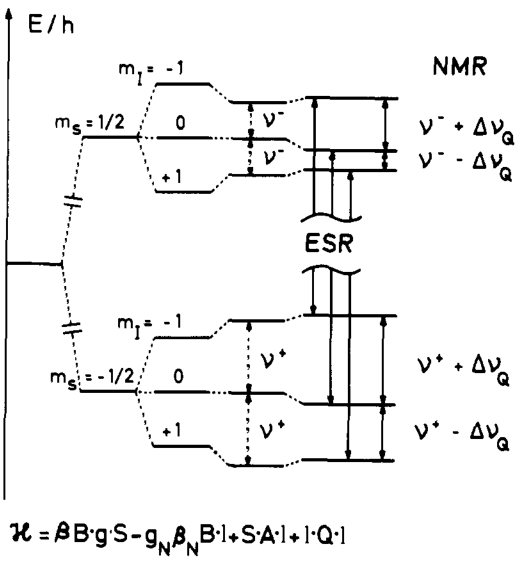

Figure 1. Level scheme of a radical fragment ($S = 1/2$, $I = 1$) in anisotropic solution ($0 < \bar{a}/2 < \nu_N$, $\Delta\nu_Q > 0$). Note that the quadrupolar interaction influences the NMR transitions (splitting of the ENDOR lines), whereas the ESR transitions remain unaffected to first order.

achieved by using isotropic solvents or by passing into the isotropic phase of the liquid crystal, i.e., by increasing the temperature. Obviously this procedure may cause some ambiguity, especially if the couplings are temperature or solvent dependent. With the aid of smectic phases, however, both the anisotropic as well as the isotropic hyperfine couplings are accessible under the same conditions.[2] One difficulty arises from the fact that smectic mesophases are not aligned by a magnetic field, but, if the liquid crystal also exhibits a nematic phase, the alignment might be preserved in the smectic mesophase when cooled down slowly from the aligned nematic phase.[3] Once aligned, the macroscopic ordering of the smectic phase persists even in the absence of the magnetic field and rotation of the sample cell does not affect the arrangement of guest and host molecules. Ordered smectic phases offer the potentiality of arbitrarily selecting the direction of orientation.[4]

Liquid crystal ESR spectra are often incompletely resolved. Hence, liquid-crystal measurements call for the ENDOR technique with its much higher spectral resolution. Moreover, electron nuclear nuclear triple resonance (TRIPLE) experiments allow the determination of relative signs of the hyperfine splitting constants.[5]

In the present paper we report on ENDOR investigations in different liquid crystals, namely, "nematic phase IV licristal", 4-cyano-4′-pentylbiphenyl, and 4-cyano-4′-octylbiphenyl, the latter of which exhibits a smectic A mesophase besides a nematic phase. For this purpose we have chosen partially labeled, i.e., deuterated or ^{13}C labeled, phenalenyl ("perinaphthenyl") radicals. The phenalenyl system is especially suitable, firstly because it is one of the most stable hydrocarbon radicals, secondly because it is readily accessible by several synthetic pathways,[6] and thirdly because it was found to achieve high degrees of alignment owing to its disk-like shape.

Finally we give an outline of our ENDOR studies on the deuterium quadrupole coupling. In this respect it has to be noted that quadrupole splittings cannot be observed by means of ESR since (to first order) the coupling shifts all levels connected by ESR transitions equally.[7] To our knowledge up to now only two papers exist in the literature dealing with the investigation of quadrupole couplings by means of ENDOR in nematic phases[8,9] and our very recent short communication describing smectic phase ENDOR studies.[10]

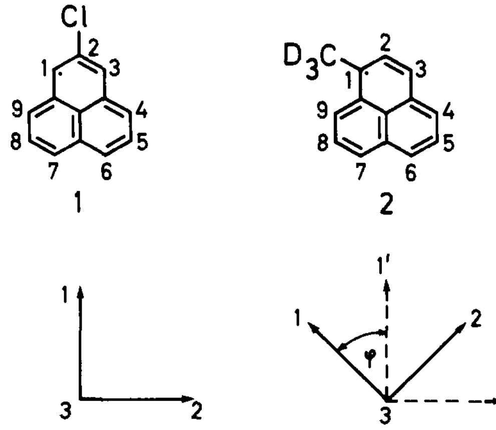

Figure 2. Numbering scheme of compounds and molecular axis systems: **1a**, 2-chlorophenalenyl; **1b**, 2-chlorophenalenyl-6-*d*; **1c**, 2-chlorophenalenyl-d_8; **1d**, 2-chlorophenalenyl-2-^{13}C-d_8; **2**, 1-methyl-d_3-phenalenyl.

