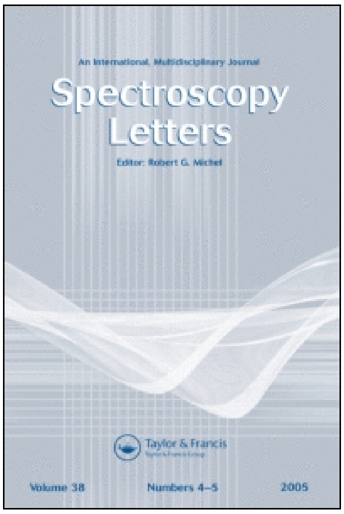

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NMR AND EPR STUDY OF THE NITROXIDE RADICAL TEMPO INTERACTION WITH PHENOLS

Key words: nitroxide radical, hydrogen bond, EPR, ^{13}C NMR, phenol.

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ABSTRACT

The 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) was used as a probe to study the changes in hydrogen bonding between the phenolic OH group and the ON group of the radical by means of NMR and EPR. ^{13}C NMR contact shifts induced by TEMPO were measured for five phenols. Formation of intermolecular hydrogen bond between a phenol and TEMPO molecule causes noticeable increase of ^{14}N hyperfine coupling

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constant in the radical and appearance of negative spin density on carbon nuclei of C-OH fragment in the phenol.

INTRODUCTION

Interactions of nitroxide radicals with various types of molecules have been monitored by NMR and EPR methods [1-6]. The 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) often was used in such experiments.

^{13}C NMR study of the interaction with aliphatic hydrocarbons [7], ethers [8] and alcohols [9] showed that TEMPO induces downfield contact shifts of aliphatic carbon signals through stereospecific collisions and the effect increases in the order $C_{quaternary} < CH < CH_2 < CH_3$. However there is negative spin density on carbon nuclei in C-OH fragments of alcohols (upfield shift) when hydroxyl group is engaged in intermolecular hydrogen bonding with radical [9]. A life time of hydrogen bonded complexes between TEMPO and alcohols was estimated as ca. 10^{-10} s [10].

EPR experiments monitored the changes in the molecule of nitroxide radical and showed that the strengthening of H-bond between a protono donor molecule and nitroxide radical causes an increase of ^{14}N hyperfine coupling constant (A_N) of the radical [11].

The aim of this work was to study the spin density distribution on carbon nuclei in several phenols which interact with TEMPO and to compare the ability of phenolic OH group to form hydrogen bond with the radical.

EXPERIMENTAL

TEMPO-radical was obtained from Aldrich and phenols from POCH (Poland).

EPR spectra were recorded on a SE/X 2452 X-band EPR spectrometer from Radiopan. The coupling constant A_N was measured with Radil JTM-48 magnetometer with an accuracy of ±0.002 mT. The EPR spectrum of this radical is a triplet and A_N was calculated as half the distance in mT between the downfield and upfield components of the signal.

^{13}C NMR spectra were recorded at 50 MHz on a Varian-200 NMR spectrometer. The chemical shifts were referenced to the position of CO signal of acetone which, as was shown earlier [12], was not influenced by the changes of radical concentration. The contact shift ($\Delta\delta$) induced by TEMPO is the difference between the shift in acetone solution with radical (δ) and without it (δ_0).

RESULTS AND DISCUSSION

^{14}N *hyperfine Coupling Constant In EPR Spectra*

Measurements of A_N were made with constant concentration of radical 0.0005 mol·dm^{-3} TEMPO in toluene. Concentrations of phenols changed from 0 to 0.05 mol·dm^{-3}.

Linear increase of the values of coupling constant upon the addition of phenols was observed at the concentrations within 0.001 ÷ 0.01 mol·dm^{-3} interval.

The value of A_N constant can serve as a measure of the strength of O-H···O-N hydrogen bond interaction [11]. Thus, for the studied phenols, one can write the following series (Table 1): 4-nitrophenol > phenol > 2,5-dinitrophenol > 2,4,6-trinitrophenol ≈ 2,6-di-tert.-butyl-phenol.

Small changes of A_N for experiments with 2,5-dinitrophenol, 2,4,6-trinitrophenol and 2,6-di-tert.-butyl-phenol could be explained by low probability of H-bond formation with TEMPO radical because of electronic effects, steric hindrances and intramolecular hydrogen bond (for the nitrophenols).

^{13}C NMR Contact Shift

The measurements of ^{13}C contact shift were carried out for constant concentration of the respective phenol 0.25 mol·dm^{-3} solution in acetone-d_6. Concentrations of TEMPO changed from 0 to 0.30 mol·dm^{-3}.

In all cases linear increase of ^{13}C nuclei chemical shifts with increasing TEMPO concentration were observed. Only for phenols which are able to form H-bond of noticeable strength an upfield shift of C-OH signals took place (FIG. 1, Table 2). For other carbons the downfield shifts were observed (FIG. 2).

Values of slopes, i.e. constant β, presented in Table 2, were calculated from equation $\delta = \delta_0 + \beta \cdot X$, where δ - chemical shifts for solutions with radical; X- concentration of TEMPO radical; δ_0- chemical shifts in acetone without radical.

In spite of the intramolecular spin density redistribution in a phenol molecule (as in the case of alcohol-TEMPO complexes [9]) the

Table 1. ^{14}N hyperfine coupling constant (A_N ±0.002 mT) of TEMPO (0.0005 mol·dm^{-3}) in solutions of phenols (0.01 and 0.05 mol·dm^{-3}) in toluene. For TEMPO solution in pure toluene A_N = 1.551±0.002 mT.

