Phenol–Acetaldehyde Oligomers. 2. One- and Two-Dimensional ^{13}C NMR and Photochemically Induced Dynamic Nuclear Polarization ^{1}H NMR Studies in Dimethyl Sulfoxide

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ABSTRACT: A number of oligomers with different stereoregularity, related to novolac resins from phenol–acetaldehyde, are investigated by one- and two-dimensional ^{1}H and ^{13}C NMR and by photochemically induced dynamic nuclear polarization (photo-CIDNP) ^{1}H NMR spectroscopy in dimethyl sulfoxide. For the racemic trimer designated IIIr complete assignment of proton and carbon signals is achieved by homonuclear carbon–carbon (INADEQUATE) and heteronuclear carbon–proton correlated spectra. For the dimer and for trimer IIIr apparent pK_a values are obtained from the pH dependence of ^{13}C chemical shifts and discussed in terms of stability of the anionic groups formed during pH titration. Photo-CIDNP spectra provide information on the stability of the radical formed during irradiation.

Introduction

In the last few years use of NMR parameters for investigating the structure and composition of phenolic resins has prompted several groups to study small oligomers as model compounds for the more complex systems.[1a–d]

All-ortho alkylidene-bridged oligophenols constitute an interesting class of compounds, as they are regarded as either components of a complex mixture of novolacs or as representative segments of the phenolic cross-linked network.

In a previous paper we studied several oligomers of phenol–acetaldehyde in chloroform solution by conventional and photo-CIDNP ^{1}H NMR, in order to obtain information on the presence of intramolecular hydrogen bonds.[1e]

In this paper complete assignment of the ^{1}H and ^{13}C NMR spectra has been obtained in dimethyl sulfoxide (DMSO) and water/dimethyl sulfoxide. NMR parameters, pH titration curves, and photo-CIDNP spectra are reported.

Materials and Methods

The source of the samples used in the present study was described elsewhere.[1c,e] Quoted pH values are meter readings, uncorrected for isotope effects. Perdeuteriated dimethyl sulfoxide was purchased from Merck and used without further purification.

NMR spectra were run on a Bruker AM-270 spectrometer controlled by an Aspect 3000 computer.

The two-dimensional INADEQUATE ^{13}C experiment was obtained with quadrature detection in both dimensions, using an extended Ernst-type phase cycle[2] in order to suppress single quantum peaks and an ca. 125° conversion pulse to reduce F_1 image peaks.[3] The spectrum was accumulated with a sweep width of 3200 Hz, covering aromatic and carbonyl resonances, over 2K data points (then zero-filled to 4K), with a τ of 4 ms, corresponding to a $J_{C\text{-}C}$ of 62.5 Hz. In the t_1 domain 512 traces were accumulated (2048 scans each), zero-filled to 2048 before Fourier transformation, leading to an (apparent) digital resolution of 1.6 and 0.8 Hz/point in F_1 and F_2, respectively; relaxation delay was 2 s. Although with the carrier frequency set between aromatic and carbonyl resonances and the sweep width of 3200 Hz the 7-11 and 8-11 pairs were folded in the F_1 dimension, simple geometrical considerations made it possible to calculate the true frequencies. On the other hand, the high digital resolution allowed a rather precise evaluation of the carbon–carbon coupling constants. The spectrum was resolution-enhanced with a $\pi/3$-shifted squared sine bell in both dimensions.

The heteronuclear shift-correlated two-dimensional spectrum was obtained with quadrature detection in both dimensions, using polarization transfer from ^{1}H to ^{13}C via $J_{^{1}H\text{-}^{13}C}$,[4] without ^{1}H–^{1}H decoupling.

