

## The Nuclear-Electron Overhauser Effect of Carbon-13 as Studied by Multi-Field Dynamic Polarization Experiments in Solutions

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Experimental dynamic nuclear polarization (DNP) studies at 176 gauss, 3420 gauss, and 13 200 gauss and at various temperatures have been concerned with the Overhauser effect of solvent carbon-13 nuclei in solutions of free radicals. Detailed measurements have been made in solutions of benzene and methyl iodide. The relative importance of scalar and dipolar coupling, the correlation times and spectral intensity functions have been of the greatest interest. The importance of the "three-spin-effect" has been investigated by applying triple-resonance irradiation. Dipolar and scalar hyperfine couplings between carbon-13 nuclei and odd electrons are of comparable magnitude, where the main difference of the DNP enhancement factors is caused by different shapes of the spectral intensity function for the fluctuations of the scalar interaction. The results are discussed in terms of the molecular structure and of the collision attitudes.

Quantitative dynamic polarization (DNP) measurements of carbon-13 nuclei suffer from a lack of sensitivity. Due to the low abundance in natural carbon and as a consequence of the relatively small magnetic moment, the  $^{13}\text{C}$  signal is under otherwise equivalent conditions about four orders of magnitude smaller than the proton signal. There is, on the other hand, a particular interest in the DNP of carbon because of its importance in the structure of organic molecules. The present paper reports first quantitative measurements of  $^{13}\text{C}$ -DNP enhancement factors in two free radical solutions, one in benzene with  $^{13}\text{C}$  in natural abundance, the other one in a 51% enriched sample of methyl iodide. The experimental difficulties have been overcome by a rather sophisticated instrumentation and by time averaging.

One main question is the nature of the interaction between electron spins of dissolved free radical molecules and solvent carbon-13 spins. A DNP study is expected to show how the molecules interact, and how far spin density is temporarily transmitted to the skeleton of solvent molecules. The possible transient hyperfine contact interaction between the molecules is to be compared with those observed with other nuclei (see preceding papers <sup>1, 2</sup>). Further applications of the DNP of  $^{13}\text{C}$  imply the question, under which circumstances an increase of the signal

to noise ratio of NMR signals is obtainable. The few  $^{13}\text{C}$ -DNP experiments that have been made hitherto only dealt either with a pure observation of an Overhauser effect or with an estimate of its relative magnitude by comparison <sup>3-5</sup>. The complexity of the frequency- and temperature dependence found with fluorine <sup>6</sup> and phosphorus nuclei <sup>2</sup>, however, has seemed to require quantitative studies in different magnetic fields. Both the strength of the intermolecular contact interaction and the magnetic field dependence of the enhancement are thought to depend critically upon the chemical environment of the nucleus in question.

A further aspect of the carbon-13 Overhauser effect shows up when the molecule contains also hydrogen. Because of the larger proton magnetic moment the interaction of  $^{13}\text{C}$  with  $^1\text{H}$  spins is no longer negligible compared to the interaction with the electrons. A saturation of the electron spin resonance leads to a dynamic polarization of the protons, which furthermore may influence the observed enhancement of the carbon-13 nuclei. The discussion of DNP experiments in such a case has to be based on a three-spin-rather than on a two-spin-treatment <sup>3, 4</sup>. In order to investigate the importance of the "three-spin-effect", and in order to eliminate the effect of proton polarization upon  $^{13}\text{C}$ , in this work triple irradiation has been applied.

<sup>1</sup> W. MÜLLER-WARMUTH, EROL ÖZTEKİN, REYNIR VILHJALMSSON, and AYTAÇ YALÇINER, Z. Naturforsch. 25 a, 1688 [1970].

<sup>2</sup> W. MÜLLER-WARMUTH, H. GRÜTZDIEK, and R. VAN STEENWINKEL, Z. Naturforsch. 25 a, 1696 [1970].



