^{13}C- and ^{1}H-ENDOR Studies of a Phenoxyl Type Radical

W. Lubitz, W. Broser, B. Kirste, H. Kurreck*, and K. Schubert
Institut für Organische Chemie, Freie Universität Berlin

Z. Naturforsch. **33a**, 1072–1076 (1978); received June 15, 1978

^{13}C- and ^{1}H-ENDOR studies on a phenoxyl type radical in fluid solution are reported. The ^{13}C-ENDOR resonance lines are comparable with those of the protons concerning amplitude, linewidth, and optimum experimental conditions. These findings are in contrast to previous ENDOR experiments on other ^{13}C-labelled systems and can be explained by assuming similar hfs anisotropies for carbon-13 and protons in this radical. From saturation measurements the relaxation parameters were determined. The hyperfine couplings are discussed in terms of McLachlan and INDO calculations. For the first time natural abundance ^{13}C-ENDOR measurements have been successful.

1. Introduction

Within the last five years non-proton ENDOR experiments in solution have proven to be very powerful extensions of the conventional H-ENDOR techniques [1, 2]. Very recently we reported on ^{13}C-ENDOR studies of ^{13}C-labelled radicals such as galvinoxyls (in the doublet and even in the triplet spin states) [3], triphenylmethyl, ketyls, and hydrocarbon anions [4]. The ENDOR-in-solution effects of these compounds are now quite well understood, can be interpreted by Freed's theory [5], and calculated in detail using a program recently developed by M. Plato [2].

For nuclei with $I = 1/2$ (^{1}H, ^{13}C) nuclear relaxation is determined by the modulation of the anisotropic hyperfine interaction caused by rotational Brownian diffusion. For carbon-13 this interaction is usually known to be much larger than for protons resulting in quite different experimental conditions required for an optimum ENDOR effect [3, 4]. However, for very small carbon-13 anisotropies, the ^{13}C-nucleus should behave similar to protons. — In the present communication we describe ^{13}C- and ^{1}H-ENDOR measurements performed on the 4-benzoyl-2,6-di-*tert*.-butylphenoxyl radical (PBP), where such a case is realized.

2. Experimental

The ENDOR spectra were recorded on a Varian E 12 ESR spectrometer equipped with a home-built ENDOR accessory, described elsewhere [6]. The PBP radical was generated from the respective phenol by lead dioxide oxidation in toluene at a high vacuum line using standard techniques [7]. The ^{13}C-labelled 4-benzoyl-2,6-di-*tert*.-butylphenol-(carbonyl-^{13}C) was prepared by a Friedel-Crafts reaction of benzoyl chloride (carbonyl-^{13}C) and 2,6-di-*tert*.-butylphenol.

4-Benzoyl-2,6-di-tert.-butylphenol-(carbonyl-^{13}C)

Benzoic acid-(carboxyl-^{13}C) (2.5 g) and 12.5 ml of thionyl chloride yield 2.2 g of benzoyl chloride-(carbonyl-^{13}C); 2.2 g of benzoyl chloride-(carbonyl-^{13}C), 1.4 g of aluminium chloride, and 2.1 g of 2,6-di-*tert*.-butylphenol yield 0.8 g of the PBP precursor. The ^{13}C-contents was $(90 \pm 3)\%$, determined by mass spectroscopy at low voltages. The chemical properties are identical to those given in Reference [8].

3. Results and Discussion

ENDOR and TRIPLE measurements

Figure 1 depicts the ENDOR spectra of the ^{13}C-labelled PBP radical in toluene at three different temperatures. According to the ENDOR resonance condition $\nu_{\text{ENDOR}} = |\nu_n \pm a_n/2|$ two pairs of H-ENDOR lines show up equally spaced around the free proton frequency $\nu_{\text{H}} = 14.02$ MHz separated by the isotropic hyperfine coupling constants (hfcs) a_{H}, and two ^{13}C-ENDOR lines around $a_{^{13}\text{C}}/2$ separated by $2\,\nu_{^{13}\text{C}} = 7.08$ MHz. The experimental hfcs are collected in Table 1. The relative signs of the hfcs were obtained from electron-nuclear-nuclear resonance (TRIPLE) measurements [9]. By comparison with similar radicals [10] the ^{1}H-hfcs could be assigned to the phenoxyl fragment. From the phenyl moiety no splittings could be resolved, being either obscured by the *tert*.-butyl proton lines or too small for detection [11].

