Free Rad. Res., Vol. 32, pp. 25–29
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Dibromonitroso Benzene Sulphonate Spin-adducts – Why No Hyperfine Coupling to Bromine?

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Accepted by Prof. J.M.C. Gutteridge

(Received 3 February 1999; In revised form 28 May 1999)

Both ^{79}Br and ^{81}Br nuclei have very large magnetic moments and hence can give rise to large hyperfine splittings. However, for the title compound, dibromonitroso-p-benzene sulphonate (DBNBS), which is a widely used spin-trap, liquid-phase spectra of radical adducts are characterised by narrow EPR features with no bromine splitting, despite the expected delocalisation of spin-density onto bromine. I find that for such radicals in the solid-state the ^{14}N parallel features are very broad, although the seven expected hyperfine features from the ^{79}Br and ^{81}Br nuclei were not clearly defined. I use these results to offer an explanation for the complete absence of any hyperfine splitting from bromine in the isotropic spectra.

Keywords: Bromine, EPR, free radicals, spin-trap, nitroxyl radicals

INTRODUCTION

Extensive solid-state EPR studies of radicals containing bromine or iodine have shown large hyperfine splittings from their nuclei.[1] However, in the liquid-phase, similar radicals have given EPR spectra with narrow features, but with no splittings from the halogen nuclei. Thus, for example, for radical I (Figure 1), formed by radiolytic electron-addition in rigid glassy solutions, maximum bromine hyperfine splittings of about 110 G were clearly defined. However, these radicals formed in fluid solution gave all the expected proton hyperfine features, but no bromine splitting.[2]

This could, of course, arise because the isotropic hyperfine coupling is, fortuitously, too small to be resolved. This is often implied in the literature by saying $A(^{81}\text{Br}) = 0$. The other possibility is that there is some unusual mode whereby the hyperfine splitting is totally lost in the liquid phase. Important examples of such radicals are the nitroxyl radicals formed from the spin-trap dibromonitroso-p-benzene-sulphonate (DBNBS) (structure 2, Figure 1). This trap is very widely used to detect active radicals, but it would be of very limited use if there was splitting or simply line-broadening from the bromine nuclei. The aim of this work is to find a general explanation for the absence of halogen coupling, and, in particular, to probe the situation for DBNBS-adducts by studying solid-state EPR spectra.

Structure I

Structure II

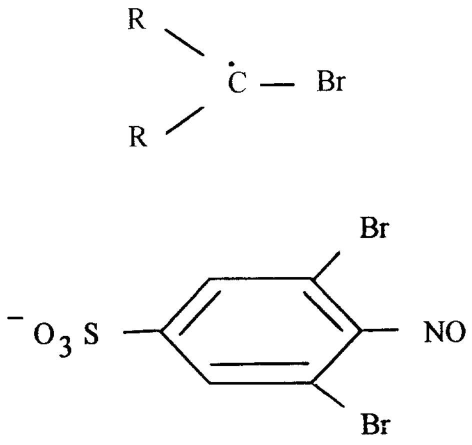


FIGURE 1 Structure I – Au α-Br alkyl radical. Structure II – DBNBS.

TABLE I EPR parameters for some α-halo radicals

Radical	Temp.	Solvent (nucleus)	Hyperfine coupling G[a]			Reference
			$A_{\parallel}$	$A_{\perp}$	A_{iso}	
$H_2\dot{C}Cl$	77K	CD_3OD	21	*ca.* 0	3	1
		(^{35}Cl)				
$Me\dot{C}HBr$	RT	Cyclopropane	—	—	0	2
		(^{81}Br)	—	—	20.47(1)	
		(^1H)			24.71(3)	
$Me\dot{C}HBr$	77K	CD_3OD	85	*ca.* 0	*ca.* 26	1
$Me_2\dot{C}Cl$	RT	C_6H_6(^{35}Cl)	—	—	0.54	4
		(^1H)	—	—	16(6)	
$Br\dot{C}(OH)Me$	RT	DMF				
		(^{81}Br)	—	—	0	2
		(^1H)	—	—	0.69(Me)	
					0.37(1H,0)	
					0.09(1H,m)	
					0.10(1H,m)	

[a] $G = 10^{-4}$T.

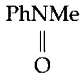
MATERIALS AND METHODS

DBNBS was prepared by standard procedures and was stored in aqueous solutions at pH 7.4. EPR spectra were measured using a JEOL-REIX X-band spectrometer. Modulation amplitutes were *ca.* 100 kHz and microwave powers were in the 1–5 mW range, in the 9.3 GHz region. Signals were accumulated in the usual way.

RESULTS AND DISCUSSION

Some typical results for a range of aliphatic chlorine and bromine-containing radicals are given in Table I. Some data for corresponding aromatic compounds are given in Table II, and for DBNBS and related spin-traps in Table III. A typical spectrum for a DBNBS radical at 77 K is shown in Figure 2.