## 1. Apparatus and Experimental Details

All dynamic polarization measurements were carried out by comparing the enhanced and unenhanced  $^{13}\text{C}$ -NMR signals. The radical ESR lines were sufficiently narrow so that considerable saturation was achieved and direct power extrapolation could be performed as usual.  $^{13}\text{C}$  nuclear relaxation measurements were made for the enriched sample in order to determine the leakage factors. For the second sample rather strong free radical concentrations were taken, in order to reduce both the leakage and the three-spin-effect to an unimportant correction. Within the frame of the present work, solutions of bis-diphenylene phenyl allyl (BPA) in methyl iodide,  $\text{CH}_3\text{I}$ , 51% enriched in  $^{13}\text{C}$ , and benzene solutions with tri-*t*-butyl-phenoxy (TBP) have been investigated. These solutions have been chosen because of their stability and the high solubility. The samples with BPA were prepared solely by dissolving the weighed amount of the radical in the liquid and by degassing via repeated evacuation. TBP was prepared by oxydation of the respective phenol.

The experiments were performed at 176, 3420 and 13 200 gauss and at various temperatures. In contrast to the usual NMR and DNP techniques, as a consequence of the low sensitivity some modifications of the common instrumentation proved necessary. In the following these will be briefly described.

### *The 176 gauss double resonance spectrometer*

Detection of  $^{13}\text{C}$ -NMR is most difficult. A special design of the spectrometer and long duration measurements of up to one week, however, made possible a detection of  $^{13}\text{C}$  signals in samples with natural abundance<sup>7</sup>. The NMR frequency of carbon-13 is 189 kHz, the ESR frequency is 493 MHz, and the proton frequency 750 kHz.

The NMR spectrometer profits by a novel detector utilizing a parametric amplifier. This receiver accomplishes the requests of low frequency NMR detection particularly well. It consists essentially of two circuits coupled by a "varicap" with a non-linear characteristic. The varicap is "pumped" by a frequency of 311 kHz, which is the difference between the intermediate frequency of 500 kHz and the NMR

frequency\*. The whole system acts like a bridge with much more favourable properties. By a proper choice of the parameters the signal to noise ratio can be considerably increased and becomes independent upon the quality factor of the input circuit. Thus broad band detection with all its advantages for our experiments can be combined with high sensitivity. Further radiofrequency amplification of the signal at the intermediate frequency is performed by single side-band detection.

For saturating the ESR, a  $\lambda/4$  cavity design has been employed. The saturation power of about 15 watts is introduced by a coaxial cable and measured by a commercial power meter. Triple resonance facilities are provided by a second NMR coil consisting of only one winding. Special attention had to be given to a mutual decoupling of the various frequencies. A scheme of the whole cavity arrangement is shown in Fig. 1.

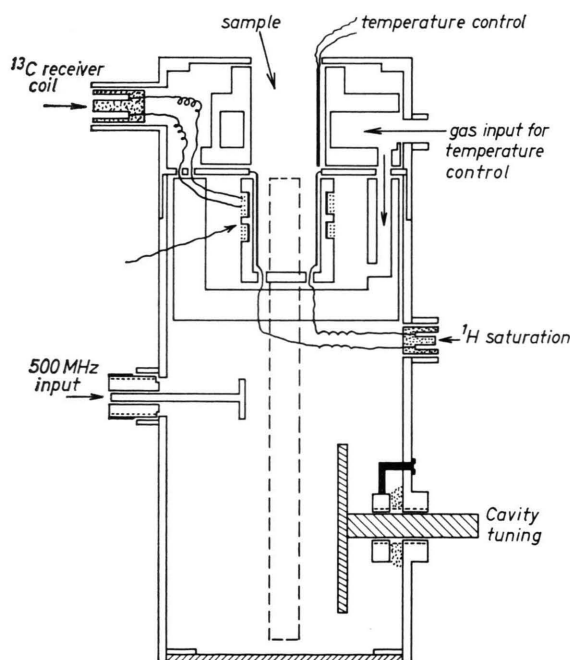


Fig. 1. Scheme of the cavity arrangement for triple resonance experiments at 176 gauss.