---

* Requests for reprints should be addressed to Prof. H. Kurreck, Institut für Organische Chemie, Freie Universität Berlin, Takustraße 3, D-1000 Berlin 33, Germany.

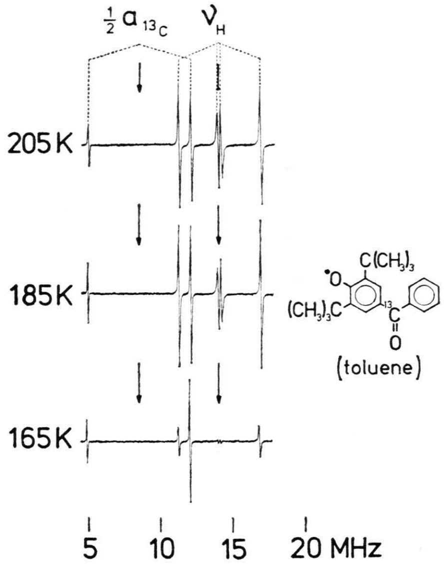


Fig. 1. ENDOR spectra of the 4-benzol-2,6-di-*tert.*-butyl-phenoxyl-(carbonyl ^{13}C) radical (PBP) in toluene at three different temperatures, microwave power: 5 mW, NMR field 4 G_{rot}, 10 kHz-fm-modulation ± 20 kHz amplitude.

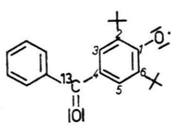
The intensity difference of the ^{13}C-ENDOR lines (Fig. 1) is caused by the hyperfine enhancement factor [12] acting on the applied NMR field, and not by cross relaxation effects [4]. An influence of internal motion on the nuclear relaxation resulting in W_{x_1} processes [5] could be excluded by our measurements. This finding is confirmed by the very small temperature dependence of the ^{13}C-hfc, which is not significantly larger than that normally found for protons caused by out-of-plane vibrations in the C-H fragment [13].

^{1}H- and ^{13}C-nuclear relaxation, ENDOR response

It is somewhat surprising and in contrast to previous ^{13}C-ENDOR results that the optimum ^{13}C- and ^{1}H-ENDOR resonances occur at about the same experimental conditions, see Figure 1. The maximum ENDOR effect for protons and for carbon-13 was obtained at 200 K and 180 K, respectively. This unusual behaviour is clearly reflected in the ENDOR spectrum taken at 165 K, showing a low intensity of the proton resonances but quite strong ^{13}C-ENDOR lines. In order to clarify this situation we have determined the proton and carbon-13 relaxation parameters from saturation measurements of the ENDOR lines at 205 K. Actually, we obtained almost equal unsaturated linewidths of (20 ± 3) kHz and effective spin lattice relaxation rates of (4 ± 1) 10^3 sec^{-1}, whereas recent measurements on ^{13}C-labelled galvinoxyls [1, 3] yielded larger linewidths for carbon-13 and drastically enhanced spin lattice relaxation rates (1—2 orders of magnitude). In the latter investigations

Table 1. Experimental and calculated isotropic hfcs in MHz for phenoxyl and PBP.

	Phenoxyl		PBP		
Pos.	Exp.[c]	Calc. INDO[b]	Exp.[d] [± 0.002]	Calc.[a] INDO[b]	McLachlan[e]
2.6 (o)	(−) 18.62	− 11.217	—	− 11.519	− 18.870
3.5 (m)	(+) 5.04	+ 5.827	+ 5.640	+ 7.022	+ 5.919
4 (p)	(−) 28.28	− 9.352	—	—	—
tert.-butyl	—	—	+ 0.207	—	—
carbonyl-^{13}C	—	—	− 17.088	− 10.472	− 17.918



[a] Instead of PBP we calculated a model without the *tert.*-butyl groups using twist angles of 40° for both the phenyl and phenoxyl rings for the INDO as well as for the McLachlan approach, see text.

[b] For the INDO calculations we used standard bond lengths (aromatic CC: 1.395, CH: 1.08, CO: 1.36; carbonyl CO: 1.21 Å) and bond angles (120°) [15]. For INDO on the phenoxyl see also [15].

[c] Taken from [16].

[d] From ENDOR on ^{13}C-labelled PBP in toluene at 205 K.