TABLE II EPR parameters for some aryl nitroxide radicals

Radical	Temp.	Solvent (nucleus)	Hyperfine coupling G[a]			Reference
			$A_{\parallel}$	$A_{\perp}$	A_{iso}	
 $\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{PhNMe}}$	RT	CH_3OH				
		(^1H)	—	—	11.7(CH_3)	3
					2.6(o,p)	
					0.9(Me)	
N-methyl-2 nitroso, 3,5,6 tetramethylbenzene	RT	C_6H_6				
		(^1H)	—	—	12.7(CH_3)	4
					3.4(p)	

[a] $G = 10^{-4}$ T.

TABLE III EPR parameters for DBNBS and related radicals

Radical	Temp.	Solvent (nucleus)	Hyperfine coupling G[a,b]		
			$A_{\parallel}$	$A_{\perp}$	A_{iso}
DBNBS + $\dot{C}H_3$	RT	H_2O			
		(^{14}N)	—	—	13.5
		(^1H)(CH_3)	—	—	14.5
		(^{81}Br)	—	—	0
DBNBS + $^{\bullet}SO_3^-$	RT	H_2O			
		(^{14}N)	—	—	12.6
		(^1H)	—	—	0.61(2,m)
			—	—	8.31(2,o)
		(^{13}C)	—	—	6.55(p)
		(^{33}S)	—	—	1.78
		(^{81}Br)	—	—	0
p-Br DBNBS + $^{\bullet}CH_3$	RT	(C_6H_6)			
		(^{14}N)	—	—	13.34
		(^1H)	—	—	12.13(3)
		(^{81}Br)	—	—	0
1,2-dichloro-derivative + CH_3Ph	RT	(PhMe)			
		(^{14}N)	—	—	12.7
		(^1H)	—	—	9.0(p)
			—	—	0.61(o)
		(^{35}Cl)			0

[a] $G = 10^{-4}$ T. [b] Data taken from Landolt-Bornstein, Volume 17, Springer-Verlag, Berlin, 1989.

(i) Analysis of EPR Spectra for DBNBS Derivatives

The liquid-phase spectra pose no problems, except for the missing bromine splittings. The features are narrow and well defined. The solid-state spectra show very broad (±1) ^{14}N parallel features and a broad central component that includes the (0) parallel feature, and the three perpendicular features. These lines are far broader than those for other nitroxyl radicals in the solid-state, not containing bromine. Unfortunately, our attempts to resolve the possible septet from the two bromine nuclei were unsuccessful. I stress that in addition to different features from ^{79}Br and ^{81}Br, a range of other factors contribute to this broadening. These include the fact that the principal axes for the bromine hyperfine coupling do not coincide with each other or with those for the ^{14}N or the *g*-tensor directions. Also, there will be various quadrupole contributions. Nevertheless, comparing the normal widths for non-bromine containing nitroxyl radicals with those now detected, gives a rough measure of

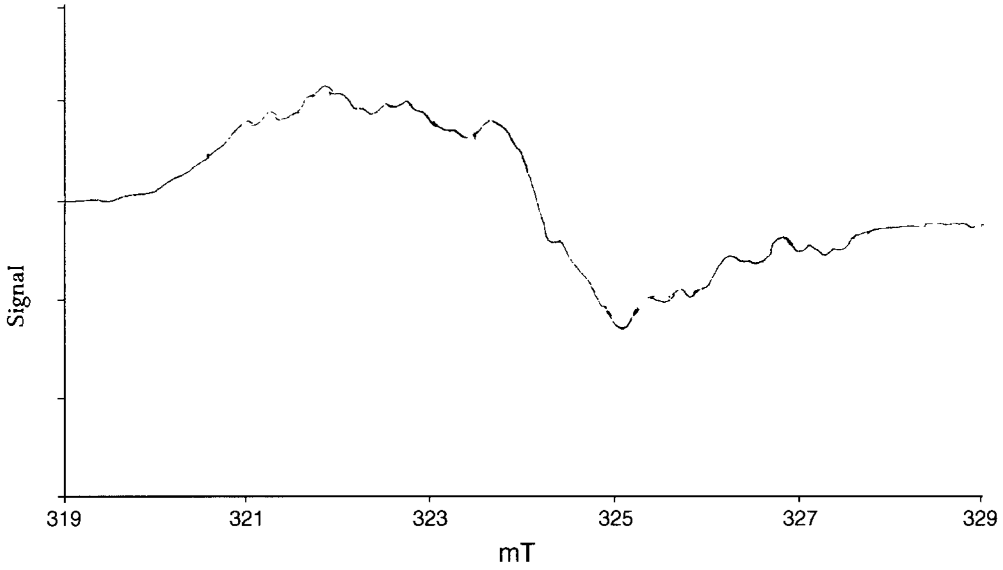


FIGURE 2 First derivative EPR spectra for the DBNBS–CD_3 adduct in CD_3OD at 77 K, showing broad features from unresolved bromine hyperfine coupling.

the overall width for the bromine septets, and hence a very rough gauge of, and A_x, A_y and A_z (^{81}Br). In an attempt to obtain narrower features we used D_2O/CD_3OD solvents, but the resolution was not improved.

