The Nitrogen Hyperfine Splitting Constant of the Nitroxide Functional Group as a Solvent Polarity Parameter. The Relative Importance for a Solvent Polarity Parameter of Its Being a Cybotactic Probe vs. Its Being a Model Process

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Abstract: Solvent polarity parameters currently fall into two classes: (1) those which involve no model reaction and which do not probe the solvent at the molecular level (in the cybotactic region) and (2) those which do involve a model reaction and which probe the solvent at the molecular level. In the former category one may find dielectric constant and dipole moment while the Kosower Z value, the Dimroth–Reichardt $E_T(30)$, and the Berson Ω value may be found in the latter. The nitrogen hyperfine splitting constants, $\mathcal{A}_N$, of di-*tert*-butyl nitroxide (**1**), 4-amino-2,2,6,6-tetramethylpiperid-1-yloxy (**2**), and 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (**3**) have been measured in a series of 31 solvents. The linear correlations between $\mathcal{A}_N$ and the polarity parameters in category (1) are poor while those between $\mathcal{A}_N$ and the polarity parameters in category (2) are good (correlation coefficient, $r \approx 0.95$). Since $\mathcal{A}_N$ involves no model reaction but is a cybotactic probe this suggests that it is more important that a solvent polarity parameter be a cybotactic probe than it is that it involve a model reaction. Since $\mathcal{A}_N$ is easily measured in almost all cases, it may prove to be a useful empirical solvent polarity parameter, especially in cases where the other parameters are difficult to determine owing to limited solubility, spectral interference, etc.

The polarity of a solvent may be described by several parameters.[1] Those which are most frequently employed are the dielectric constant, ϵ, dipole moment, μ, Winstein–Grunwald Y value,[2] Kosower Z value,[3] and Dimroth–Reichardt $E_T(30)$ value.[4] The ϵ and μ parameters are fundamentally different from the remaining three in two important ways.

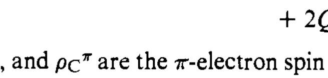
First, ϵ and μ do not directly probe the cybotactic region[5a] of the solvent. The dielectric constant is not a probe of the cybotactic region because it is a macroscopic property of the bulk solvent. The dipole moment of the *solvent* is a property of an individual solvent molecule (particularly when determined by microwave spectroscopy in the gas phase, which values are generally regarded as being most accurate). However, *when μ is employed as a solvent polarity parameter* for an ensemble of solvent molecules in the liquid phase it becomes a polarity parameter of the bulk solvent and does not probe the cybotactic region. (If the magnitude, direction, and perhaps the intramolecular contributions of μ for the solvent molecule are known, this information may help provide a qualitative description of the cybotactic region surrounding some particular solute but this would still not be a probe of this region.) On the other hand, if the dipole moment of a *solute* could be accurately measured at high dilution in a series of solvents, its variation might be the basis for a solvent polarity parameter which would directly probe the cybotactic region.[5b] Conversely, Y, Z, and $E_T(30)$ values derive from experiments which do probe the cybotactic region of the solvent since these parameters are based on effects which the cybotactic region has on solute molecules.

Secondly, Y, Z, and $E_T(30)$ are what might be called model parameters of solvent polarity since each of these parameters results from a particular effect the solvent polarity has on a certain (model) chemical process of a certain compound (e.g., in the case of Y the formation of an ion pair from neutral *tert*-butyl chloride and in the case of Z the conversion of the ion pair of 1-ethyl-4-carbomethoxypyridinium iodide to a neutral species). Conversely, ϵ and μ might be called nonmodel parameters of solvent polarity since no model reaction is involved in their determination.

If the solvent polarity parameter is to be used to determine the effect of solvent polarity on some aspect of a reaction (e.g., reaction rate), then it would seem to be better to use a cybotactic probe, rather than one which is not, since the reaction of interest will be mainly influenced by the cybotactic region and not the bulk solvent. Likewise, it would seem to be better to use a model probe rather than one which does not involve a model reaction. Furthermore, a model probe in which the model reaction, which defines the polarity parameter, bears some resemblance to the reaction of interest would be expected to be a better choice than one in which it does not.[6]

Of the five polarity parameters considered above two, ϵ and μ, are both noncybotactic and nonmodel parameters and the remainder are both cybotactic and model parameters. None is a nonmodel and cybotactic parameter nor is any a model and noncybotactic parameter. Consequently, using these parameters it is not possible to estimate the relative importance of these two factors (i.e., noncybotactic vs. cybotactic as compared to model vs. nonmodel).

However, it has been known for some time that the ^{14}N isotropic hyperfine splitting constant, $\mathcal{A}_N$, in the electron spin resonance (ESR) spectrum of certain nitroxide free radicals is sensitive to the polarity of the solvent in which they are dissolved.[7-15] In terms of valence bond theory two canonical structures (Ia and Ib) can be drawn for the nitroxide functional group.