Carrier frequency and sweep width in both domains were chosen to cover only the aromatic region. In t_2 domain 1500 Hz were sampled over 2 K data points, then zero-filled to 4 K. In t_1 domain 200 Hz over 256 traces were accumulated (32 scans per trace) and then zero-filled to 512 before Fourier transformation, which lead to a digital resolution of 0.4 Hz/point both in F_1 and F_2; relaxation delay was 2 s. The delay for polarization transfer was 3.125 ms, corresponding to a $J_{^{1}H\text{-}^{13}C}$ of 160 Hz. The spectrum was resolution-enhanced with a $\pi/3$-shifted squared sine bell in both dimensions.

Photo-CIDNP spectra were obtained with a Bruker HX-360 spectrometer controlled by an Aspect 2000 computer.

Results and Discussion

1. Resonance Assignment. The compounds discussed in the present study are listed in Chart I.

^{13}C NMR spectra of a number of oligophenols from acetaldehyde in chloroform have been published previously.[1] The assignment of signals was based mainly on proton-decoupling techniques and comparison with ^{13}C NMR spectra of model compounds. Owing to the complexity of the ^{1}H NMR spectra, the assignment of pairs B, D and L, M (see Chart I) could not be unequivocally determined.

In order to obtain a complete resonance assignment in DMSO solution, a two-dimensional ^{13}C INADEQUATE experiment was performed, which provided the carbon–carbon connectivities for IIIr. The contour plot is shown in Figure 1, while the traces corresponding to the individual connectivities are reported in Figure 2. The experiment was optimized for detection of sp^2–sp^2 ($^{1}J_{C\text{-}C} \approx$ 60–70 Hz)

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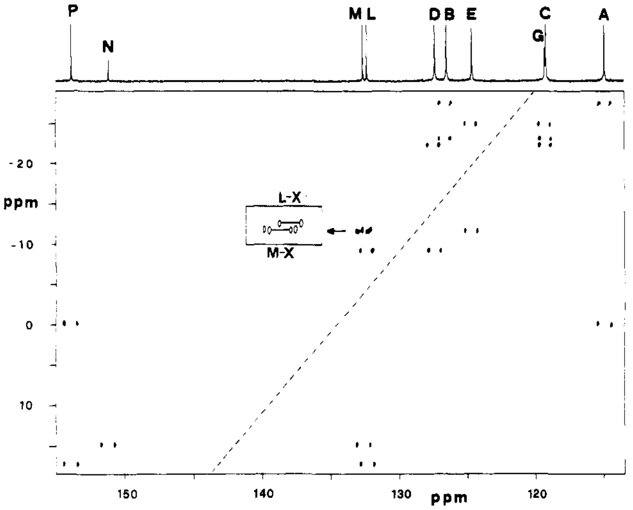
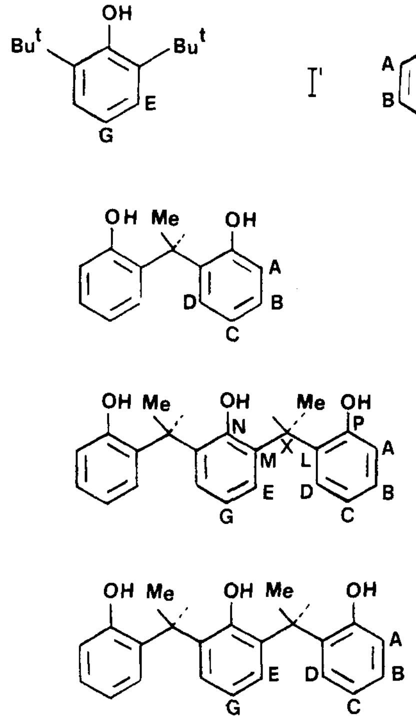


Figure 1. ^{13}C two-dimensional INADEQUATE experiment, 67.88 MHz, on IIIr, 1 M in DMSO. Absolute value intensity contour plot showing coupled ^{13}C pairs, separated according to the sum of chemical shifts (double-quantum frequency). In addition to the connectivity between E and M, the insert shows the sp^3–sp^2 connectivities between the methine carbons of the bridges (whose signal is folded near 132 ppm) and L and M aromatic carbons. For reference, the conventional ^{13}C spectrum is reported above the contour plot.