[e] For the McLachlan calculation [14] we used $\lambda = 1.2$ and standard HMO parameters except h_{O} (phenoxyl) = 1.9, k_{CO} (phenoxyl) = 1.6, giving optimum results for phenoxyl [17]. For the elucidation of H and ^{13}C-hfcs from the spin densities we used the following equations and polarization parameters: $a_{\mathrm{H}} = Q_{\mathrm{CH}}\varrho_{\mathrm{C}}^{\pi}$ with $Q_{\mathrm{CH}} = -75.6$ MHz [17],
$a_{^{13}\mathrm{C}} = \left(S_{\mathrm{C}} + \sum_{j=1}^{n} Q_{ij}\right)\varrho_i^{\pi} + \sum_{j=1}^{n} Q_{ji}\varrho_j^{\pi}$ with $S_{\mathrm{C}} = -35.6$, $Q_{\mathrm{CC'}} = +40.5$, $Q_{\mathrm{CO}} = +49.6$, $Q_{\mathrm{C'C}} = -38.3$, $Q_{\mathrm{OC}} = -75.9$ MHz from [18], [17].
Taking account of the *tert.*-butyl groups by using an "inductive" model, the Coulomb integrals at positions 2 and 6 have been changed in some further calculations ($h_{\mathrm{C}_{2,6}} = -0.5$), yielding changes in spin densities of less than 10%.

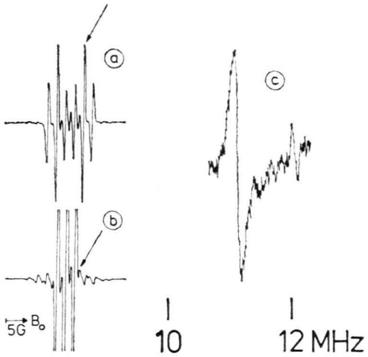


Fig. 2. a) ESR spectrum of the ^{13}C-labelled PBP radical.
b) ESR spectrum of the unlabelled radical showing ^{13}C-satellite lines, the arrows in a) and b) depict identical ESR components in the spectrum.
c) Part of the ENDOR spectrum obtained by saturating the carbon-13 satellite ESR line indicated in b), time constant 30s, single sweep. For details see text.

the higher temperatures required to obtain optimum ^{13}C-ENDOR effects were attributed to the much larger hfs anisotropy of the carbon-13, entering quadratically in the relaxation rates. These rates determine ENDOR linewidths, amplitudes, and the optimum experimental conditions (temperature/viscosity; external fields) [2, 5]. In the PBP radical under study the hfs anisotropy seems to be comparable in magnitude with that of the protons. Unfortunately a precise elucidation of the ^{13}C-hfs tensor components in glassy toluene matrix failed, since at least three nuclei ($2 \times {}^{1}$H, $1 \times {}^{13}$C) with different hfs anisotropies contribute to the spectrum. However, it is obvious that the ^{13}C-hfs anisotropy is obscured by the large linewidth and therefore should not be considerably larger than that of a meta proton. This prompted us to seek a theoretical interpretation of the low carbonyl ^{13}C-hfs anisotropy.

Interpretation of isotropic ^{1}H- and ^{13}C-hfcs and hfs anisotropies

A comparison between the hfcs of the meta and *tert.*-butyl protons in the PBP radical and those in similar phenoxyls [10] shows that the spin distribution is not very much altered even by the 4-benzoyl substituent, see Table 1. A HMO/McLachlan calculation [14] performed on the PBP radical (for details see Table 1, caption) yields very small π-spin populations at the labelled ^{13}C position (-0.006) and in the phenyl ring ($< |0.002|$). The observed quite large negative ^{13}C-hfc therefore arises mainly from $\pi - \sigma$ spin polarization caused by spin density at the neighbouring para carbon ($+0.280$) and oxygen ($+0.088$) atoms. The isotropic meta ^{1}H- and carbonyl ^{13}C-hfcs derived from the McLachlan spin densities by use of the equations and parameters given in the table caption are in very good agreement with the experimental results.

From the π-spin populations at the carbon-13 position and the three neighbouring centres we could calculate the anisotropic ^{13}C-hfs tensor [19]. The resulting value of $\mathrm{Tr}\,A_{\mathrm{C}}'^{2} = 14.0\ \mathrm{MHz}^2$ is comparable with that calculated for a meta proton ($\mathrm{Tr}\,A_{\mathrm{H}}'^{2} = 13{,}1\ \mathrm{MHz}^2$), yielding an explanation for the similar ENDOR behaviour of both nuclei.

Using a more consequent theoretical approach we have also performed MO calculations in the INDO framework [15]. For this reason a Fortran program has been developed on the basis of the QCPE programs 136 and 223 allowing CNDO and INDO calculations also for larger molecules, which are additionally shown in a diagram for geometrical control.