Long time measurements requested of course an extremely high stability of the double resonance spectrometer. All frequencies were crystal-stabilized.

<sup>3</sup> K. H. HAUSSE and F. REINBOLD, *Phys. Lett.* **2**, 53 [1962].

<sup>4</sup> J. P. IMBAUD, *C. R. Acad. Sci. Paris* **261**, 5442 [1965].

<sup>5</sup> D. F. S. NATUSCH and R. E. RICHARDS, *Chem. Commun.* **1966**, 579.

<sup>6</sup> K. H. HAUSSE and D. STEHLIK, *Adv. Magnetic Resonance* **3**, 79–139, Academic Press, New York 1968.

<sup>7</sup> H. GRÜTZEDIEK and W. MÜLLER-WARMUTH, *Z. Naturforsch.* **24a**, 459 [1969].

The magnetic field produced by Helmholtz coils was kept constant by an extra proton resonance controller. Most procedures for measuring NMR signals run automatically so that the spectrometer works preferably at night and stores the results. Since the main information required in this study concerns relative amplitudes of enhanced and unenhanced  $^{13}\text{C}$  signals rather than their shapes, most measurements were stored in a home-made two-channel analyzer. For purpose of time averaging this instrument converts signal voltages into frequency pulses which are counted and thus stored. Based on an extremely stable time scale two measurements are successively made and repeated as often as necessary in order to obtain a reasonable signal to noise ratio: one measurements at the resonance value of the magnetic field, the other one at a value outside resonance. The final signal is then proportional to the difference of the two counters. A three-channel version of the same instrument determines relaxation times by measuring the area under the relaxation function. Much more time has to be invested in a measurement with a commercial "Computer of Averaging Transients" (CAT), which was also used occasionally in order to obtain the whole signal information. Examples are given in Fig. 2.

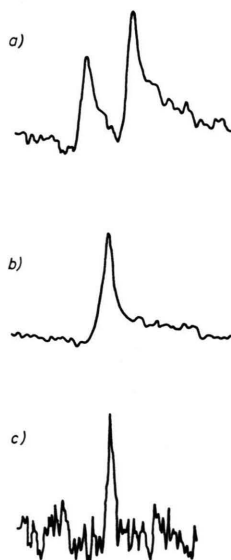


Fig. 2. Examples of weak field  $^{13}\text{C}$ -NMR and DNP measurements in a solution of the TBP radical in benzene (natural abundance) as obtained with at CAT. a) Enhanced signal under double resonance conditions, total measuring time: 4 hours. b) Enhanced signal under triple resonance conditions, 1 hour; the doublet splitting is removed by simultaneous saturation of the  $^1\text{H}$  spins. c) Unenhanced signal, 50 hours.

### *Double resonance spectrometers operating at 3420 and 13 200 gauss*

Compared with 176 gauss there are less problems with double and triple resonance experiments in stronger magnetic fields.

The spectrometers are consequently of the more familiar type. We have used a pulse spectrometer with phase sensitive detection at 3.63 MHz (ESR frequency 9.58 GHz) and high resolution techniques at 14.14 MHz (37 GHz).

By repeating the pulse sequences after the re-establishment of thermal equilibrium the whole trace consisting of the free decay and the echo was stored in the CAT and then recorded (Fig. 3). One or two passages were generally sufficient to record the enhanced signals. The unenhanced signal was measured by 10 ( $\text{CH}_3\text{I}$  enriched in  $^{13}\text{C}$ ) or 100 passages ( $\text{C}_6\text{H}_6$ , natural abundance of  $^{13}\text{C}$ ), respectively. As one realizes from Fig. 3, the narrow pulse shapes are greatly distorted and broadened by the accumulation method. The enhancement factors were