Theory

Partial alignment of a radical in a nematic mesophase causes a shift in the observed hyperfine splittings

$$\Delta a = \frac{2}{3}\sum_{i,j} O_{ij}A'_{ij} \qquad (1)$$

where O_{ij} and A'_{ij} are the elements of the traceless ordering and anisotropic hyperfine tensors.[11] In the principal axis system of the ordering matrix, eq 1 can be rewritten in the form

$$\Delta a = O_{33}A'_{33} + \frac{1}{3}(O_{11} - O_{22})(A'_{11} - A'_{22}) \qquad (2)$$

The director of a nematic phase is aligned in the direction of the magnetic field, whereas a smectic phase is neither aligned nor realigned after a variation of the orientation. The observed hyperfine splittings of a radical in a monodomain sample of a smectic A phase depend upon the angle γ between the director and the magnetic field:[4]

$$|\bar{a}(\gamma)| = [\tilde{A}_\perp^2 + (\tilde{A}_\parallel^2 - \tilde{A}_\perp^2)\cos^2\gamma]^{1/2} \qquad (3)$$

where $\tilde{A}_\parallel = \bar{a}(0°) = a + \Delta a$ and $\tilde{A}_\perp = \bar{a}(90°) = a - \frac{1}{2}\Delta a$ with Δa given by eq 1 or 2. While each set of equivalent protons gives rise to one pair of ENDOR lines

$$\nu_{\mathrm{ENDOR}} = |\nu_H \pm \bar{a}/2| \qquad (4)$$

deuterium ENDOR lines may additionally show a splitting $\delta_Q = 2|\Delta\nu_Q|$ due to the quadrupole interaction of the deuterium nucleus ($I = 1$)[9] (see Figure 1):

$$\nu_{\mathrm{ENDOR}} \approx |(\nu_D \pm \bar{a}/2) \pm \Delta\nu_Q| \qquad (5)$$

$$\Delta\nu_Q = Q'\left[O_{11} + \frac{1}{3}\eta(O_{22} - O_{33})\right] \qquad (6)$$

where $Q' = \frac{3}{4}e^2q_{11}Q/h$ and $\eta = (q_{22} - q_{33})/q_{11}$, assuming that axis 1 is parallel to the C–D bond direction.

Experimental Section

Generation of the Radicals. 2-Chlorophenalenyl (**1a**) and the labeled compounds **1b–d** were prepared by a carbenoid reaction of acenaphthylene (acenaphthylene-5-*d*,[12] acenaphthylene-d_8) with chloroform (chloroform-^{13}C) and potassium *tert*-butoxide. The radicals were generated in the ESR sample cell, after evaporation of the solvent, liquid crystal "nematic phase IV licristal" (Merck, Darmstadt; nematic mesophase 289–349 K) was added and the sample thoroughly degassed. The carbenoid reaction can, in principle, also be performed directly in the liquid crystal, but the former procedure proved to give the more stable solutions of the phenalenyls. A more detailed description of the generation of the chlorophenalenyls has been given elsewhere.[6] 1-Methyl-d_3-phenalenyl (**2**) was obtained by heating the

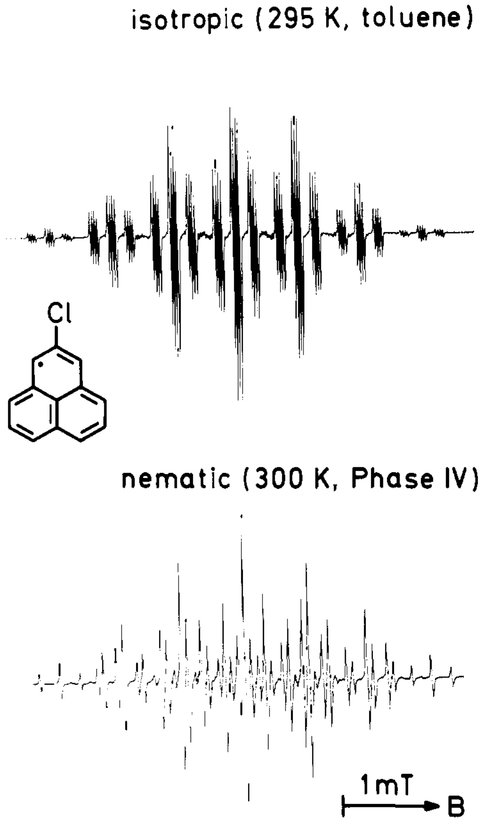

Figure 3. ESR spectra of 2-chlorophenalenyl (**1a**) in isotropic solution (top) and in a nematic mesophase (bottom).

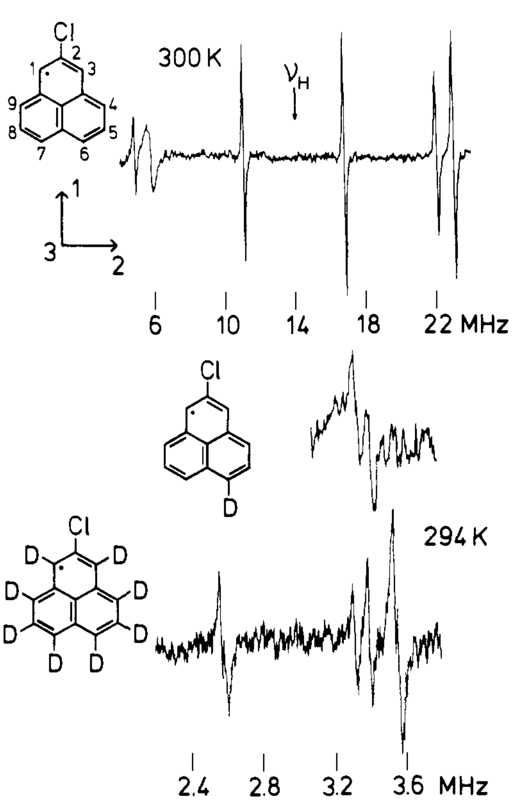

Figure 4. ^{1}H ENDOR spectrum of **1a** (top) and ^{2}H ENDOR signals of **1b** (center) and **1c** (bottom) in the nematic mesophase of "nematic phase IV".