In the original CNDO/INDO program molecular orbitals (MO) are filled up in order of increasing energy within the Hückel as well as in the SCF parts. Since the ordering of levels may differ in the Hückel and SCF calculation, it is advisable, to allow a free choice of starting electron configurations. For this reason we adapted the QCPE program to include this possibility.

Calculations have been performed on the CDC CYBER 175 of "Wissenschaftliches Rechenzentrum Berlin". Taking full account of the computer space available, it is possible to handle molecules up to a limit of 62 atoms and 182 atomic orbital basis functions.

The INDO calculations on the benzoyl phenoxyl radical, which has been chosen as model for the PBP, failed to converge when the first SCF cycle was based on a Hückel ground state constructed according to the usual "aufbau" rules. A well behaved SCF convergence was, however, obtained by choosing starting configurations corresponding to close-lying Hückel excited states. The resulting SCF energy minima were compared and it was found that three configurations gave almost the same values, and were lowest-lying. Of these three the state giving the best overall agreement with experimentally observed spin density distribution was chosen as the true ground state of the molecule. For this choice, the Hückel "starting" state was constructed by leaving the 36th level for β spin empty (usually the HOMO) and filling up the 37th level (usually the LUMO). All other Hückel levels for α and β spins were occupied in the usual manner. Using this model the spin densities in the phenoxyl moiety turned out to be similar to those in the unsubstituted phenoxyl radical.

The results obtained by INDO for the unsubstituted phenoxyl and the PBP radical are given in Table 1. For the calculation we have omitted the *tert.*-butyl groups ortho to the oxygen in order to avoid steric complications, vide infra. The ^{1}H-hfcs in the phenyl ring are quite small ($|a| < 0.7$ MHz), but somewhat larger than the experimental upper linewidth limit observed for the smallest couplings in the ENDOR spectrum (≈ 0.3 MHz).

Altering the assumed mean twist angles (40°) in the wide range of 0 to 90°, $a_{^{13}\text{C}}$ and $a_{3,5}$ are changed within less than ± 40 and $\pm 20\%$, respectively. The overall agreement between experimental and calculated hfcs is rather poor, especially for $a_{^{13}\text{C}}$, which attains only about 60% of the observed value. This may be attributed to the fact that the measured couplings in the unsubstituted phenoxyl radical are also reproduced quite badly by the INDO method, see Table 1. Especially for the para position, where the benzoyl group is attached to in the PBP radical, the calculation disagrees with experiment by a factor of more than 3.

Calculations on the complete PBP radical using standard geometries revealed that the through-space interaction between the *tert.*-butyl groups and the oxygen also results in a large change of spin densities in the phenoxyl ring and at the ^{13}C carbonyl position. Such effects have not been found experimentally. Therefore we believe the geometry of radicals like PBP may be altered in the region of ortho *tert.*-butyl groups. However, we think it not reasonable to allow large deviations from standard geometries — even if the total energy is lowered — since the calculation neglects influences of the environment of the radicals in solution. Moreover, an optimization of molecular geometries with respect to total energy often did not improve the hfs constants. However, it has to be borne in mind that the INDO approach in itself is too approximate [15] to give results which are in perfect agreement with experiment. The excellent results usually achieved by HMO/McLachlan calculations can be accounted for by individually optimized parameters, see e.g. [17].

Considering the quality of the INDO calculations, it seemed rather hopeless to achieve acceptable results for the ^{13}C- and ^{1}H-hfs anisotropies. A crude estimate, taking account of the INDO p_z-spin populations at the carbonyl carbon and the three neighbouring atoms, ($\text{Tr}\, A_{\text{C}}'^{2} \approx 200\ \text{MHz}^{2}$) indicates that, in contrast to the McLachlan approach, the INDO calculation is unable to give this very low ^{13}C-hfs anisotropy which is expected from the observed ENDOR relaxation behaviour.

