

Nitroxide Radicals as Hydrogen Bonding Acceptors. An Infrared and EPR Study.

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Dedicated to Prof. Domenico Spinelli on the occasion of his 70th birthday

The equilibrium constants for the formation of hydrogen-bonded complexes with phenol, benzyl alcohol and diphenyl amine of a persistent nitroxide radical (TEMPO) have been measured for the first time by IR spectroscopy in solution. By making use of the data obtained with IR measurements it was possible to quantitatively determine the effect of hydrogen bonding on the nitrogen hyperfine-splitting constant. On this basis it is shown that EPR spectroscopy can be used as an alternative to IR spectroscopy for the determination of the thermodynamic parameters of hydrogen bond formation with nitroxides by following the dependence of the

experimental EPR nitrogen hyperfine splitting of these radicals upon changing the nature of the solvent. The experimental data obtained from both IR and EPR spectroscopy indicate that nitroxides are versatile hydrogen bond acceptors giving hydrogen bonds of strength similar to that of ethers or esters. The corresponding Abraham's $\beta_{\frac{H}{2}}$ values have been determined as 0.46.

KEYWORDS:

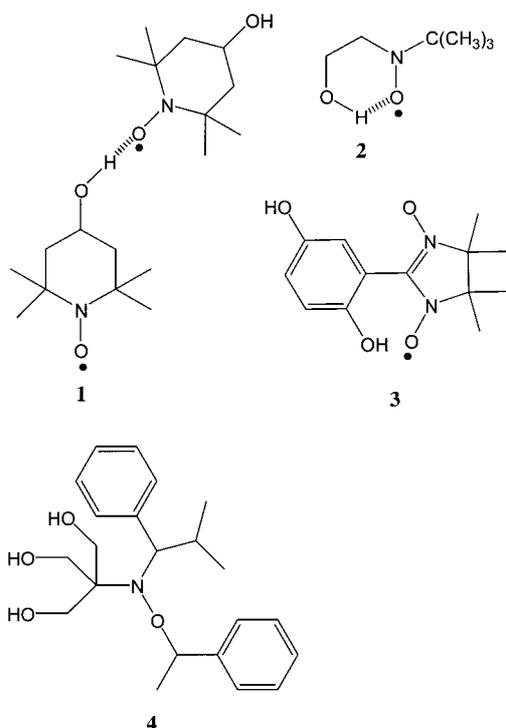
EPR spectroscopy · hydrogen bonds · magnetic properties · nitroxides · radicals

The possibility that hydrogen bonding to the nitroxide functional group could occur was first recognized by Rozantsev in the case of 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (4-hydroxy-TEMPO (1), Scheme 1).^[1] Due to the sizeable dipole moment of the nitroxyl function (3.1 D for TEMPO) 4-hydroxy-TEMPO easily forms O–H...·O–N intermolecular hydrogen bonds, both in solution and in a single crystal. The formation

of intramolecular hydrogen bonding O–H...·O–N has also been reported in the case of the hydroxy-substituted nitroxide (2).^[2]

The possibility that the nitroxide function can accept hydrogen bonding has several important implications. For instance, nitronyl nitroxides (3) have been used to prepare organic radical solids exhibiting intermolecular ferromagnetic interactions where the formation of hydrogen bonds has been exploited to control the molecular arrangement of organic radicals.^[3] Interestingly, it has been found that hydrogen bonds are able not only to control the crystal packing of radical species but also to generate and propagate ferromagnetic interactions. These have been obtained in the solid state, both by means of intermolecular homoatomic^[4] and of intermolecular heteroatomic hydrogen bonds.^[5] In the latter case spin transmission occurs in a supramolecular structure via a diamagnetic compound.

Another application of hydrogen bonding with nitroxides has been reported in the field of free-radical living polymerisation. It has been found that alkoxyamines (4) derived from nitroxides capable of giving intramolecular hydrogen bonding undergo C–O bond cleavage faster than the corresponding non-hydrogen bonded analogues, thus accelerating nitroxide-mediated radical polymerisation.^[6]



Scheme 1. Structures of 1–4.