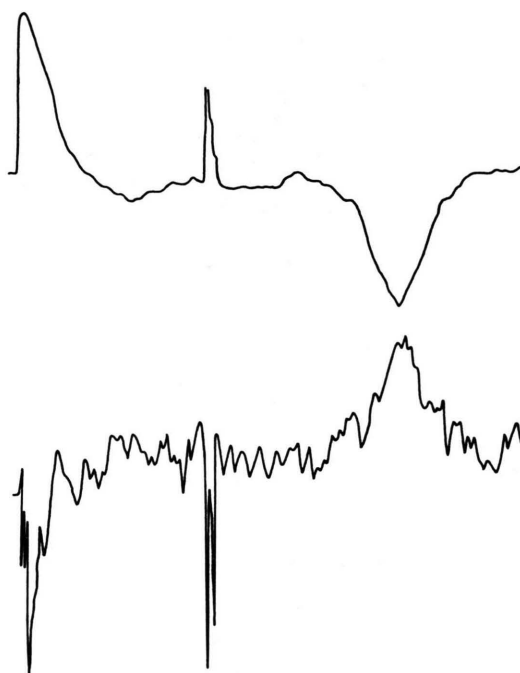


Fig. 3.  $^{13}\text{C}$ -spin echo signal of the benzene solution at 3.63 MHz and  $-3^\circ\text{C}$  (natural abundance). Compared with the enhanced signal (at the top), the unenhanced trace is repeated 100 times using a CAT, and the overall-gain is about twice as much.

\* For more details it is referred to the thesis of H. GRÜTZDIEK (unpublished), Universität Mainz 1970.

therefore determined from a comparison of the spin echoes throughout. An advantage of pulse spectroscopy is that relaxation times can be measured with the same procedure.

As an example of measurements at 13 200 gauss, in Fig. 4 the enhanced  $^{13}\text{C}$  spectrum of  $\text{CH}_3\text{I}/\text{BPA}$  is shown. In this picture below, the quartet is collapsed into one line, and the total intensity is slightly lower by triple irradiation.

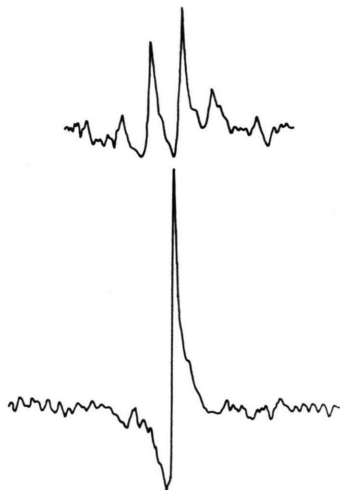


Fig. 4.  $^{13}\text{C}$ -spectrum of methyl iodide in a solution of BPA: at the top without triple irradiation, below when the proton resonance is simultaneously saturated. By the Overhauser effect the spectrum is about 25 times enhanced.

## 2. Experimental Results and their Interpretation

The DNP enhancement factors of the carbon-13-NMR measured at various temperatures with the different spectrometers are given in Fig. 5. On the

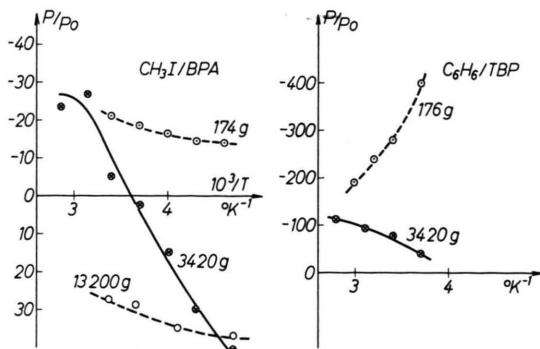


Fig. 5. Enhancement factors of the  $^{13}\text{C}$ -DNP as a function of reciprocal temperature as measured at different magnetic fields. As usual, (negative) enhancements with signal inversion are plotted in the positive direction.

left hand side, the results of the methyl iodide solution are drawn, on the right hand side those of benzene. These data are less accurate than comparable measurements of DNP enhancement factors of  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  because of the time averaging procedures. Especially in the case of benzene an error of  $\pm 30\%$  can well be assumed. The results for  $\text{CH}_3\text{I}$  show negative enhancements in weak fields and positive enhancements in strong fields. The enhancements of  $\text{C}_6\text{H}_6$  are always negative, the values at 13 200 gauss are smaller and not included because of bad accuracy.