(ii) Expected Values for the Bromine Hyperfine Splitting

I have tackled this problem in two ways, one being to scale the known isotropic coupling constants for some chloro-derivatives of this type with those for similar bromo-radicals. The other was to use the resolved solid-state spectra for some bromo-derivatives, to provide the isotropic splitting. These can be related to radicals, $R_2\dot{C}Br$, having a formal unit spin on carbon (Table I). I then attempted to relate these results to the DBNBS derivatives, by making estimates of the spin-densities on carbon for the attached Br atoms in DBNBS adducts. This assumes that the spin reaches bromine via π-delocalisation. This may not be correct, as discussed below.

Some results for certain chlorine derivatives are included in Tables I and II. The most direct result is that for $(CH_3)_2\dot{C}$–Cl, which gave *ca.* 3 G for the chlorine isotropic hyperfine coupling. For the aromatic derivatives (Table II), the radical $H_2\dot{C}$–C_6H_4–Cl gave $A(\text{Cl}) = 0.34$ G. If we guess that the spin-density of the *para*-carbon is close to those on the *ortho*-carbons, then, from the ^{1}H splitting, we get a spin-density of *ca.* 17% on the *para*-carbon. Hence, for unit spin on carbon, we get *ca.* 3 G, in good agreement. For the radical $Ar\dot{C}Cl_2$, the splitting is already 3 G.[3] However, no splittings were found for the ring protons, suggesting that the benzene ring is twisted through *ca.* 90°, thus blocking π-delocalisation. These results are in satisfactory agreement. By multiplying this value of 3 G by the ratio of the ^{35}Cl and ^{81}Br nuclear spins, we get a predicted value of *ca.* 15 G for ^{81}Br. This can be compared with the result obtained by analysis of the solid-state spectra for $Me_2\dot{C}BR$ (Table I). This gives $A_{\text{iso}}(^{81}\text{Br}) = 25$ G, in reasonable agreement. Using a value of 20 G as a yardstick, we now need to estimate the spin-density on the $>$C–Br carbon atoms in DBNBS-adducts. If we use the results for radicals in which the $-SO_3^-$ group is replaced by –H or –CH_3, we get *ca.* 4%. This gives a predicted isotropic splitting of *ca.* 0.8 G for bromine.

Such splittings would normally be readily resolved. Using this value we find that $A_{\parallel}(^{81}\mathrm{Br})$ should be *ca.* 1.3 G. For seven lines, this gives *ca.* 7.8 G as the predicted total parallel splitting. In fact, with proton splittings of *ca.* 1.3 G on the parallel features, this is reasonable, although the resolution is poor.

An Alternative Structure

The normal structure expected for Ar–N(O$^\bullet$)–R radicals is one in which the groups are nearly planar, with good π-overlap. However, for the dibromo-derivatives, such a structure is surely sterically impossible. Hence the Ar group is expected to twist, relative to the –N(O$^\bullet$)–R group, the most favourable conformation on steric grounds being that with $\theta = 90°$. This would compete with the stabilising effect of π-delocalisation, and a compromise orientation is therefore possible. However, there is now direct overlap between the semi-occupied π-orbital and the two bromine atoms. This will introduce an unpredictable, but large extra hyperfine coupling, and hence is unlikely to be a major factor.

Possible Relaxation Mechanism

I suggest that the reason why the bromine coupling is completely lost is not because the isotropic coupling is exactly zero, but because the quadrupole coupling controls the nuclear orientation. This situation is common in NMR spectroscopy, because the nuclear magnetic coupling is often much less than the electric quadrupolar coupling. This locks the nucleus to the molecular axes, and when the molecule rotates fast enough to average out the anisotropic coupling as usual, but it also induces rapid nuclear spin flips so that only a single feature is observed. On cooling initial broadening would occur prior to reaching the normal spectra.

This is a very rare phenomenon in EPR spectroscopy because the electron-spin is much greater than the nuclear-spin, and usually also greater than the quadrupole coupling. Hence, normally, when the radical tumbles, the nucleus remains locked to the strong static magnetic field acting via the unpaired electron. In the present case, for the π-type radical, the quadrupole axes lie along the C–Br bond directions, attempting to lock the nucleus along these axes. When the magnetic field is along the π-axis, for the bromoalkyl radicals, the hyperfine coupling is large, and the magnetic field is in control. However, the reverse applies for fields along the y and z axes, where the hyperfine coupling is small. Hence the EPR features are quite unusual for solid-state radicals.[1]

For DBNBS radicals, I suggest that the quadrupular couplings remain large, but the hyperfine couplings are now very small. Hence the electric field dominates in all directions, so there is no possibility for resolution in the liquid-phase. Fortunately, at low temperatures, this is not the case at least for the chloro-derivatives. The lines are broadened, but resolution is still observed.

CONCLUSIONS

I conclude that this quadrupole effect is responsible for the loss of bromine hyperfine splitting in the liquid-phase. It is, of course, fortunate that it does, since, otherwise, there would be far more hyperfine features and by analogy with the chloro-derivatives, the features would be broad, making this species useless as a spin-trap.

I thank Professor C. Rhodes and Dr. N. Nazhat for helpful discussions.

References

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