An Electron Spin Resonance Study of 1,2,3,4-Tetrahydro-3-methyl-2,4-dioxo-1-quinazoliyloxyl Radical

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Synopsis. The ESR spectra of the title radical have been obtained in various solvents, and the assignments have been made. It is found that the solvent effects on the hyperfine coupling constants(hfc) for hydrogens on the benzene ring were small, while the nitrogen hfc ($a_{N(1)}$) remarkably increased in polar solvents. The solvent dependence of the nitrogen hfc has been explained in terms of a substantial contribution of dipolar resonance structures through the N-O bond.

Oxidation with lead dioxide converts 1-hydroxy-3-methyl-2,4(1*H*,3*H*)-quinazolinedione (**1**) into its *N*-oxyl radical (**2**) which has the half-life of about 1.5 h at room temperature in solution. The ESR spectrum of this radical consists of nine lines (Fig. 1). Baldock et al.[1] have ascribed the stability of the radical to the canonical resonance structures (**2a** and **2b**) in Scheme 1.

They assigned the spectrum to the two nitrogen atoms. However, this is questionable since the simulated spectrum on the basis of their hfc-values does not reproduce the observed one at all.

It has been recognized that the stability of free radicals is controlled by both mesomeric and steric

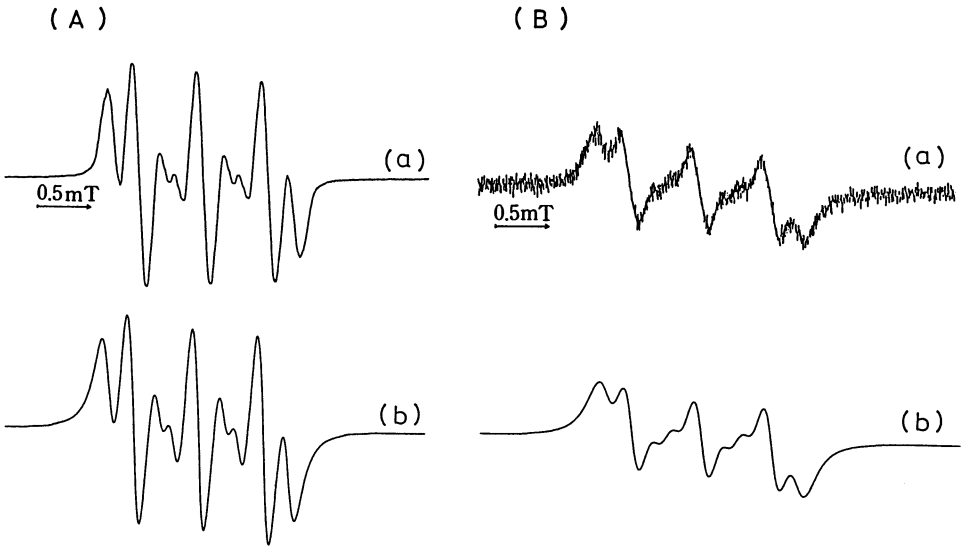
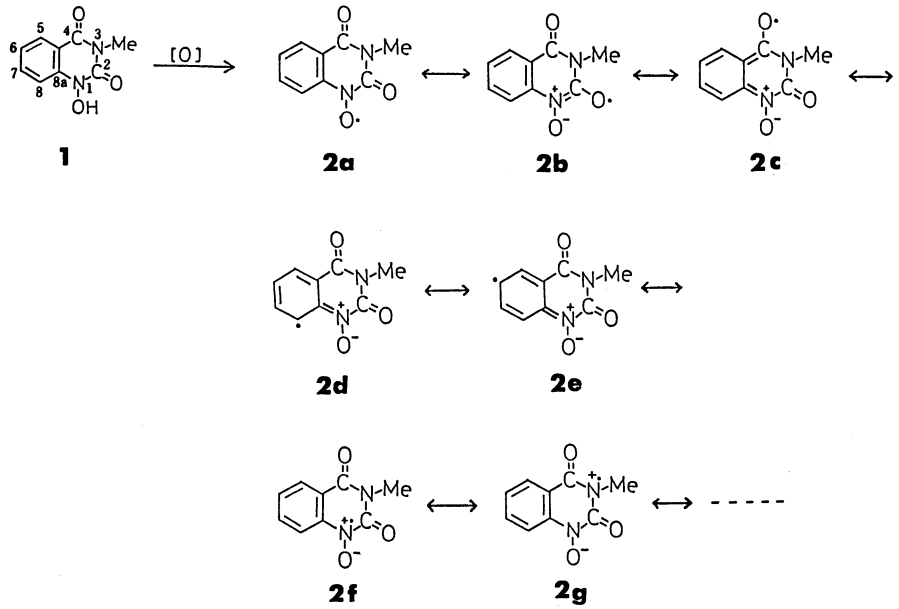


Fig. 1. ESR spectra of *N*-oxyl radical **2** in CCl_4 (A) and acetonitrile (B). (a): experimental spectra, (b): spectra simulations using parameters given in Table 1.