The carbon-13  $T_1$ -values of the  $\text{CH}_3\text{I}$  solutions were between 1.2 and 2.8 sec at 176 gauss, between 1.4 and 2.4 sec at 3400 gauss, and between 2.5 and 5.4 sec at 13 200 gauss compared with 9 to 15 sec in the pure solvent. The spin lattice relaxation times of the benzene solution were in the range of 5 to 12 sec. By a comparison of the relaxation rates at different frequencies it has been established that the interaction of  $^{13}\text{C}$  with the quadrupole nucleus iodine most likely does not play a role in the solution.

In order to determine the details of the translational diffusion of the molecules, as in the preceding paper<sup>2</sup>, the proton-DNP of  $\text{CH}_3\text{I}/\text{BPA}$  has also been studied. Fig. 6 shows the proton-electron coupling

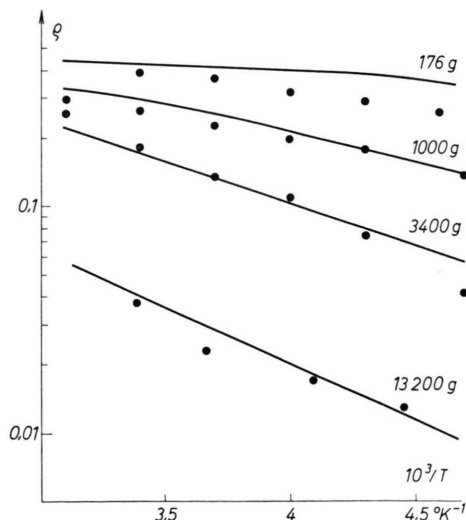


Fig. 6. Proton-electron coupling parameters of  $\text{CH}_3\text{I}$  solutions as measured at different temperatures and magnetic fields.

parameter  $\rho$  and its interpretation by applying Eq. (1) of Ref. <sup>1</sup>. It has again been assumed that no scalar coupling exists for the protons although the systematic departures at weak field values could in-



	CH <sub>3</sub> I/BPA	C <sub>6</sub> H <sub>6</sub> /THP
$\tau_t(23^\circ)$ in $10^{-11}$ sec	6.0	2.9
$E_A$ in kcal/mole	2.0	3.2
$K$	0.74	0.92
$\tau_{sk}/\tau_t$	0.54	0.48
$f_{sk}(x)$ (approximation)	$(0.56 e^{-0.95x} + 0.26 e^{-0.2x} + 0.18 e^{-0.01x})^2$	$(0.29 e^{-18x} + 0.55 e^{-0.45x} + 0.16 e^{-0.01x})^2$

Table 1. Numerical parameters describing the  $^{13}\text{C}$ -DNP by the nuclear-electron Overhauser effect as obtained from the experiments.

dicates, within the limits of accuracy, a weak scalar contribution. This, however, would practically not change the dipolar intensity functions thus determined. To relate the translational correlation time  $\tau_t$  to the temperature we again use Eq. (2) of Ref. <sup>2</sup>. The particular parameters  $\tau_t(23^\circ)$  and  $E_A$ , which were derived from the proton results, will be indicated in Table 1 further below. The proton-electron Overhauser effect of free radical solutions in benzene was already investigated <sup>8,9</sup>. We take (Table 1) suitable average values of  $\tau_t$  and  $E_A$ , considering also relaxation <sup>10</sup> and self-diffusion data <sup>11,12</sup>. The Arrhenius law with the activation energies given in Table 1 is only a proper approximation in the investigated temperature range.