Chart I

I I' II IIIr IIIm



rather than the sp^3–sp^3 carbon connectivities ($^1J_{\text{C-C}} \approx 30$ Hz). However, while the latter are not observed, the two sp^3–sp^2 connectivities between the X methine carbons of the bridges (whose signal is folded near 132 ppm) and L and M aromatic carbons are neatly detected.

The two signals at 151.2 and 153.9 ppm are assigned to the phenolic carbons N and P, respectively, on the basis of their chemical shifts and relative intensities (2:1); therefore, the C–C connectivities have been deduced starting from these two signals. In Figure 1 all ^{13}C doublet pairs are easily recognized; the most significant rows of the 2D data matrix are shown in Figure 2.

The ^{13}C assignments obtained in the INADEQUATE experiment make it possible to assign conversely the ^{1}H resonances, via the heteronuclear correlations created in the spectrum shown in Figure 3.

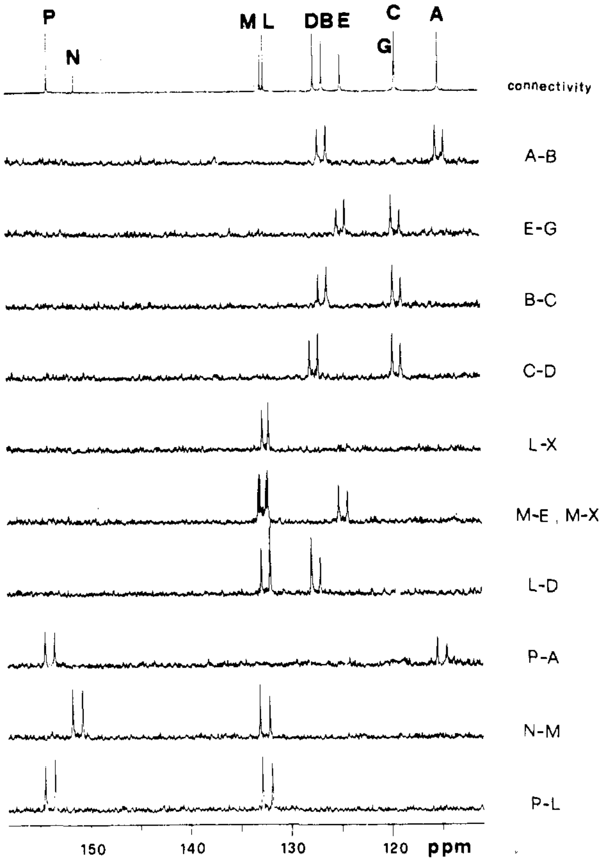


Figure 2. Plot of the individual rows of the 2D INADEQUATE data matrix, corresponding to coupled ^{13}C pairs of IIIr in DMSO solution. For reference, the conventional ^{13}C spectrum is reported in the top row.

Table I
^{13}C NMR Parameters for IIIr, As Obtained from the 2D Spectra Shown in Figures 1–3

^{13}C	δ, ppm^a	^{13}C–^{13}C	^1J, Hz	^{13}C	δ, ppm^a	^{13}C–^{13}C	^1J, Hz
P	153.9	P–L	66.5	E	124.7	B–C	55.6
N	151.2	N–M	65.7	G	119.4	C–D	56.3
M	132.7	P–A	64.2	C	119.3	E–G	56.3
L	132.4	M–E	60.3	A	115.0	M–X	42.3
D	127.4	L–D	61.0	X	30.4	L–X	44.3
B	126.6	B–A	56.3				

[a] From internal TMS.

Table II
^{1}H NMR Parameters for IIIr, As Obtained from the 2D Spectra Shown in Figure 3

^{1}H	δ, ppm^a	^{1}H–^{1}H	^1J, Hz	^{1}H	δ, ppm^a	^{1}H–^{1}H	^1J, Hz
X	4.90	A–B	8.0	E	7.14	C–D	7.5
G	6.92	A–C	1.2	B	7.19	E–G	7.7
C	6.94	B–C	7.5	D	7.28		
A	6.98	B–D	1.7				

[a] From internal TMS.