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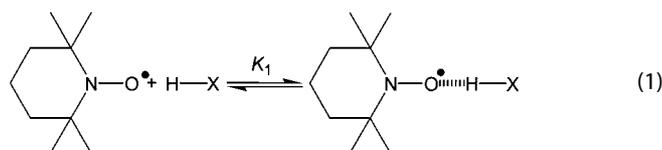
The interaction of nitroxides with polar protic solvents via intermolecular hydrogen bonds is also responsible for the lowering of their reactivity with respect to alkyl radicals.^[7]

The formation of hydrogen bonds with oxygen-centred radicals is also considered important in the stabilisation of catechol semiquinone radicals, and is regarded as the main effect controlling the activity of natural catechols as antioxidants.^[8]

Very recently the synthesis and structural characterisation by single-crystal neutron diffraction of a phenol-nitroxide hydrogen-bonded complex has been reported by Davidson and co-workers.^[9] This study demonstrates that nitroxides are versatile hydrogen bond acceptors over a wide range of geometries.

Despite the great interest in the capability of nitroxides (and in general of oxygen-centred radicals) to accept hydrogen bonding, to the best of our knowledge no experimental determination of the strength of X–H...O–N(C) hydrogen bond in solution has yet been reported in the literature, although it has been estimated by theoretical calculations.^[10]

As infrared spectroscopy is the traditional technique used to investigate hydrogen bonds,^[11] we decided to employ FT-IR in order to measure the equilibrium constant K_1 for the formation of hydrogen-bonded complexes between 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) and different hydrogen bond donors (HBD), Equation (1).



Equilibrium constants for hydrogen bond complexation have also been determined by following the dependence of the experimental EPR nitrogen hyperfine splitting on changing the solvent composition. With due prudence, the proposed method represents an alternative to IR spectroscopy for the determination of the hydrogen bond strength in radicals.

Results

FT-IR Measurements

Our first aim was to select the best IR absorption feature for this study. Initially we chose the N–O stretch at 1340 cm^{-1} , which however is relatively weak and is too close to other more intense absorptions.^[12] Moreover, the N–O stretch is weakly sensitive to changes in environment as previously reported by Symons and co-workers for di-*tert*-butylnitroxide.^[13] They attributed such insensitivity not to the weakness of the solvent interactions but to structural reasons due to the existence in the nitroxide of an antibonding π -electron, with resulting competing effects from solvent perturbations. The similarity of the results obtained in the present study with TEMPO confirms that this is a general behaviour characteristic of all nitroxides. Therefore, we decided to investigate the behaviour of the stretching of the hydrogen

donor bond, that is, O–H or N–H, rather than that of the acceptor bond.

The infrared spectrum of a hydrogen bonded complex with an X–H...Y bond typically shows a very intense absorption due to the proton-stretching motion, shifted to lower frequency relative to the X–H absorption in the corresponding free species. IR spectroscopy allows both the free- and hydrogen-bonded species to be observed.

The experiments were carried out using four different hydrogen donors; two of them containing an hydroxyl group (benzyl alcohol and phenol) and two containing the aminyl group (diphenylamine and dibenzylamine). In the last case, experiments could be carried out only with diphenylamine because of the low absorption coefficient characterising dialkyl amines.

As an example Figure 1, shows the IR spectra of phenol recorded at room temperature in the $3100\text{--}3700 \text{ cm}^{-1}$ range in CCl_4 . Only the signal of the free phenol could be detected in the absence of TEMPO, while in the presence of TEMPO both the free (sharp peak) and complexed (broad peak) phenol were observed.