In the interpretation of  $^{13}\text{C}$  dynamic polarization data in principle a three-spin equation <sup>6</sup> has to be used rather than two-spin-equation (2) of the preceding paper <sup>1</sup>. The polarization of the carbon-13 spins is not exclusively determined by their interaction with the electron spins of the radical (coupling parameter  $\varrho_C^S$ ), but it is also affected by the time-dependent interaction with the protons ( $\varrho_C^H$ ). Applying the same terminology as before the enhancement factor can be written

$$\frac{P_C}{P_{C_0}} = 1 - \varrho_C^S f_C^S s \frac{|\gamma_S|}{\gamma_C} + \varrho_C^H f_C^H \varrho_H^S f_H^S s \frac{|\gamma_S|}{\gamma_C}. \quad (1)$$

Here  $\varrho_H^S$  is the coupling parameter of the solvent protons with the electron spin, and  $f_C^S$ ,  $f_C^H$ ,  $f_H^S$  are the various leakage factors. By saturating both the electron and the proton spins simultaneously and observing the  $^{13}\text{C}$  signal (triple resonance experiment) the influence of the protons is reduced and

the enhancement becomes

$$\left(\frac{P_C}{P_{C_0}}\right)_{\text{TR}} = 1 - \varrho_C^S f_C^S s \frac{|\gamma_S|}{\gamma_C} + \varrho_C^S f_C^S s^H \frac{\gamma_H}{\gamma_C}. \quad (2)$$

The third term in Eq. (2) is generally negligible against the second term because of the much smaller  $\gamma_H/\gamma_C$  ratio.

An inspection of Eq. (1) shows that the influence of the third term is expected to be most important in weak magnetic fields and at high temperatures. It becomes the smaller the stronger the electron spin concentration of the solution is. Therefore all measurements at 176 gauss were made under triple resonance conditions in order to derive the  $\varrho_C^S$ -values from  $P/P_0$ . The magnitude of the three-spin-effect was estimated from Fig. 2 being 3.6 in this particular case. By combining Eqs. (1) and (2) the same ratio can be expressed in terms of the various  $\varrho$  and  $f$  parameters. This leads finally to a value of  $\varrho_C^H f_C^H \approx 0.06$ .

An example of the three-spin-effect in a strong magnetic field is Fig. 4. From this and further similar measurements it turns out that by saturation of the proton resonance the total intensity of the spectrum is reduced by about 10%. As one expects from Eq. (1), the third term is always positive. Therefore it decreases negative enhancements and increases positive ones. At 3400 gauss no triple irradiation facilities were available. The application of concentrated solutions has certainly guaranteed a rather small error by the influence of the protons.

From the enhancement factors of Fig. 5 and the relaxation times, the  $\varrho_C^S$ -values were calculated. In Fig. 7 they are plotted against  $x = \omega_S \tau_t$ , where  $\tau_t$  is the correlation time of translational diffusion obtained from the proton data.

<sup>8</sup> K. D. KRAMER, W. MÜLLER-WARMUTH, and J. SCHINDLER, J. Chem. Phys. **43**, 31 [1965].

<sup>9</sup> R. A. DWEK, J. G. KENWORTHY, D. F. S. NATUSCH, R. E. RICHARDS, and D. J. SHIELDS, Proc. Roy. Soc. London A **291**, 487 [1966].

<sup>10</sup> W. MÜLLER-WARMUTH and V. PRINTZ, Z. Naturforsch. **21a**, 1849 [1966].

<sup>11</sup> R. HAUSER, G. MAIER, and F. NOACK, Z. Naturforsch. **21a**, 1410 [1966].

<sup>12</sup> G. J. KRÜGER and R. WEISS, Z. Naturforsch. **25a**, 777 [1970].