solution of the respective phenalene in "phase IV", in the liquid crystal 4-cyano-4′-pentylbiphenyl (nematic phase 295–308 K), or in 4-cyano-4′-octylbiphenyl (smectic A phase 294–307 K, nematic phase 307–314 K) in the presence of atmospheric oxygen for a few minutes. Subsequently the solutions were carefully degassed on a high vacuum line. For more details, including the synthesis of the phenalenyl precursor, see ref 13a.

To obtain a monodomain sample of the smectogen 4-cyano-4′-octylbiphenyl, the sample was heated to the temperature range of the nematic phase, and while in a magnetic field (0.33 T) the temperature was slowly lowered at a rate of about 1 K/min until the smectic phase was formed. Judging from the measured hyperfine couplings, no higher degree of alignment was found within experimental error when applying a stronger magnetic field than that used for the X-band ESR experiments. Furthermore, realignment of the director in the smectic phase by the magnetic field was not found, at least in a temperature range not too close to the smectic–nematic transition point (using 3.5 mm o.d., 2.5 mm i.d. tubes). However, in a very recently published analysis of ESR line shapes angular-dependent effects were found which depend upon the size, shape, and preparation of the sample.[13b]

Instrumentation. The ESR spectra were recorded on an AEG-12X-ESR spectrometer. The ENDOR and TRIPLE spectrometer consists basically of an AEG-20XT-ESR spectrometer; the ENDOR accessory was built up in this laboratory. A detailed description of our CW ENDOR spectrometer was given elsewhere;[14] an HP 8660 B frequency synthesizer served as radio-frequency source. Temperature variation was achieved with an AEG temperature control unit; temperature data are accurate within ±1 K.

Results

ESR and ENDOR of 2-Chlorophenalenyl (1a). The hyperfine line pattern of the ESR spectrum of 2-chlorophenalenyl changes drastically when passing from the isotropic to the nematic phase of the liquid crystal "phase IV"; see Figure 3. (In Figure 3, the ESR spectrum taken in toluene is reproduced since the spectrum taken in the isotropic phase of "phase IV" is less well resolved owing to the higher viscosity of the solvent.) The isotropic solution spectrum shows the hyperfine interaction with one set of six equivalent protons (largest splitting), one set of two equivalent protons, and additionally with the chlorine nucleus (^{35}Cl/^{37}Cl, $I = 3/2$) giving rise to a splitting of each component into four lines ($|a_{\mathrm{Cl}}| = 0.64$ MHz). In the nematic phase, the equivalence of the six protons is lifted and a resolved chlorine hyperfine structure is no longer seen ($|\bar{a}_{Cl}| \leq 0.1$ MHz). Actually the ESR spectrum can be interpreted by assuming one set of four and two sets of two equivalent protons contributing to the line pattern.

An accurate determination of the hyperfine coupling constants was possible from the ENDOR experiments in the isotropic and anisotropic phases of the liquid crystal. Moreover, the relative signs of all couplings were accessible from our general TRIPLE resonance experiments. The ENDOR spectrum of **1a** taken in the nematic phase of "phase IV" (Figure 4, top) clearly indicates the inequivalence of the protons belonging to the largest splitting, being in agreement with the ESR results. The isotropic proton hyperfine coupling constants of **1a** and the shifts measured in the nematic phase ($\Delta a = a_{\mathrm{nem}} - a_{\mathrm{iso}}$) are collected in Table II. It is noteworthy that the isotropic proton couplings are equal to those of the unsubstituted phenalenyl within experimental error.[6]

^{2}H ENDOR of 2-Chlorophenalenyl-*6-d* (1b) and -*d*$_8$ (1c). Quadrupole Splittings. Previously deuterium quadrupole splittings of (unsubstituted) deuterated phenalenyl could be observed by using ENDOR in liquid crystals.[9] The quadrupole splittings were found to be equal for both groups of deuterons ((42.2 ± 0.5) kHz, "phase IV", 293 K). In order to examine the influence of substitution, we have studied the chlorinated phenalenyls **1b** and **1c**. All of the expected ^{2}H ENDOR lines of **1c** could be detected, each of them showing a quadrupole splitting; see Figure 4 (bottom; only the high-frequency side of the ^{2}H ENDOR spectrum is shown). Surprisingly, the magnitudes of the splittings deviate considerably from the value reported for phenalenyl-*d*$_8$: 25, 79, and 24 kHz (±2 kHz,