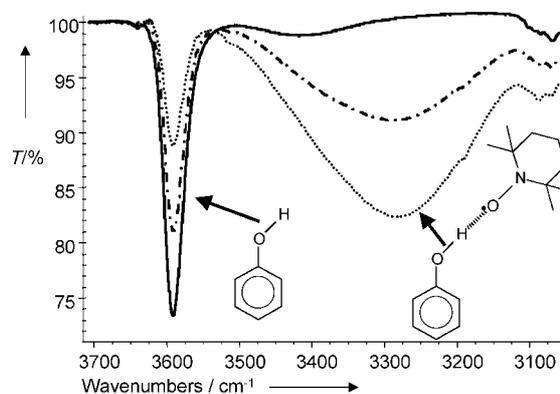


Figure 1. FT-IR spectra of phenol in a CHCl_3 solution in the absence (solid line) and in the presence of different amounts of TEMPO (dash-dot line: TEMPO/PhOH 1/1; dotted line TEMPO/PhOH 2/1).

In order to determine the equilibrium constant K_1 for the formation of the hydrogen-bonded complex of the hydrogen donor with TEMPO, the integrated absorbance of the peak due to the free species was used. By plotting the concentration of the free species as a function of the concentration of nitroxide, the equilibrium constants for hydrogen bonding, reported in Table 1, were obtained

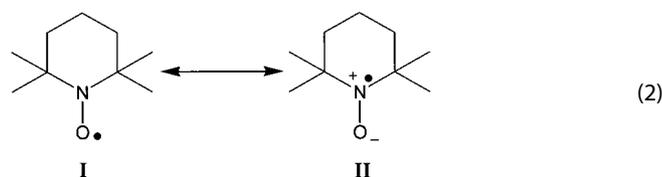
Table 1. Room temperature (296 K) equilibrium constants K_1 for the formation of the hydrogen-bonded complexes of TEMPO, determined by FT-IR and EPR spectroscopy.

HBD	K_1 (IR) [M^{-1}]	K_1 (EPR) [M^{-1}]
Cyclohexanol	–	$1.9 \pm 0.10^{[b]}$
Diphenylamine	$2.2 \pm 0.19^{[a]}$	$2.4 \pm 0.16^{[b]}$
Benzyl alcohol	$3.7 \pm 0.35^{[a]}$	$4.5 \pm 0.46^{[b]}$
Phenol	$9.0 \pm 0.70^{[a]}$	$7.9 \pm 0.90^{[c]}$
Hexafluoropropanol	–	$32.1 \pm 1.18^{[c]}$

[a] In CHCl_3 . [b] In cyclohexane. [c] In toluene.

EPR Measurements

It is well established that the nitrogen hyperfine-splitting constant a_N of nitroxides is sensitive to the polarity of the solvent in which they are dissolved.^[13, 14] This solvent dependence can be explained on the basis of the two canonical forms I and II of the nitroxide function (Equation 2). The greater the solvent polarity, the more favoured will be structure II, bearing larger electron density on the oxygen and spin density on the nitrogen atom.



Two distinct contributions to the solvent effect on the a_N value can be identified: the macroscopic electrostatic contribution and that due to hydrogen bond formation with the solvent. The dependence of EPR nitrogen hyperfine splittings on solvent properties can be expressed as a linear combination of these two terms.^[13, 14] Actually, Mukerjee and co-workers^[15] reported that the a_N value for the di-*tert*-butyl nitroxide in aprotic solvents could be fitted to an equation of the form of Equation (3)

$$S = \beta + \gamma Q / (1 - CQ) \quad (3)$$

obtained by using the continuum model for the dielectric. This relation was used for estimating polarity effects, other than electrostatic, in protic solvents, thus allowing us to isolate the stronger and more specific hydrogen bonding effect from the general medium effect. In particular, if S is the solvatochromic experimental quantity (in the present case a_N) it was found that S obeys Equation (3), where β and γ are constants (1.5224 mT and 0.02085 mT, respectively), $Q = (D - 1)/(2D + 1)$ is a function of the dielectric constant D . The term C is defined as $2\alpha/a^3$, where α and a represent the solute polarisability and effective radius, respectively. In view of the uncertainties associated with the solute parameters α/a^3 , C has been determined as an adjustable coefficient equal to 0.79.