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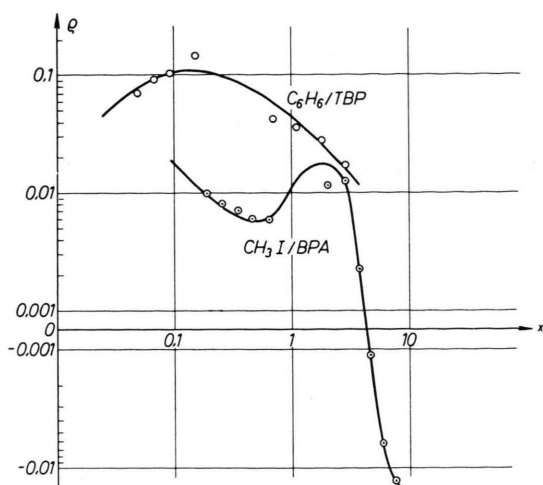


Fig. 7. The  $\rho$ -values for carbon-13 as a function of  $x = \omega_S \tau_t$ . The solid lines are the result of an interpretation, which uses the spectral intensity functions of Fig. 8 for the scalar interaction with the radical electron.

Further interpretation is essentially very similar to the procedure given for the  $^{31}\text{P}$ -DNP in the preceding paper<sup>2</sup>. We explain the results by a mixed scalar and dipolar interaction and search for a scalar intensity function that — inserted in Eq. (1) of Ref. 2 — yields correct  $\rho$ -values. The intensity function of the fluctuations of the scalar hyperfine interaction between carbon-13 and the free radical electron is again approximated by a series of three exponentials. The functions thus obtained are plotted in Fig. 8 together with the familiar spectral intensity function  $f_t(x)$  for the fluctuation of the dipolar interaction. The efficiency of this fit can be controlled by the solid lines of Fig. 7. The numerical parameters describing the carbon-13 DNP are listed in

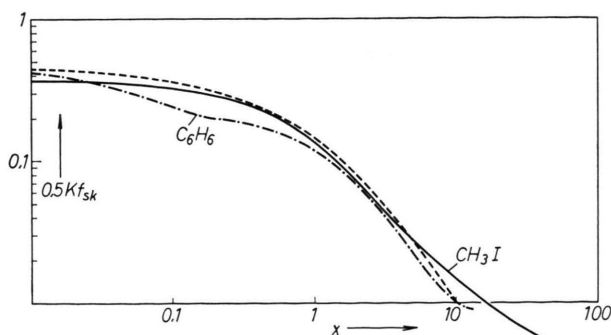


Fig. 8. Scalar contact coupling strength and intensity functions ( $0.5 K f_{sk}$ ) for  $\text{CH}_3\text{I/BPA}$  (—) and  $\text{C}_6\text{H}_6/\text{TBP}$  (---). For comparison, the dipolar intensity function  $0.5 f_t$  (— · —) is plotted in the same scale.

Table 1: the afore-mentioned parameters of the diffusion ( $\tau_t$  and  $E_A$ ),  $K$  the relative importance of scalar and dipolar coupling,  $\tau_{sk}$  the scalar correlation time in units of  $\tau_t$  and the analytical approximation of the intensity function. The definitions of these quantities can be found in the preceding paper<sup>2</sup>. The scalar contributions to the carbon-electron interaction characterized by  $K$  are not very accurately determined because extreme narrowing is not reached, even at 176 gauss and high temperature.

### 3. Discussion

Although many more systems have to be studied in order to obtain structural information from  $^{13}\text{C}$ -DNP measurements, the present work has revealed some common features. First of all, the existence of time-dependent scalar hyperfine couplings seems to be a characteristic property of intermolecular interactions between carbon-13 nuclei and radical electrons. This compares with  $^{19}\text{F}$  and  $^{31}\text{P}$  nuclei. The interaction is of the short range type and occurs during a collision of two diffusing molecules. Both the relative importance of scalar coupling and the scalar correlation time are comparable with other cases that have been investigated via the  $^{19}\text{F}$  or  $^{31}\text{P}$ -Overhauser effect.

