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SOLVENT EFFECTS ON THE NITROGEN HYPERFINE SPLITTING CONSTANT OF THE t-BUTYL-t-BUTOXY NITROXYL RADICAL

Edward G. Janzen and Gregory A. Coulter
Department of Chemistry
Guelph-Waterloo Centre for Graduate Work in Chemistry
University of Guelph
Guelph, Ontario, CANADA, N1G 2W1

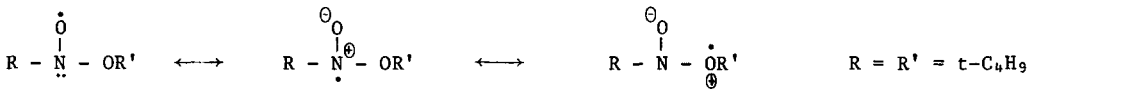
ABSTRACT: A decrease in nitrogen hyperfine splitting constant (N-hfsc) with increasing solvent polarity is reported for t-butyl t-butoxy nitroxyl radical produced by trapping t-butoxyl radical with 2-methyl-2-nitrosopropane.

The N-hfsc for dialkyl and alicyclic nitroxyl radicals has been shown to increase with increase in solvent polarity (1-4). This relationship is due to the increasing spin density on nitrogen with increase in solvent polarity:

(I) (II)

In connection with an esr study of a 5-membered cyclic alkoxy nitroxyl radical (5) it was noted that literature values of the N-hfsc's of the t-butyl t-butoxy nitroxyl radical (BOBN) indicated a small solvent effect and in the opposite direction from dialkyl and alicyclic nitroxyls. This question has been investigated using most of the thirty solvents selected by Knauer and Napier in their extensive study on the use of the N-hfsc as a solvent polarity parameter (4).

The experimental method has been described previously (6). Di-t-butylperoxalate (0.01M) was used as a room-temperature t-butoxyl radical source. Trapping by 2-methyl-2-nitrosopropane (0.01M) provided t-butyl t-butoxy nitroxyl radicals (BOBN) in most solvents.



(III) (IV) (V)

In some cases only the radical derived from the solvent was trapped (see Table 1). Spectra consisting of typical nitroxyl triplets were observed with the range of N-hfsc only 1.5 gauss.

Figure 1 shows a plot of a_N (BOBN) vs. the Dimroth-Reichardt solvent polarity parameter, $E_T(30)$, used by Knauer and Napier (4,7). It is clear that if all the data is used (a) the correlation is poor (b) the slope is negative and (c) the point for THF is anomalous.

TABLE 1

	Solvent	a_N(BOBN)[a]	$E_{T(30)}$[b]	a_N(DTBN)[a]
1.	hexane	27.44	30.9	15.13
2.	cyclohexane	27.34	31.2	15.05
3.	carbon tetrachloride	27.16	32.5	15.33
4.	carbon disulfide	27.10	32.6	15.29
5.	toluene	27.06	33.9	15.35
6.	benzene	27.12	34.5	15.40
7.	diethylether	27.27	34.6	15.33
8.	1,4-dioxane	27.01	36.0	15.45
9.	tetrahydrofuran	26.13	37.4	15.37
10.	chlorobenzene	26.99	37.5	15.47
11.	bromobenzene	26.98	37.5	15.48
12.	1,2-dimethoxyethane	27.02	38.2	15.42
13.	chloroform	(c)	39.1	15.86
14.	pyridine	26.85	40.2	15.61
15.	methylene chloride	26.90	41.1	15.75
16.	acetophenone	26.89	41.3	15.56
17.	1,2-dichloroethane	26.86	41.9	15.65
18.	acetone	26.95	42.2	15.53
19.	N,N-Dimethylformamide	(c)	43.8	15.63
20.	t-butyl alcohol	27.11	43.9	15.86
21.	dimethyl sulfoxide	26.73	45.0	15.69
22.	acetonitrile	26.84	46.0	15.67
23.	nitromethane	26.67	46.3	15.76
24.	i-propyl alcohol	27.06	48.6	15.97
25.	benzyl alcohol	26.79	50.8	16.27
26.	acetic acid	(d)	51.9	16.42
27.	ethyl alcohol	26.97	51.9	16.03
28.	methyl alcohol	(a)	55.5	16.21
29.	ethylene glycol	(d)	56.3	16.36
30.	water	(d)	63.1	17.17
31.	.1N NaOH	26.92	--	17.11