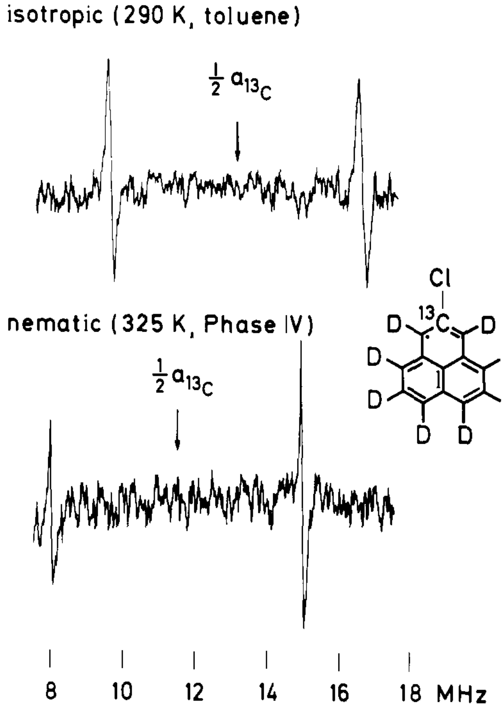

Figure 5. ^{13}C ENDOR spectra of **1d** in isotropic solution (top) and in a nematic mesophase (bottom; B_{NMR} = 0.9 mT in the rotating frame).

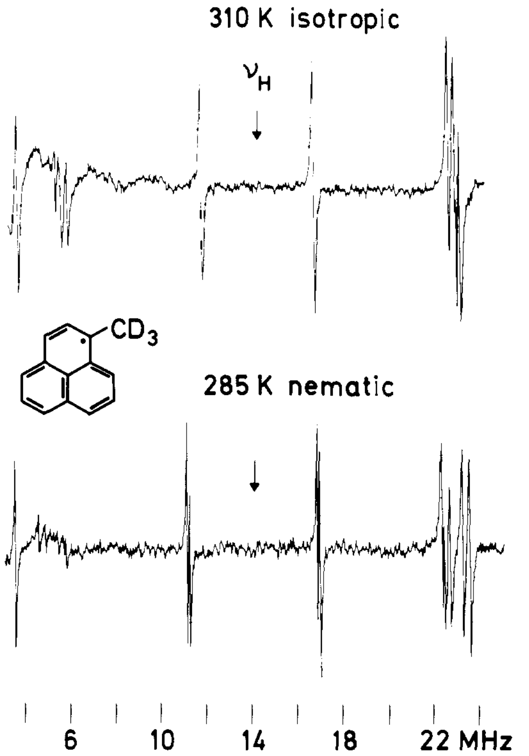

Figure 6. ENDOR spectra of 1-methyl-d_3-phenalenyl (**2**) in the isotropic (top) and in the nematic phase (bottom) of 4-cyano-4′-pentylbiphenyl.

294 K, in order of increasing $|\bar{a}_D|$). The assignment to molecular positions was achieved by investigating the specifically labeled compound **1b**; see Figure 4 (center). Actually, this assignment had been predicted beforehand on the basis of an analysis of the corresponding proton coupling shifts (vide infra).

^{13}C ENDOR of 2-Chlorophenalenyl-*2-^{13}C-d_8* (1d). The most interesting nonproton nucleus for the organic chemist is the ^{13}C isotope. Recently successful ^{13}C ENDOR studies have been reported and some general statements concerning the optimum ENDOR response could be given.[15] In order to check the possibility of performing ^{13}C ENDOR experiments in liquid crystals, we have studied 2-chlorophenalenyl-*2-^{13}C-d_8* (**1d**). Actually, ^{13}C ENDOR lines of **1d** could be detected in isotropic (toluene, 290 K) as well as in nematic solutions ("phase IV", 325 K); see Figure 5. It has to be noted that ^{13}C ENDOR lines were not observable at temperatures near the melting point of the solvent since a somewhat higher temperature/viscosity ratio was required as compared to the optimum ^1H ENDOR conditions;[15] no ^{13}C ENDOR spectrum could be recorded in the isotropic phase of "phase IV" owing to the limited radical stability at higher temperatures. According to the ENDOR resonance condition $\nu_{ENDOR} = |\nu_N \pm a_N/2|$ and $\nu_{^{13}C} < |a_{^{13}C}/2|$ two ^{13}C ENDOR lines show up, equally spaced around $a_{^{13}C}/2$ and separated by $2\nu_{^{13}C}$ = 7.01 MHz. In isotropic solution, $\bar{a}_{^{13}C} = -26.08$ MHz was measured (toluene, 290 K), and a significant shift was found in the nematic phase, $\bar{a}_{^{13}C} = -23.00$ MHz ("phase IV", 325 K); the negative sign of the ^{13}C hyperfine coupling constant could be deduced from a TRIPLE experiment. To our knowledge, this is the first successful ^{13}C ENDOR experiment in a liquid crystal.

ESR and ENDOR of 1-Methyl-d_3-phenalenyl (2). The isotropic fluid solution ESR and ENDOR spectra of 1-methyl-d_3-phenalenyl (**2**), very recently published and interpreted,[13a] show that the equivalence of the five perimeter protons belonging to the largest splitting is removed by the methyl group even in isotropic solution. On passing into the nematic mesophase, the hyperfine line pattern of the ESR spectrum becomes very complex (solvent: 4-cyano-4′-pentylbiphenyl), obviously caused by a more pronounced inequivalence of the protons. As a matter of fact, the limited resolution of ESR prevents an unambiguous interpretation of the spectrum.