In the examples studied in this work dipolar and scalar couplings were of comparable magnitudes (Fig. 8). The theoretical limits of the enhancements for predominant dipolar or scalar interaction, resp., have by far not been reached. On the contrary, small differences of either function produce a relatively small increase or decrease in the enhancement (Fig. 7) depending upon the particular spectral range. Mixing of scalar and dipolar coupling causes different values of  $\rho$  and even different signs of the DNP as can be read from Fig. 8. Single field and temperature measurements therefore do not provide a relative measure of the scalar contribution. Although benzene shows much larger negative enhancements in the 176 gauss field, and although the DNP of methyl iodide becomes inverted at  $x \approx 4$ , the scalar coupling of  $\text{C}_6\text{H}_6$  turns out to be a little bit larger. Preliminary experiments with a number of further solvents and free radicals have shown that the  $^{13}\text{C}$ -DNP behaves always similar in the medium field range; the enhancements are sometimes positive, sometimes negative, but never very large.

It seems therefore that the collision attitude of the interacting molecules being reflected by the particular shape of the scalar intensity function is more responsible for an enhancement factor at a certain field and temperature value than the hyperfine coupling constant or the correlation time. The change of the sign of enhancement that has been observed by other workers<sup>5</sup> if halogen atoms are substituted into hydrocarbon molecules is probably also due to an influence upon the spectral function.

Since the carbon atoms are well shielded in the solvent molecules a direct overlap of the unpaired radical electron orbital with the  $^{13}\text{C}$  nucleus does not explain the scalar interaction. The measured  $K$ -values and the comparison with  $^{19}\text{F}$ -DNP data obtained from substituted fluorobenzene<sup>13</sup> suggest, however, that in the case of benzene an interaction between the  $\pi$ -systems of the two molecules is responsible. By this mechanism the unpaired  $\pi$ -electron may temporarily be transferred into an unoccupied  $\pi$ -orbital of the benzene. Spin density is then transmitted to the carbon nuclei via  $\pi$ - $\sigma$ -exchange polarization. To have more information on this possible mechanism the  $^{13}\text{C}$ -DNP of substituted benzenes is being studied. Furthermore the scalar intensity function has certain similarities with that obtained from  $^{19}\text{F}$ -DNP studies of hexafluorobenzene solutions<sup>14</sup>. In the case of benzene, however, the increase of  $f_{\text{sk}}(x)$  at small  $x$  values is more pronounced, and the decay at large  $x$  is a little faster.

In methyl iodide the carbon atom is surrounded by four substituents and is therefore more or less completely shielded against the radical. During a

collision of the molecules the C—X bonds might be perturbed and a partial spin exchange between the odd electron and the paired electrons take place.

Through the s-character of the bonding orbitals spin density is then transmitted to the carbon nucleus. The rather isotropic arrangement of the carbon environment is mirrored in the smooth character of the spectral intensity. This function is in some way very similar to that of the solution of the same free radical in  $(\text{C}_2\text{H}_5\text{O})_3\text{PO}$ , where the phosphorus nucleus is also equally shielded<sup>2</sup>.

Since the observed contact interaction is an average over all relative orientations of colliding molecules, the particular shape of the intensity function may either reflect the presence or absence of different coupling mechanisms, or the isotropy or anisotropy of the collision attitudes. This holds especially for benzene, where  $f_{\text{sk}}$  looks a bit step-like. The long range part of this function (small  $x$ ) could perhaps be explained by some tendency of molecular complexing, whilst the short range part (large  $x$ ) reflects the point of contact during a short random collision. One would expect aromatic solvents with their delocalized  $\pi$ -systems to have longer correlation times than small aliphatic molecules. The observed correlation times do not necessarily mean a contradiction to this concept, since they only represent average values of the interaction time, and the long range contribution, which is absent in  $\text{CH}_3\text{I}$ , may be identified with the property of the  $\pi$ -system. It would be interesting to study this behaviour for a larger number of compounds.