(a) all measurements in gauss
(b) ref. 7
(c) solvent derived radicals trapped exclusively
(d) no spectrum obtained

FIGURE 1
a_N(BOBN) vs. E_T(30)

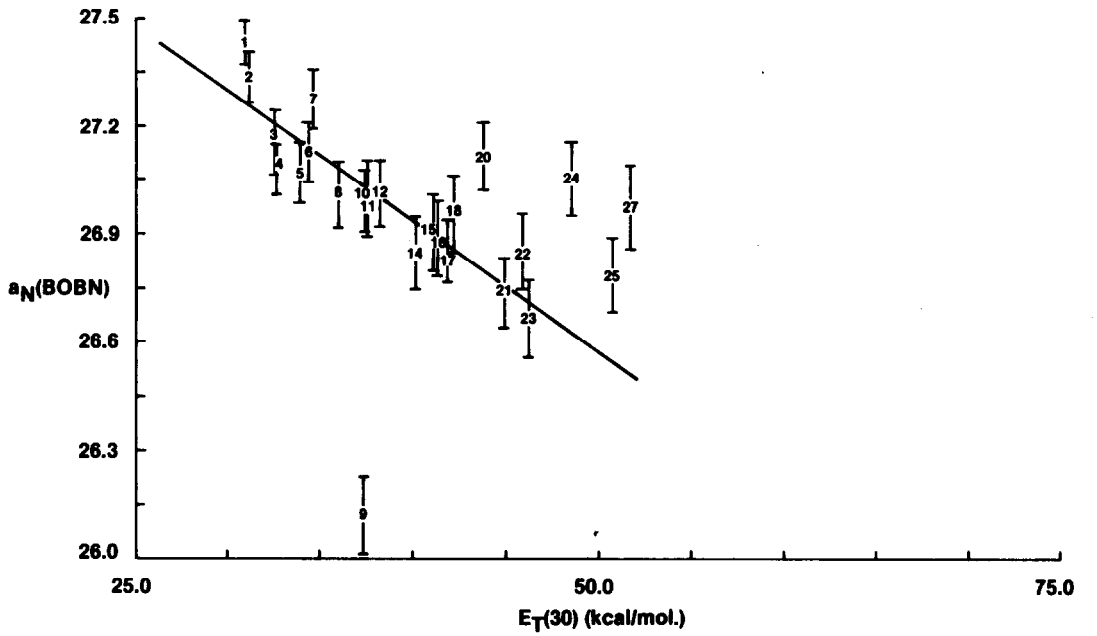
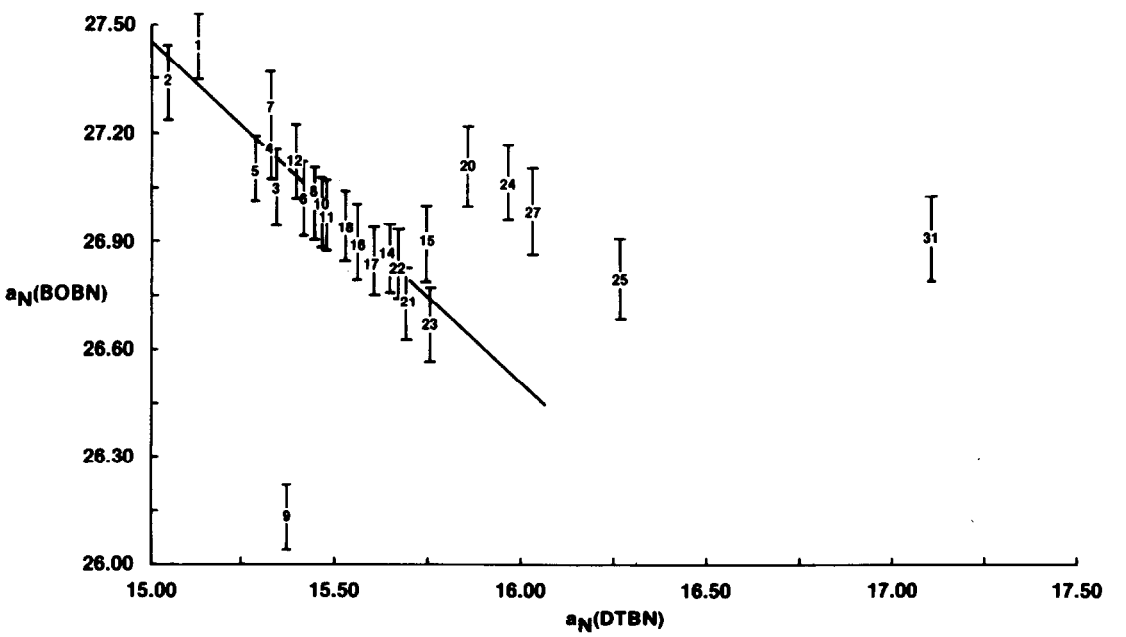