The relevant NMR parameters, i.e., chemical shifts and coupling constants, are quoted in Tables I and II.

The assignment of the ^{13}C resonances is in agreement with that reported by Soika et al. for the trimer of phenol–formaldehyde.[1d]

Two species of one bond ^{13}C–^{13}C coupling constants are observed, depending on the hybridization of the C–C bond: an average value of 43 Hz for the sp^2–sp^3 bond and 60 Hz for the sp^2–sp^2 bond. In addition the different substitution

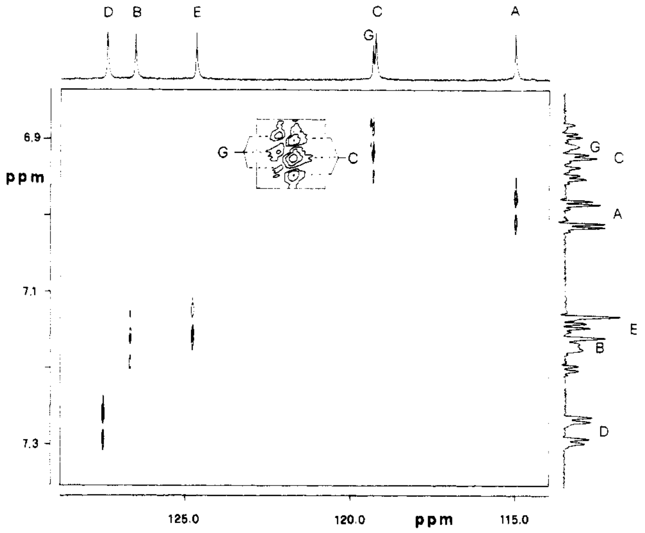


Figure 3. Two-dimensional ^{13}C–^{1}H heteronuclear correlated experiment, 67.88 MHz, on IIIr, 1 M in DMSO. Contour plot showing the fine structure of the aromatic proton multiplets in the F_1 dimension. The insert shows a horizontal expansion, with more levels, of the two nearby G and C carbon–proton multiplets. ^{1}H and ^{13}C reference spectra are plotted on the corresponding axes.

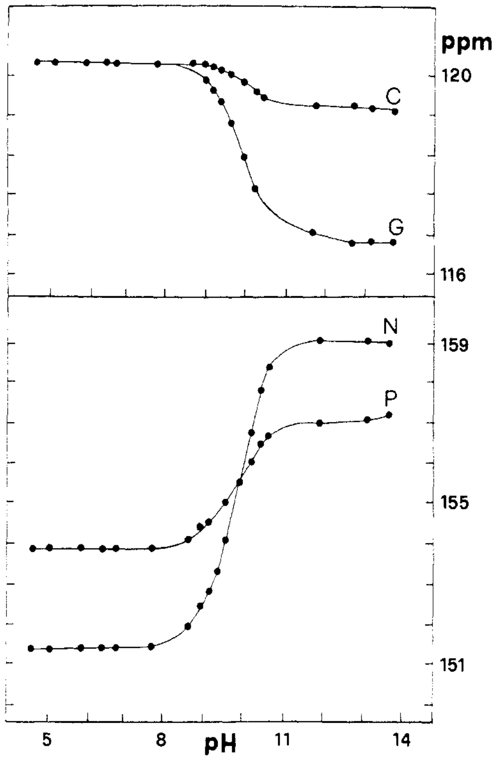


Figure 4. pH titration curves of the aromatic resonances of trimer IIIr in 1 M solution of water and DMSO (ratio 3:1): para carbons (C and G) and α carbons (N and P). Curves result from free interpolation between points.

on the sp^2–sp^2 hybridization gives average values of 65 Hz for CH=COH and C=COH, 60 Hz for CH=CC, and 56 Hz for CH=CH.