In Equation (3) the only variable parameter is the bulk dielectric constant D which can be easily calculated by Equation (4), where the polarity index H is defined as the ratio between the molar concentrations of the OH groups in the chosen solvent and in water (55.4 M).^[15]

$$D = 0.484 + 77.673H \quad (4)$$

Therefore, the contribution of the general medium effect on a_N is obtained from the alcohol concentration by means of Equations (3) and (4).

As an example, Figure 2 reports the experimental dependence (circles) on the benzyl alcohol concentration $[\text{PhCH}_2\text{OH}]$ of the nitrogen hyperfine splitting a_N of TEMPO, in cyclohexane at 296 K, together with (dotted line) the dependence calculated using the above procedure, namely considering only the general

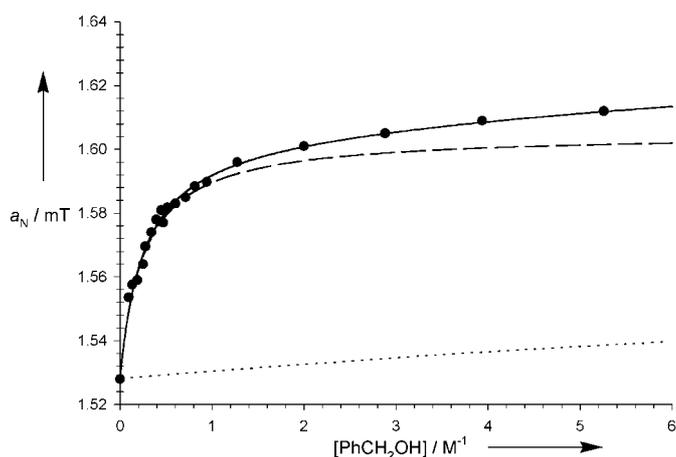


Figure 2. Experimental dependence of a_N on the benzyl alcohol concentration (●) at 296 K in cyclohexane. The lines represent the theoretical dependence of a_N on $[\text{PhCH}_2\text{OH}]$ calculated by taking into account only the general medium effect (dotted line), only the formation of hydrogen bonding (dashed line) and both effects (solid line).

medium effect. It is apparent that the experimental data deviate significantly from the theoretical model if the formation of hydrogen bonds is not taken into account.

Once the contribution from the general medium effect is known, EPR spectroscopy can be used to determine quantitatively the effect of hydrogen bonding on the a_N value. Since the rate of formation and breaking of the hydrogen bonds is very large on the time scale of EPR spectroscopy, the experimental spectrum represents the concentration-weighted average of the spectra due to the free and hydrogen-bonded species. Therefore, the equilibrium binding constant for the formation of hydrogen bonds with TEMPO can be estimated with the Equation (5).

$$a_N = a_{\text{free}}X_{\text{free}} + a_{\text{bound}}X_{\text{bound}} \quad (5)$$

Here a_{free} and a_{bound} represent the values of the nitrogen splitting for the free- and hydrogen-bonded nitroxides, respectively, and X_{free} and X_{bound} are the corresponding molar fractions.

Figure 2 also shows the theoretical dependence of a_N (dashed line) on the benzyl alcohol concentration calculated by considering only the effect of hydrogen bonding, namely by using Equation (5) where X_{free} and X_{bound} have been obtained by using the equilibrium constant K_1 determined by IR spectroscopy (3.7 M^{-1}).^[16] Figure 2 shows that a good fitting of the experimental data at low alcohol concentration is obtained even when only the hydrogen bonding interaction is considered, while at higher concentrations, the general medium effect must also be introduced. When considering both hydrogen bonding and general medium effects, a very good fitting (solid line) of the experimental data is obtained at any alcohol concentration.

Therefore, by keeping the HBD concentration low the equilibrium constants for the formation of hydrogen bonding could be obtained by fitting the EPR data to Equation (5), as shown by Table 1 reporting the K_1 values for the other investigated hydrogen donors. The good agreement with the

FT-IR results data suggests that EPR can be usefully employed to measure equilibrium constants of complexation.