FIGURE 2
a_N(BOBN) vs. a_N(DTBN)



If the data for the hydroxylic solvents and THF is removed the correlation is excellent (see line of best fit on Figure 1). A comparison between a_N(BOBN) and a_N(DTBN) as a function of solvent is shown in Figure 2. The same conclusions can be reached indicating that the response of a_N to solvent polarity is quite different for the two nitroxyl radicals (the line of best fit in Figure 2 excludes hydroxylic solvents and the point for THF).

Correlation Coefficients from a Linear-Unweighted Least-Squares Calculation

	a_N(BOBN) vs. E_T(30) (Figure 1)	a_N(BOBN) vs. a_N(DTBN)* (Figure 2)	a_N(DTBN)* vs. E_T(30) (Figure 1, ref. 4)
all data	-0.44	-0.28	+0.94
non OH solvents (also excluding THF)	-0.91	-0.94	+0.84**

* DTBN = di-t-butyl nitroxyl radical ** excluding only non-hydroxylic solvents

Two explanations for the solvent effect on a_N(BOBN) can be proposed: a larger contribution of resonance structure V with increase in solvent polarity and/or an increase in planarity with increase in solvent polarity. The effect of hydroxylic solvents on a_N(BOBN) is puzzling. Although hydrogen bonding would be expected to enhance contributions from resonance structure V, a_N(BOBN) is found to be larger than predicted from the line passing through the other 19 points. Perhaps the contributions from IV and V are both enhanced and the effects on a_N(BOBN) cancel. Also small changes in structure of the nitroxyl function (planar/nonplanar) are expected to have relatively large effects on a_N(BOBN) which may offset substantial changes in spin density. In the case of THF other nitroxyl triplets with large N-hfsc were noted. The structure of these radicals is not known at this time. The point identified with THF in Figure 1 and 2 may not be due to the t-butyl t-butoxy nitroxyl radical. Further studies on this point are underway.

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References

1) R. Briere, H. Lemaire and A. Rassat, Bull. Soc. Chim. Fr. 3273 (1965).
2) Th. A.J.W. Wajer, A. Mackor and Th. J. deBoer, Tetrahedron, 25, 175 (1969).
3) E.F. Ullman, L. Call and J.H. Osiecki, J. Org. Chem., 35, 3623 (1970).
4) B.R. Knauer and J.J. Napier, J. Am. Chem. Soc., 98, 4395 (1976).
5) E.G. Janzen, C.C. Lai and R.V. Shetty, Tet. Letts. 1201 (1980).
6) G.A. Russell, E.G. Janzen and E.T. Strom, J. Am. Chem. Soc., 86, 1807 (1964).
7) K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, Justus Liebigs Ann. Chem., 661, 1 (1963).

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