2. pH Titration. The chemical shift changes associated with the proton abstraction in phenols is of general interest with respect to the electron density distribution in these systems, as well as for structure characterization and ^{13}C NMR signal assignments in oligophenolic compounds.

A series of ^{13}C NMR spectra has been collected for samples of II and IIIr in solution of water and DMSO (ratio 3:1), in the pH range 4.7–13.7.

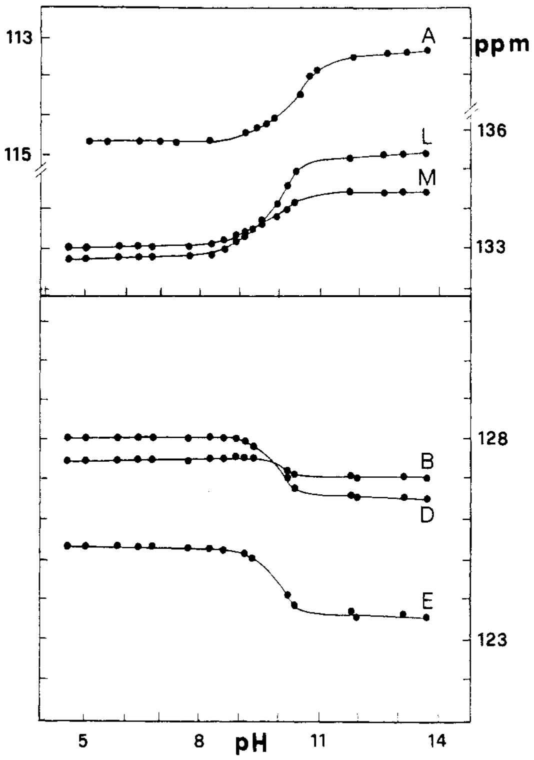


Figure 5. pH titration curves of the aromatic resonances of trimer IIIr in 1 M solution of water and DMSO (ratio 3:1): ortho carbons (A, L, and M) and meta carbons (B, D, and E). Curves result from free interpolation between points.

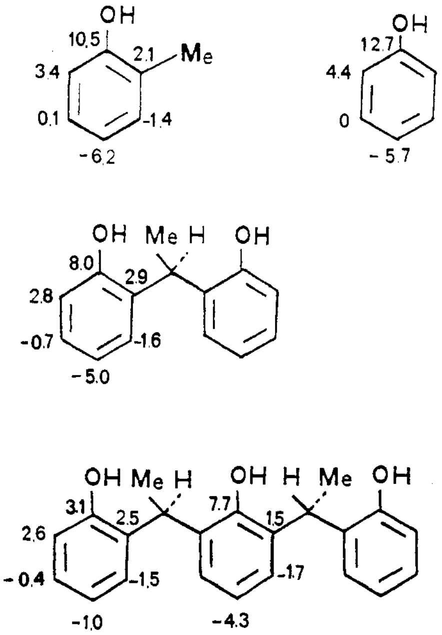


Figure 6. Deprotonation-induced ^{13}C NMR shifts in ppm.

The first dissociation constants (pK_a) have been determined by fitting the experimental chemical shifts to the equation

$$pH = pK_a + (1/s) \log [(\delta_{HA} - \delta)/(\delta - \delta_A)]$$

where δ is the experimental chemical shift, δ_{HA} is the chemical shift for the fully protonated species, δ_A is for the species with one phenolic ring unprotonated, and s equals 1 for groups having single one-proton titration behavior. The second and third dissociation constants are outside the pH range investigated.