The ENDOR investigation of **2** in liquid-crystalline solutions provides an excellent example of the high resolution power of this technique. In fact, eight pairs of ^1H ENDOR lines could be resolved in the nematic phase of "phase IV" (294 K) besides the high-frequency ^2H ENDOR line belonging to the CD_3 group, i.e., all of the protons have become inequivalent. However, while "phase IV" is an excellent solvent for ^1H ENDOR at room temperature, the decreasing viscosity at higher temperatures results in larger line widths and a correspondingly poorer resolution in the isotropic phase. In this respect, the liquid crystal 4-cyano-4′-pentylbiphenyl is superior, which is clearly demonstrated by the ENDOR spectra of **2** taken in the isotropic and nematic phases of this solvent; see Figures 6 and 7. ^1H ENDOR line widths down to 30 kHz could be obtained.

It stands to reason that in the present case, with several inequivalent protons showing only small differences of their couplings, the shifts cannot be unambiguously assigned to the corresponding isotropic splittings since the ordering sequence of the hyperfine coupling constants might be altered on passing from the isotropic to the nematic phase. By observing the temperature dependence of the coupling constants in the nematic phase, only a tentative assignment was possible. Very recently we have found a possibility of overcoming this kind of difficulty by using smectic mesophases instead of nematic phases, e.g., the smectic A phase of 4-cyano-4′-octylbiphenyl.[10] As was pointed out in the Introduction, the direction of orientation of the smectic phase with respect to the magnetic field can be arbitrarily selected. Making use of this fact, the coupling constant shifts derived from the ENDOR spectra of **2** taken in the anisotropic solution could be accurately assigned to the isotropic coupling constants by stepwise rotating the sample cell and observing the changes of the splittings. The shifts $\Delta a = \frac{2}{3}[\bar{a}(0°) - \bar{a}(90°)]$ and the isotropic couplings $a = \frac{1}{3}[\bar{a}(0°) + 2\bar{a}(90°)]$ are collected in Table III.

Table I. Anisotropic Proton Hyperfine Tensors of Phenalenyl (MHz)[a]

position	A'_{11}	A'_{22}	A'_{33}	A'_{12}
		A		
1,3	−2.654	4.316	−1.662	∓7.727
4,9	−4.118	5.779	−1.662	±6.882
6,7	9.265	−7.603	−1.662	∓0.845
2	0.324	2.020	−2.344	0.000
5,8	1.596	0.748	−2.344	±0.735
		B		
1,3	−4.043	4.371	−0.329	∓7.468
4,9	−4.199	4.528	−0.329	±7.378
6,7	8.735	−8.406	−0.329	∓0.091
2	−0.015	2.088	−2.073	0.000
5,8	1.562	0.511	−2.073	±0.911

[a] Calculated according to ref 21 with $Z = 3.18$, $R_{\mathrm{C\text{-}H}} = 108.5$ pm, $R_{\mathrm{C\text{-}C}} = 139.7$ pm, and spin populations from ref 28. In model A, all π spin density contributions are included; in model B, only contributions with $R_{ij} \leq 210$ pm are taken into account. For the axis system, see Figure 2 (left).

In Figures 6 and 7, also the high-frequency ^{2}H ENDOR line of **2** is reproduced. In the isotropic phase (310 K) one single line is observed, whereas this line is split by (18 ± 2) kHz in the supercooled nematic phase (280 K, 4-cyano-4′-pentylbiphenyl; high-resolution conditions); see Figure 7 (bottom left). This splitting undoubtedly has to be attributed to a quadrupole splitting. Obviously the (anisotropic) deuterium quadrupole coupling of a methyl group is not averaged to zero even in the case of free rotation; see Discussion.

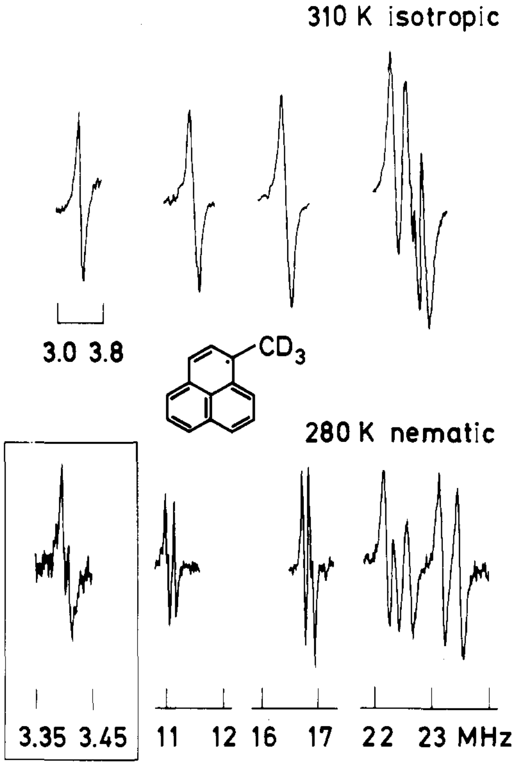

Figure 7. ^{1}H and ^{2}H ENDOR lines of **2** in the isotropic (top) and nematic phase (bottom) of 4-cyano-4′-pentylbiphenyl shown on an expanded frequency scale. Bottom left: high-frequency ^{2}H ENDOR line of **2** showing a quadrupole splitting ($B_{\mathrm{NMR}} = 0.40$ mT, 3-kHz amplitude of the 5-kHz frequency modulation).