^{13}*C-ENDOR of the unlabelled PBP radical*

The excellent signal-to-noise ratio of the ^{13}C-ENDOR lines (Fig. 1) encouraged us to check, whether these lines might even show up when using a sample of the unlabelled PBP radical. The result of our experiment is given in Fig. 2, depicting part of the ENDOR spectrum of unlabelled PBP at 185 K, showing the H-ENDOR line at 11.12 and the ^{13}C-ENDOR line at 12.05 MHz. The intensity difference between the ^{13}C- and ^{1}H-ENDOR resonances is caused by the fact that the ^{13}C-ESR satellite line chosen (see Fig. 2b) is partly obscured by a large ESR component belonging to the spectrum from PBP without any carbon-13 coupling. ^{13}C-ENDOR resonances from ESR settings on ^{13}C-satellites (see Fig. 2a, b) others than those belonging to the carbonyl carbon could not be observed. This can readily be explained by the fact that the ^{13}C-hfs anisotropies of the carbon-13 nuclei in the phenoxyl moiety should be much larger, calling for a drastical change in temperature/viscosity of the solution and external fields. Actually it is known from recent non-proton ENDOR studies that linewidths are much larger for nuclei with larger anisotropies and the ENDOR effects are smaller [1, 2].

To our knowledge this is the first detection of ENDOR-in-solution resonance lines from carbon-13 in natural abundance. It has to be pointed out that in these preliminary measurements the ENDOR lines could only be detected because the positions, i.e. NMR frequencies, and optimum experimental conditions were known beforehand from the results of the respective labelled sample. None the less we feel encouraged for extending the studies of natural abundance carbon-13 ENDOR-in-solution.

Acknowledgements

The authors are grateful to Prof. K. Möbius from Institut für Molekülphysik der Freien Universität Berlin for the use of the ENDOR spectrometer, and to Dr. M. Plato and Dr. C. Winscom (same institute) for their kindful help concerning some theoretical questions. This work was supported by "Deutsche Forschungsgemeinschaft" (SFB 161 and Normalverfahren), which is gratefully acknowledged. W. Broser and H. Kurreck wish to thank "Fonds der Chemischen Industrie" for financial support.

[1] W. Lubitz, Thesis, Freie Universität Berlin 1977.
[2] M. Plato, to be published.
[3] B. Kirste, H. Kurreck, W. Lubitz, and K. Schubert, J. Amer. Chem. Soc. **100**, 2292 (1978).
[4] H. J. Fey, W. Lubitz, H. Zimmermann, M. Plato, K. Möbius, and R. Biehl, Z. Naturforsch. **33a**, 514 (1978).
[5] a) J. H. Freed, J. Chem. Phys. **43**, 2312 (1965); b) J. Phys. Chem. **71**, 38 (1967); c) J. H. Freed, D. S. Leniart, and J. S. Hyde, J. Chem. Phys. **47**, 2762 (1967); d) J. H. Freed, ibid. **50**, 2271 (1969); e) J. H. Freed, D. S. Leniart, and H. D. Connor, ibid. **58**, 3089 (1973).
[6] K. Möbius and R. Biehl in "Multiple Electron Resonance Spectroscopy", M. M. Dorio and J. H. Freed, Edts., Plenum Press, New York, in press.
[7] D. E. Paul, D. Lipkin, and S. I. Weissman, J. Amer. Chem. Soc. **78**, 116 (1956).
[8] N. V. Portnykh, A. A. Volod'kin, and V. V. Ershov, Izv. Akad. Nauk. SSR, Ser. Khim. **1966**(2), 2243.
[9] R. Biehl, M. Plato, and K. Möbius, J. Chem. Phys. **63**, 3515 (1975).
[10] K. Scheffler and H. B. Stegmann, "Elektronenspinresonanz", Springer-Verlag, Berlin 1970, p. 339—359, and ref. cited.
[11] R. D. Allendoerfer and A. H. Maki, J. Magn. Reson. **3**, 396 (1970).
[12] S. Geschwind in "Hyperfine Interactions", A. J. Freeman, R. B. Frankel, Edts., Academic Press, New York, 1967.
[13] A. H. Reddoch, C. L. Dodson, and D. H. Paskovich, J. Chem. Phys. **52**, 2318 (1970).
[14] A. D. McLachlan, Mol. Phys. **2**, 271 (1959).
[15] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theorie", McGraw-Hill, New York, 1970.
[16] T. J. Stone and W. A. Waters, J. Chem. Soc. **1964**, 213; B. T. Allen and W. Vanneste, Nature **204**, 991 (1964).
[17] K. Dimroth, A. Berndt, F. Bär, R. Volland, and A. Schweig, Angew. Chem. **79**, 69 (1967).
[18] M. Karplus and G. K. Fraenkel, J. Chem. Phys. **35**, 1312 (1961).
[19] H. M. McConnell and J. Strathdee, Mol. Phys. **2**, 129 (1959).