Scheme 1.

factors.[2] Knauer and Napier[3] have shown that the linear correlation between the E_T-value and the nitrogen hfc of aliphatic nitroxide radicals in various solvents exists, and the hfc variation is a useful empirical solvent polarity parameter. In cases where molecules in question have polarized resonance structures, it seems necessary to take into account special interactions between solute and solvent molecules in order to explain the solvent dependency of hfc.

In this paper, we would like to report a modified assignment of **2** and the solvent dependency of the hfc.

Experimental

Materials. The reagent grade solvents were purified and distilled in the usual manner just before use. The solvents were purged with nitrogen. The substance **1** was prepared according to the method by Baldock et al.[1] and recrystallized from ethanol; mp 246—247 °C (lit,[1] 254—257 °C). The product was checked by IR and NMR spectra.

Procedure. Radical **2** was prepared by oxidation of **1** (ca. 10^{-4} mol dm^{-3}) with PbO_2 in various solvents. ESR spectra were obtained with a JEOL JES-FE 3XG equipped with a 100 kHz field modulator. The magnetic field sweep was calibrated using Fremy's salt.[4] Computer-simulated spectra were obtained according to an attached program by using a DEC RT-11 computer. The accuracy of the coupling constants obtained from these simulations was within 4 μT.

Results and Discussion

The ESR spectra of **2** in CCl_4 and acetonitrile are shown in Fig. 1. Since the dielectric loss for acetonitrile is large and **1** is sparingly soluble in acetonitrile, the spectrum was very weak and not well-resolved. The spectra in other solvents are rather similar to that in CCl_4. As may be seen in Fig. 1, the spectrum consists of nine lines. Baldock et al.[1] assumed the planar structure for this molecular skeleton, and showed two canonical forms **2a** and **2b**. They ascribed the nine-line spectrum to the two nitrogen atoms (a=612, 210 μT), hydrogen atoms causing only broadening. If these hyperfine coupling constants are used, a nine-line spectrum with the same intensity and approximately the same peak-to-peak distance could be expected. The spectra in Fig. 1 are, however, quite different.

We have inspected these spectra and simulations have been made so as to reproduce the observed spectra best. Representative computer simulated spectra are shown in Fig. 1. The hfc values of N(1), H(6,8), and H(5,7) are given in Table 1. From these data, some interesting points may be noticed. (1) The hfc $a_{N(1)}$ increases as the solvent polarity increases, and the value is considerably small compared with those of similar nitroxide radicals.[3,5] (2) The dependencies of the hfc of the hydrogen atoms in the benzene ring on the solvent polarity are small compared with that of the nitrogen. However, there is a trend that $a_{H(6,8)}$ increases, while $a_{H(5,7)}$ decreases as the solvent polarity increases. (3) The hyperfine structure due to N(3) was not observed. Here, we wish to comment the above findings.

If radical **2** is planar (as could be presumed by the CPK model), a considerable flow of lone-pair electrons to the benzene rings would be expected and we could write down various types of polar structures besides **2a** and **2b**, as shown in Scheme 1. Botrel and coworkers[6] have calculated the electron densities of 4-[2-(1-methyl-4-pyridino)ethyl]phenolate by means of the CNDO/SCI method in which solvation is taken into account. They have shown that polar structures are favored in polar solvents. By applying McRae's formula, we have also shown that solvent-induced solute polarization plays an important role in the cis-trans thermal isomerization of push-pull azobenzenes, recently.[7] In Fig. 2, the nitrogen and hydrogen hfc's are plotted against the E_T-value which could be regarded as a measure of solvent polarity parameter. The $a_{N(1)}$ clearly shows a trend to increase with the increase in the E_T-value. If the contributions of the canonical polar structures such as **2b** and **2c**

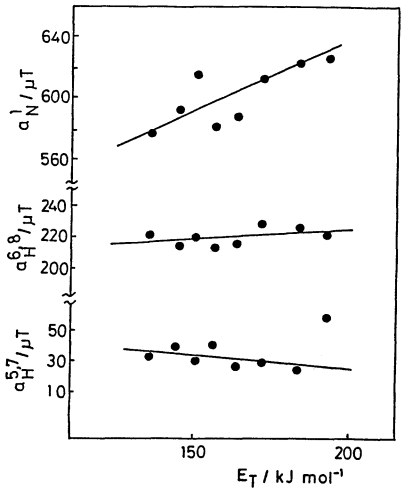


Fig. 2. Relationship between the nitrogen and hydrogen coupling constants and solvent polarity parameters, E_T.