Discussion

The shifts of the hyperfine couplings and the quadrupole splittings observed for 2-chlorophenalenyl deviate considerably from those of phenalenyl.[9,16-19] The effect of the chloro substituent might be explained by an influence on the spin and charge density distributions and/or on the preferred orientation of the radicals in the liquid crystal with respect to the director. In the following it will be shown that only the latter effect accounts for all of the observations.

(1) The isotropic hyperfine coupling constants remain unaltered, indicating that the spin density distribution is not noticeably affected by chloro substitution. This is in agreement with an HMO/McLachlan calculation (using $h_{\mathrm{Cl}} = 2.0$, $k_{\mathrm{C\text{-}Cl}} = 0.4$[20]) which gives a maximum deviation of 1.4% for the spin populations.

(2) The observed coupling constant shifts can be reproduced by a calculation of the anisotropic contributions based on the theory of McConnell and Strathdee[21] and by using eq 2 with $O_{11} \neq O_{22}$; vide infra. Since $O_{11} > O_{22}$ is found, the molecules are preferentially oriented with the C–Cl bond axis parallel to the magnetic field direction. The shifts obtained for the methyl substituted phenalenyl **2** can be interpreted in a quite analogous manner.

(3) The relatively large deuterium quadrupole splitting of 79 kHz might be ascribed to an increased electric field gradient due to the inductive effect of the chloro substituent. However, the investigation of the specifically labeled compound **1b** established that the respective deuterons have to be assigned to positions 6 and 7 rather than to positions 1 and 3. In fact, the results concerning the quadrupole splittings can be accounted for on the basis of a pure orientational phenomenon; see eq 6 and the discussion presented below.

Analysis of the Coupling Constant Shifts. Since the observed hyperfine coupling constant shifts due to the partial alignment of radicals in liquid crystals depend on the ordering tensor as well as on the anisotropic hyperfine tensor (see eq 1), knowledge of one of the tensors is required for a quantitative interpretation. The elements of the anisotropic proton hyperfine tensors can be calculated by using the integrals given by McConnell and Strathdee[21] if the spin density distributions and the geometry of the radical are known. However, in the conventional treatment with standard parameters the shift Δa_{HI} in phenalenyl is considerably overestimated.[16] Possible reasons for this deficiency have been extensively discussed in the literature,[11,16,22] but none of the proposed modifications is completely satisfying. The agreement with the experimental data is improved by assuming a reduction (>10%) of the C–H bond distance or the effective nuclear charge Z (from $Z = 3.18$ to $Z = 2\zeta \sim 2.6$[22]) or by using a restricted model which takes into account only π spin density at the adjacent and next-nearest carbon atoms ($R_{ij} \leq 210$ pm).[17] Although this last procedure is somewhat arbitrary, it gives the most satisfying result in the case of phenalenyl (not necessarily in other cases), probably owing to a compensation of various errors inherent in the method. The calculated elements of the anisotropic proton hyperfine tensors obtained by both the conventional (A) and the restricted model (B) are collected in Table I. In the following it will be shown that the tensor elements calculated by the restricted method (B) also give the better results for the substituted phenalenyls.

While in the case of phenalenyl the ordering parameter O_{33} can simply be obtained from the relation $O_{33} = \Delta a/A'_{33}$ because of its threefold symmetry, the ordering parameters for 2-chlorophenalenyl (**1a**) have to be determined by a least-squares fit procedure using eq 2. With the hyperfine tensor components from the restricted model (B), $O_{33} = -0.30 \pm 0.01$ and $O_{11} - O_{22} = +0.29 \pm 0.01$ are obtained; the same value for $O_{11} - O_{22}$ is obtained from model A provided that $O_{33} = -0.30$ is assumed. It should be noted that the ordering parameter O_{33} agrees with that found for unsubstituted phenalenyl under the same experimental conditions.[9] The observed

Table II. Isotropic Proton Hyperfine Coupling Constants of **1a** ("Phase IV", 350 K; ±0.01 MHz) and Experimental ("Phase IV", 294 K) and Calculated Shifts (MHz)

position	a_{iso}	Δa_{exp}	$\Delta a_{\text{calcd}}^{(A)}$	$\Delta a_{\text{calcd}}^{(B)}$
1,3	−17.64	−0.78	−0.18	−0.71
4,9	−17.64	−0.78	−0.46	−0.74
6,7	−17.64	+1.70	+2.13	+1.75
5,8	+5.10	+0.74	+0.79	+0.72