With cyclohexanol, 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) and phenol we have also measured the dependence of the nitrogen hyperfine-splitting of TEMPO on HBD concentration at various temperatures in order to determine the thermodynamic parameters for the formation of hydrogen bonding with this nitroxide. Figure 3 reports the dependence of a_N , in toluene, on

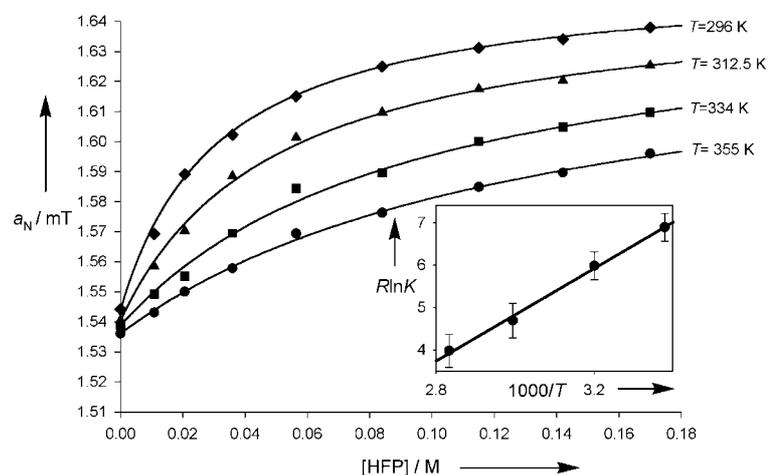


Figure 3. Experimental dependence of a_N on the HFP concentration (filled symbols) at different temperatures in toluene. The lines represent the theoretical dependence of a_N on the alcohol concentration calculated by taking into account only the formation of hydrogen bonding, and were obtained by numerical fitting of the experimental data by using Equation 5. K_1 and a_{bound} were determined as adjustable parameters.

the HFP concentration in the temperature range 296–355 K (filled symbols). Numerical fitting of each curve to Equation (5) provided the value of the equilibrium constant at each temperature, from which the thermodynamic parameters ΔH and ΔS for the formation of hydrogen-bonded complex were calculated (see Table 2).

Table 2. Thermodynamic parameters for the formation of hydrogen bond complexes, Equation (1), determined by EPR spectroscopy.

HBD	ΔH [kcal mol ⁻¹]	ΔS [cal mol ⁻¹ K ⁻¹]
HFP	-5.45 ± 0.24	-11.5 ± 0.74
Cyclohexanol	-4.00 ± 0.19	-12.3 ± 0.89
Phenol	-4.69 ± 0.28	-11.5 ± 0.65

Discussion

The data obtained in the present investigation indicate that hydroxyl derivatives form hydrogen bonds with TEMPO of strengths similar to those formed with ethers and esters. Actually, the equilibrium constants for the intermolecular hydrogen bond formation between phenol and ethyl acetate^[17] or dimethyl ether^[18] in CCl₄ at room temperature are 8.8 and 7.8 M⁻¹, respectively, very close to the values 9.0 M⁻¹ (IR) and 7.9 M⁻¹ (EPR) measured for the complexation by TEMPO in this work. A more

quantitative estimate of the capability of nitroxides to act as hydrogen bond acceptors can be obtained by determining the corresponding Abraham's β_2^H values.^[19] These provide a general, thermodynamically related scale of solute hydrogen-bonded basicity, and can be determined by following the procedure reported in ref. [19] from the equilibrium constant K_1 measured in this work by FT-IR for the hydrogen-bond formation of TEMPO with both phenol and HFP.^[20] From the determined β_2^H value of 0.46, it can be inferred that TEMPO is a good hydrogen bond acceptor, comparable to other important HBA derivatives such as alcohols, ethers and carbonyl groups^[21] as characterised by β_2^H values in the range 0.45–0.50.^[19]