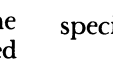
Table 1. Nitrogen and Hydrogen Coupling Constants (in μT) for **2** in Various Solvents at 25 °C

Solvent	$E_T(30)$[a]	$a_{N(1)}$	$a_{H(6,8)}$	$a_{H(5,7)}$
CCl_4	136	577	222	33
Benzene	145	592	216	40
Dioxane	151	616	218	30
Chlorobenzene	157	581	213	41
Chloroform	164	587	216	27
Dichloromethane	172	613	230	29
N,*N*-Dimethylformamide	184	623	227	25
Acetonitrile	193	627	223	58

a) kJ mol^{-1}.

are dominant as proposed,[1] the reverse should be true. Therefore, the proposed canonical resonance structures alone cannot give a resonable explanation for the solvent dependency. It would be natural to consider that, among the canonical forms in Scheme 1, **2f** plays the most important role. Then, the solvent dependency on $a_{N(1)}$ could be understood well.

The hfc $a_{N(1)}$ for **2** ($\approx$600 μT) is considerably small compared with those of similar nitroxide radicals. For example, a_N is ca. 1500 μT, 1000 μT, and 900 μT, for di-*t*-butyl nitroxide radical[3] diphenyl nitroxide radical,[5] and phenyl nitroxide radical,[9] respectively. The remarkably small value of $a_{N(1)}$ can be ascribed to the contibution of **2b** and possibly **2c** for which the unpaired electron moves to the adjacent carbonyl oxygen.[8] It should be noted that the hfc due to the N(3) atom has not been observed. This indicates that the contribution of **2g** is negligibly small. There is a possibility that the hetero-ring is not coplanar, or that sp^2 hybridizations are imperfect(decrease of s-character). This might be responsible for the small value of $a_{N(1)}$, and $a_{N(3)}=0$. According to our view, however, the steric hindrance is not so severe for **2** that the mesomeric stabilization through coplanar structure will overwhelm the steric factor, and **2a—f** will play an important role, thus accounting for our results. Negligible contribution of **2g** could be ascribed to the strong electron-attracting carbonyl groups adjacent to the N(3) atom rather than to the imperfect sp^2-hybridization.

On the assumption that the hybridization of the nitrogen atom in the phenyl nitroxide radical is sp^2, Kikuchi and Someno[9] estimated the spin densities on the benzene ring (0.128 for the 2,4-positions and 0.043 for the 3 position) and compared these with the calculated values on the basis of McLachlan's method. By referring to their results, we have assumed that $a_{H(6)} \approx a_{H(8)} \gg a_{H(5)} \approx a_{H(7)}$. This assumption may be valid because of the contribution of **2d** and **2e**. Applying the relationship $a_H = Q^H_{CH} \cdot \rho_c$,[10] where Q^H_{CH} (=2250 μT) is a constant, and using the data in Table 1, we have estimated the spin densities $\rho_{C(6,8)}=0.096$ and $\rho_{C(5,7)}=0.018$. As stated above, there are trends that $a_{H(6,8)}$ increases, while $a_{H(5,7)}$ decreases with an increase in the solvent polarity. Mukai et al.[5] reported similar results for the 2,6-di-*t*-butyl-4-methylphenoxyl radical and explained trends in terms of a variation in the π-electron spin density due to an electrostatic interaction between the radical and the solvent molecules. The $a_{H(5,7)}$-value in acetonitrile clearly deviates upward even if the large experimental uncertainty, as pointed out above, is taken into account, and this exceptionally large $a_{H(5,7)}$ causes to change the pattern of the ESR spectrum compared with that in other solvents (Fig. 1). The reason is not clear; however, we can say that a specific solvation of acetonitrile to the  group might be operating and might modify the spin density on H(5) and H(7), as has been discussed by Leach and Tabner.[11]

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