Table III. Isotropic Proton Hyperfine Coupling Constants of **2** and Experimental and Calculated Shifts (MHz)[a]

position	a_{iso}	Δa_{exp}	$\Delta a_{\text{calcd}}^{(A)}$	$\Delta a_{\text{calcd}}^{(B)}$
3 (or 4)	−17.883	−1.017	−0.64	−0.87
4 (or 3)	−17.350	−0.926	−0.48	−0.86
6 (or 7)	−17.299	+0.031	+0.62	+0.14
7 (or 6)	−16.763	−0.009	+0.34	+0.12
9	−17.486	+0.890	+1.74	+1.11
2	+4.979	+0.835	+0.82	+0.81
5	+4.950	+0.650	+0.69	+0.69
8	+4.920	+0.946	+0.92	+0.93

[a] The experimental data were obtained by ENDOR in the smectic A phase of 4-cyano-4′-octylbiphenyl (285 K; ±0.01 MHz). The calculations are based on models A (with $O_{33} = -0.35$ and $O_{11} - O_{22} = 0.24$) and B (with $O_{33} = -0.39$ and $O_{11} - O_{22} = 0.20$), respectively.

and calculated shifts are given in Table II, clearly showing that model B yields a much better agreement with the experimental data than model A.

The interpretation of the coupling constant shifts of 1-methyl-d_3-phenalenyl (**2**) is somewhat more complicated since the principal axis system of the ordering tensor cannot be derived from simple symmetry arguments, and eq 1 has to be used with $O_{12} \neq 0$. However, some conclusions may be drawn without a calculation. Table III shows the following results concerning the shifts: about −1 MHz for two protons, zero for two protons, and +1 MHz for one proton. Since the shift is essentially determined by the average angle between the C–H bond axis and the direction of the magnetic field, the shift of +1 MHz has to be assigned to the singular position 9. The ordering parameters were determined by a least-squares fit procedure using the tensor elements of Table I, and a principal-axis transformation yielded an axis system rotated by $\phi = 45°$ (see Figure 2); the calculated shifts and the ordering parameters are given in Table III. That means that 1-methylphenalenyl is preferentially aligned with its "long axis" parallel to the long axes of the solvent molecules, similar to 2-chlorophenalenyl. The preferential alignment in the case of chloro- and methyl-substituted phenalenyls is evidently due to steric interactions with the solvent molecules, whereas a similar alignment effect found for phenalenyl-1-carboxylic acid in 4-pentoxybenzoic acid was ascribed to the formation of hydrogen-bonded dimers with the liquid-crystalline solvent.[11]

Interestingly, the analysis of the coupling constant shifts of **2** provides the possibility of an assignment of the shifts and isotropic coupling constants to molecular positions. This is achieved by a comparison of observed and calculated shifts (the assignment to positions 3 and 4 or 6 and 7 might be interchanged); the correlation of the shifts and the isotropic couplings is known from the study in the smectic phase (vide supra). It has to be noted that neither HMO/McLachlan nor INDO calculations were useful in the assignment of the coupling constants to molecular positions.[13a] The results given in Table III demonstrate that the proton in position 9 has no abnormal hyperfine coupling as might be expected by considering a peri interaction with the methyl group.

Deuterium Quadrupole Couplings. According to the arguments presented at the beginning of this section, the different deuterium quadrupole splittings obtained for the different positions in 2-chlorophenalenyl solely reflect the orientational dependence of the quadrupole coupling. It can be shown that the weighted average of the quadrupole splittings for the six deuterons in the positions of high spin density should be equal to the splitting found for unsubstituted phenalenyl. In fact, the result $\delta_Q = (42 \pm 2)$ kHz is in agreement with the value of $\delta_Q = (42.2 \pm 0.5)$ kHz for phenalenyl.[9] The evaluation of the out-of-plane component of the deuterium quadrupole tensor is straightforward ($|e^2q_{33}Q/h| = \frac{2}{3}\delta_Q/O_{33}$), giving $e^2q_{33}Q/h = (-94 \pm 5)$ kHz with the sign taken from ref 9. The remaining tensor components were obtained from eq 6, yielding $e^2q_{\text{CD}}Q/h = (174 \pm 10)$ kHz for the component along the C–D bond axis and $\eta = 0.08 \pm 0.04$. These values compare well with those reported for planar deuterated molecules in the singlet ground state ($e^2q_{\text{CD}}Q/h = 181$ kHz for benzene, 177 kHz for naphthalene[23]) and in the triplet state (177 kHz for quinoline, 179 kHz for quinoxaline[24]).

The interpretation of the quadrupole splitting of the deuterons in the methyl group of 1-methyl-d_3-phenalenyl is not so straightforward. The quadrupole coupling constant is averaged to a small value, but not to zero, by the rotation of the methyl group. This rotation can be pictured as a cone-shaped motion of the C–D bond axes, and the electric field gradient component along the symmetry axis is given by[25]

$$q_{\text{av}} = \left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)q_{\text{CD}} - \frac{1}{2}\eta\sin^2\theta\, q_{\text{CD}} \qquad (7)$$

where θ is the angle between the bond axis and the symmetry axis. Insertion of the tetrahedral angle (109° 28′) for θ and neglect of the second term in eq 7 ($\eta \sim 0$) yields $q_{\text{av}} = -\frac{1}{3}q_{\text{CD}}$. Since the principal axes of the averaged quadrupole coupling tensor and of the ordering tensor of **2** do not coincide, the appropriate tensor transformation has to be performed. With the ordering parameters given in Table III, $|e^2q_{\text{av}}Q/h| = 43$ kHz and finally $|e^2q_{\text{CD}}Q/h| = 130$ kHz were obtained. This value should only be regarded as an approximation, since the error of δ_Q is at least 10% and further ambiguity might have been introduced by inaccuracies of the ordering parameters. For comparison, a deuterium quadrupole coupling constant of 165 kHz is reported for the methyl group in toluene.[26]