SUBSTANCE	A_N, mT	
	0.01 M	0.05 M
1. phenol	1.565	1.607
2. 4-nitrophenol	1.595	1.633
3. 2,5-dinitrophenol	1.556	1.574
4. 2,4,6-trinitrophenol	1.552	1.557
5. 2,6-di-tert.-butyl-phenol	1.552	1.554

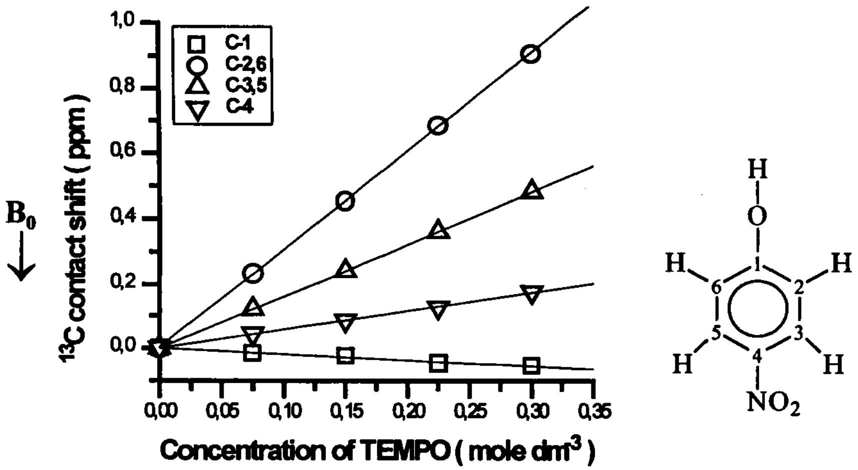

FIG.1 The dependence of ^{13}C contact shift for 4-nitrophenol on concentration of TEMPO. Zero on the contact shift scale means the chemical shift in acetone without the radical.

Table 2. Values of constant β (± 0.02 ppm·dm^3/mol).

SUBSTANCE	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1. phenol	- 0.20	2.50	1.54	1.40				
2. 4-nitrophenol	- 0.22	2.99	1.60	0.57				
3. 2,5-dinitrophenol	0.12	0.80	2.87	2.26	0.6	2.7		
4. 2,4,6-trinitrophenol	11.50	5.20	0.08					
5. 2,6-di-tert.-butyl-phenol	0.28	0.37	0.68	1.17			0.1	1.6

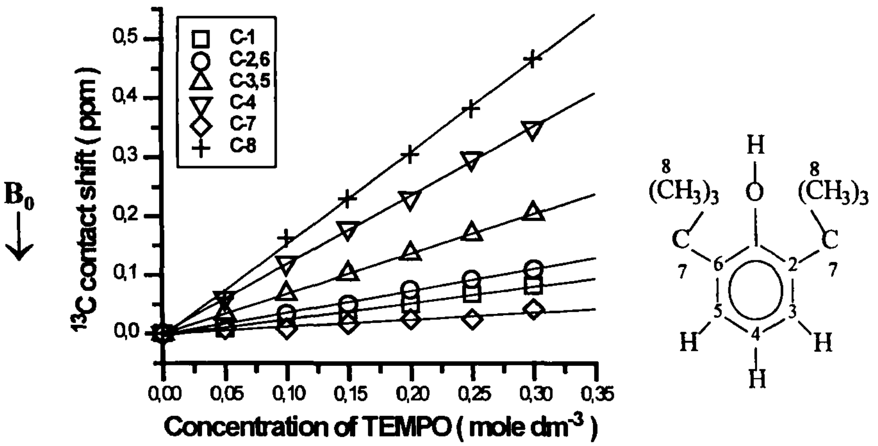

FIG.2 The dependence of ^{13}C contact shift for 2,6-di-tert.-butyl-phenol on concentration of TEMPO. Zero on the contact shift scale means the chemical shift in acetone without the radical.

values of contact chemical shifts can be also related to the probability for the carbon nuclei to come closer to N-O fragment of the radical. Thus, small values of β are observed for quaternary carbons (0.1-0.8) and significantly larger for CH carbons (up to 2.99). Extremely large values for 2,4,6-trinitrophenol could be tentatively explained by electron-donor/acceptor (EDA) type π-stacking interaction [13].

The interaction of nitrophenols with radicals will be subject to further studies.

Calculation Of Electrostatic Potentials

Optimised geometry and net atomic charges for the molecules of phenols were calculated using the semiempirical AM1 method [14]. Subsequent substitution by nitro groups results in stronger polarisation of the O-H group and positive charge at hydrogen atom increases in the order: mono-< di-< trinitrosubstituted phenol (Table 3).

CONCLUSION

The results of ^{14}N hyperfine coupling constant measurements in EPR spectra and ^{13}C NMR contact shifts showed that only p-nitrophenol and phenol are able to form H-bond of noticeable strength with TEMPO radical.

The strength of this interaction is larger for p-nitrophenol than for nonsubstituted phenol in agreement with the higher positive proton charge in this substance, as calculated by AM1 method.

However, because of the formation of intramolecular hydrogen bond in the nitro-ortho-substituted phenols and steric hindrances in

Table 3. Net atomic charges (ρ) on hydrogen atom in O-H group of phenols as calculated by AM1 method.

SUBSTANCE	ρ
1. phenol	+ 0.217
2. p-nitrophenol	+ 0.229
3. 2,5-dinitrophenol	+ 0.237
4. 2,4,6-trinitrophenol	+ 0.288
5. 2,6-di-tert.-butyl-phenol	+ 0.220

2,6-di-tert.-butyl-phenol the possibility to form intermolecular bond is much smaller.

On the other hand, formation of intermolecular hydrogen bond between phenol and TEMPO molecule causes noticeable increase of A_N value and appearance of negative spin density on carbon nuclei of C-OH fragment in phenol. In all other cases positive spin density is produced as a result of stereospecific collisions.

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