The chemical shift versus pH curves for trimer IIIr are shown in Figure 4 and Figure 5. In Figure 6 the titration

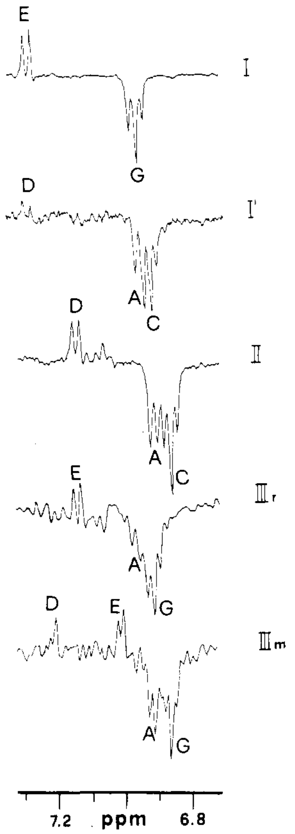


Figure 7. Aromatic region of the 360-MHz photo-CIDNP difference spectra of monomers I and I′, dimer II, and trimers IIIr and IIIr in 10 mM DMSO solution.

shifts obtained for the dimer and trimer IIIr are compared with those of phenol and *o*-cresol described in the literature.[5,6]

The chemical shifts arising from different pH are small when compared to the rate of the proton exchange reaction

$$\mathrm{AOH} \rightleftharpoons \mathrm{AO}^- + \mathrm{H}^+$$

Hence, during the entire pH titration only one spectrum is observed, which corresponds to the weighted average of the species present in solution.

Most of the carbon atoms are strongly affected by the pH variation, both in the dimer and in the trimer. Qualitatively, similar changes in chemical shifts have been observed for phenols and *o*-cresol. However, in IIIr only the carbon atoms of the inner ring exhibit titration shifts quantitatively similar to those of the model compounds, while the carbon atoms of the external rings show smaller shift variations. These features suggest that in IIIr the most stable anion is that with the inner ring ionized. In this case, the monoanion can be stabilized by two H bonds from the adjacent phenolic moieties.

3. Photo-CIDNP Spectra. In a series of oligophenol compounds we observed that a H atom can be abstracted from the phenolic units when the sample is laser irradiated in the presence of a suitable dye.[1e] A radical pair is formed initially in the triplet state and, after its conversion to the singlet state, recombines. Before recombination, a H transfer between adjacent phenolic moieties can take place, in order to give the most stable radical.[7]

By combination photo-CIDNP experiments performed on several oligomers from phenol–acetaldehyde in chloroform and in dimethyl sulfoxide, it appears that the solvent choice influences only the magnitude of the CIDNP signals but does not affect the signal sign, consistently with previous observations.[8] Negative signals are observed for protons in both ortho and para positions to the phenolic group and positive resonances for protons in the meta position.

In particular, the photo-CIDNP spectrum (Figure 7) of monomer I shows strong emissions for the para signals and weak absorptions for the meta, indicating accessibility of the OH group to the flavin in this solvent. The photo-CIDNP spectrum of I′ shows weak emission for both para and ortho resonances, whereas in chloroform no photo-CIDNP effect was seen at all.[1e] Since the dye used for investigating the monomers in DMSO (3-*N*-(carboxymethyl)lumiflavin) is very similar to that previously used in chloroform (3-*N*-methyllumiflavin), the steric hindrance deriving from the bulky substituents in the ortho positions is not the primary factor that prevents the observation of photo-CIDNP effects in chloroform. Most likely, the strong polarization observed in DMSO is due to the absence of self-association, which lowers the accessibility of the OH groups to the flavin.

As for the dimer, the same features are observed in both solvents.

In the trimers polarization is observed for both the internal and external rings, while in chloroform the polarization of the external rings was very weak. It is tempting to suggest that the H transfer to the most stable radical before recombination is less efficient in dimethyl sulfoxide than in chloroform.

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Registry No. I, 128-39-2; I′, 88-69-7; II, 87804-18-0; $\mathrm{III_r}$, 87804-20-4; $\mathrm{III_m}$, 87804-19-1; (phenol)(acetaldehyde) (copolymer), 27814-11-5.

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