Isotropic and Anisotropic ^{13}C Hyperfine Coupling. Finally, a short comment on the ^{13}C coupling in **1d** shall be given. The measured shift of +3.08 MHz ($O_{33} \sim -0.26$) for carbon in position 2 agrees roughly with the corresponding shift reported for unsubstituted phenalenyl (+2.46 MHz, 4,4′-dimethoxyazoxybenzene).[16] The isotropic coupling (−26.08 MHz) deviates significantly from that of the unsubstituted compound (−21.99 MHz) which might be due to different spin polarization properties of the C–Cl bond as compared to the C–H bond. The relative ease in obtaining ^{13}C ENDOR resonances (line width ~ 200 kHz) is accounted for by considering the hyperfine anisotropies[15,27] being comparable in magnitude for carbon-13 in position 2 and a proton in position 1.

Conclusions

Concluding, we can state that ENDOR in nematic and smectic mesophases yields valuable information about the alignment of radicals, anisotropic hyperfine interactions, and quadrupole couplings. We have shown that a chloro or methyl substituent in phenalenyl produces a marked additional alignment effect. The complete quadrupole coupling tensor of the ring deuterons and the quadrupole coupling of methyl deuterons could be determined. It must be pointed out, however, that the numerical reliability of the analysis is limited by possible errors of the ordering parameters which were obtained by using calculated hyperfine tensors. Unfortunately, to our knowledge there is no better procedure available for these calculations. For the ring positions, the same deuterium quadrupole couplings were found as for comparable molecules in singlet or triplet spin states within experimental error, indicating that there is no significant dependence of quadrupole couplings on the electron spin state in these systems. The observed quadrupole splittings of ^2H ENDOR lines depend strongly on the orientation of the C-D bond and thus might give information about the geometry of the radical.

The use of smectic A phases of liquid crystals has proved to be superior to the conventionally applied nematic phases in ^1H ENDOR studies, since the isotropic coupling constants and the shifts can be measured under the same experimental conditions. This is especially advantageous if the difference of coupling constants is small or in the case of strongly temperature or solvent dependent isotropic hyperfine couplings.

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Detailed Studies of Trigger Wave Initiation and Detection[1d]

Kenneth Showalter,*[1a,c] Richard M. Noyes,*[1b,c] and Harold Turner[1c]

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403, the Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506, and the Max Planck Institut für Biophysikalische Chemie, D-3400 Göttingen-Nikolausberg, West Germany.

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Abstract: A Belousov-Zhabotinsky solution in a marginally stable but excitable steady state can propagate trigger waves of oxidation that move undamped through the solution. Such a wave can be initiated by a positive square wave pulse of 0.8 V or more applied to a silver electrode previously biased negatively with respect to a platinum electrode in the same solution. The critical pulse duration necessary to initiate a wave can be measured within a few tenths of a millisecond and has been determined as a function of composition of the solution and of other relevant parameters. Passage of a trigger wave can be followed by recording potentials between platinum electrodes in its path. Because velocity of propagation at any point is a positive function of time since the last previous wave passed that point, three or more successive waves separated by no more than a few minutes will tend to approach more uniform separations as they propagate. If a pulse is applied to an electrode less than 50 s after the solution underwent an induced oxidative excursion (IOE), the incipient wave may be "localized" for up to 2 min before it leaves the electrode to propagate as a trigger wave; pulses applied 50 s or more after an IOE generate waves without delay. Repetitive pulses at a frequency of about 0.8 min^{-1} or less each generate a wave, but it is not possible to generate waves at a frequency greater than this no matter how frequently pulses are applied. Dissolved oxygen increases the concentration of bromide ion in the solution apparently by affecting the stoichiometry of oxidation by ferriin of a malonic-bromomalonic acid mixture; this increased bromide makes the system less sensitive to trigger wave initiation. An agar gel impregnated with silver nitrate solution can also initiate trigger waves. If a pair of silver electrodes is connected by a wire, a trigger wave impinging on the first can be discontinuously advanced so that future propagation is as though the wave had continued in the same direction but had been at the second electrode at the time it actually reached the first. All of these observations can be interpreted by a chemical mechanism previously developed to explain other features of this remarkable system. The behavior reported here exhibits several features similar to those observed during transmission of signals by a nervous system, and it may suggest useful analogies to neurophysiologists.

Introduction

Several unusual features can be exhibited by a Belousov[2]-Zhabotinsky[3] solution containing malonic and sulfuric acids, bromate, and ferroin catalyst. Temporal oscillations in a uniform solution are now well understood[4,5] and have been modeled.[6]

Because of a prior perturbation of an initially uniform os-

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