Important information on the energetics of hydrogen bond complexation by nitroxides is also provided by the thermodynamic parameters determined by EPR. The formation of hydrogen bonding, characterized by an enthalpy change of -4.0 kcal mol⁻¹ with cyclohexanol and even more exothermic with HFP (-5.45 kcal mol⁻¹), is in the range normally observed for the formation of O-H...O hydrogen bond with other oxygen-containing HB acceptors.^[22] This is also true for the loss of entropy, namely -11.5 and -12.3 e.u. for the cyclic and the fluorinated alcohols, respectively, whose values are close to those measured for the formation of other hydrogen-bonded complexes (for instance, the ΔS of formation of the complex between the 2-methoxyphenol and ethyl acetate is -10.7 e.u.).^[22]

Conclusions

We have measured for the first time using IR and EPR spectroscopies in solution the equilibrium constants and the thermodynamic parameters for the formation of hydrogen-bonded complexes with different HB donors of a representative member (TEMPO) of a very important class of persistent radicals. The experimental data indicate that nitroxides are versatile hydrogen bond acceptors giving hydrogen bonds of strength similar to that of ethers or esters. With due prudence, the proposed EPR method represents an alternative to IR in the determination of the energy of hydrogen bonds in radicals from the measure of hyperfine coupling constants at low concentrations of the HB donor. These measurements can be quite helpful in designing new organomagnets and also in determining the effect of hydrogen bonding on the reactivity of nitroxides or of other oxygen-centred radical species, such as the peroxy radicals involved in the autoxidation of hydrocarbons in biological systems and in many commercial products.

Experimental Section

Materials: TEMPO, HFP, benzyl alcohol and phenol (loose crystals) were purchased from Aldrich. Anhydrous diphenylamine (Fluka) and chloroform (Aldrich) were packaged under nitrogen. All chemicals were of the highest purity and used as received.

FT-IR Measurements: Spectra were recorded on a Nicolet Protégé FT-IR 460 ESP spectrometer and processed with OMNIC software. The spectrometer was equipped with an air purifier for the elimination of CO₂ and H₂O from the sample housing. Trace background spectra were subtracted from the infrared spectra of each sample. Spectra were recorded at 25 °C using an EZ-fill sealed cell from Spectra-Tech, which had KBr windows and a pathlength of 0.1 mm. The cell was assembled on a back plate and held in place by a compression ring. The cell was filled in the holder and connected to two 1 mL syringes through Luer fittings. The syringes were filled by slowly pulling the solution from the filled syringe to the empty one. All measurements were carried out with freshly prepared solutions. Teflon stoppers were used to minimise any evaporation loss. Resolution of 1 cm⁻¹, 64 scans and an automatic receiver gain were used. The absorbance spectrum of the HBD was obtained by subtracting the absorbance of the solvent from the spectrum of the solution.

The extinction coefficients of free HBDs were determined in CHCl₃ using dilute solutions in order to avoid deviation from linearity due to self-association: phenol (0.01–0.08 M, $\epsilon = 54.2$), benzyl alcohol (0.02–0.09 M, $\epsilon = 25.0$), diphenylamine (0.05–0.20 M, $\epsilon = 26.6$). The equilibrium constant for the formation of hydrogen-bonded complexes was obtained in CHCl₃ by measuring the change in the intensity of the free HBD absorption by varying the amount of TEMPO in the solution (0.05–0.25 M). The integrated absorption intensity was calculated only for the band attributed to the free species.

EPR Measurements: The EPR spectra were recorded on a Bruker ESP300 spectrometer equipped with an NMR gaussmeter for field calibration and Bruker ER033M field-frequency lock. The temperature was controlled with a standard variable temperature accessory and was monitored before and after each run with a copper-constantan thermocouple. The sample consisted of a deoxygenated cyclohexane, toluene or isooctane solution of TEMPO (0.1 mM) in the presence of a known amount of HBD. The instrument settings were as follows: microwave power 0.79 mW, modulation amplitude 0.04 mT, modulation frequency 100 kHz, scan time 180 s, 2 K data points. The nitrogen hyperfine splittings were determined by computer simulation using a Monte Carlo minimisation procedure.^[23]

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