Ia Ib

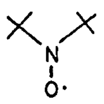
The greater the polarity of a solvent the more structure Ib is favored, increasing the electron density on oxygen, but increasing the spin density on nitrogen. According to the theory of Karplus and Fraenkel[16]

$$\mathcal{A}_N = (S^N + Q_{NO}^N + 2Q_{NC}^N)\rho_N^\pi + Q_{ON}^N\rho_O^\pi + 2Q_{CN}^N\rho_C^\pi \qquad (1)$$

where ρ_N^π, ρ_O^π, and ρ_C^π are the π-electron spin densities at the nitrogen, oxygen, and adjacent carbon atoms, respectively; S^N represents the contribution to the splitting from the nitrogen 1s electrons; and the Q's represent the contributions of the 2s electrons (e.g., Q_{ON}^N is the σ-π parameter for the nucleus of the nitrogen resulting from the interaction between the ON bond and the π-electron density on the oxygen). These constants have been estimated by Ayscough and Sargent[17] for diphenyl nitroxide (I, $R_1 = R_2 = Ph$), giving $\mathcal{A}_N = 35.61\rho_N^\pi - 0.93\rho_O^\pi$, using McLachlan[18] HMO spin densities (Q_{CN}^N is negligibly small). Kubota et al.[19] have estimated them for the anion radicals of a series of heterocyclic amine *N*-oxides giving $\mathcal{A}_N = 42.57\rho_N^\pi - 18.98\rho_O^\pi - 6.66\rho_C^\pi$. Kikuchi and Someno[10] estimated them for phenyl nitroxide (I, $R_1 = Ph$, $R_2 = H$), giving $\mathcal{A}_N = 30.5\rho_N^\pi - 13.6\rho_O^\pi$. Finally, Cohen and Hoffman[20] have estimated them for di-*tert*-butyl nitroxide and 2,2,6,6-tetramethylpiperidine-*N*-oxyl giving $\mathcal{A}_N = 23.9\rho_N^\pi + 3.6\rho_O^\pi$. In any case increasing the spin density on nitrogen and decreasing it on oxygen would increase the magnitude of $\mathcal{A}_N$. Thus, changing the solvent in which the nitroxide is dissolved from one which is less polar to one which is more polar should increase the magnitude of $\mathcal{A}_N$.

This effect, in fact, has been observed. Mukai et al.[9] studied the variation of the ^{14}N hyperfine splitting in diphenyl nitroxide (DPNO, I, $R_1 = R_2 = Ph$) with 22 solvents and in di-*p*-anisyl nitroxide (DPANO, I, $R_1 = R_2 = Ph\text{-}OCH_3$) with 21 solvents. In both cases the ^{14}N hyperfine splitting was considered to be a function of the dipole moments of the solvents and a straight line was fitted by inspection. We have performed an unweighted linear least-squares analysis on these data and calculated correlation coefficients (Table II, lines 10-17). While a trend of increasing nitrogen hyperfine splitting with increasing solvent dipole moment is apparent, the correlation is very poor when all the solvents are considered as a group (lines 10 and 14), and is poor to fair when only similar solvents are considered as a group (lines 11-13, 15-17) except for DPANO in nonhydrogen-bonding solvents (line 15) where the correlation is good ($r \geq 0.95$). Lemaire and Rassat[11] studied the variation of the ^{14}N hyperfine splitting in di-*tert*-butyl nitroxide as a function of the Kosower *Z* value of the solvents used. Except for two solvents, the hyperfine splitting constants are not reported in this paper. However, we have estimated them from a graph which is presented and performed a linear unweighted least-squares analysis. The correlation so obtained is a good one (Table II, lines 25-26, 28). However, only six solvents were examined in this study (4 hydrogen bonding) so there is some question as to whether the large value of *r* might be fortuitous. Wajer, Mackor, and deBoer[15] examined the nitrogen and α-hydrogen (N-H) hyperfine splitting constants of *tert*-butyl nitroxide (I, R_1 = *tert*-butyl, $R_2 = H$) in a series of 11 solvents. The correlation between $\mathcal{A}_N$ and $E_T(30)$ in this case is fair (Table II, line 40). An excellent linear correlation results if $\mathcal{A}_N/\mathcal{A}_{NH}$ is plotted against $E_T(30)$ (Table II, line 39).[21] However, this correlation involves the introduction of an additional parameter, $\mathcal{A}_{NH}$.

The nitrogen hyperfine splitting, $\mathcal{A}_N$, is a solvent polarity parameter for cases in which the nitroxide functional group is used as a solvent polarity probe. Furthermore, this parameter is based on a cybotactic nonmodel probe. If this parameter gives a good linear correlation with the cybotactic, model solvent polarity parameters, then this would suggest that the cybotactic nature of a solvent polarity probe is considerably more important than its model reaction character. On the other hand, if the correlation is a poor one, this would suggest the converse, or that both properties are important. Consequently, we decided to measure $\mathcal{A}_N$ for three nitroxides, di-*tert*-butyl nitroxide (**1**), 4-amino-2,2,6,6-tetramethylpiperid-1-yloxy (**2**), and 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (**3**), in a wide variety of solvents and to determine the degree of correlation of $\mathcal{A}_N$ with cybotactic, model reaction solvent polarity parameters.



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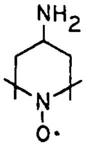

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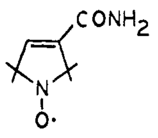

3

Experimental Section

Chemicals. Di-*tert*-butyl nitroxide (**1**), bp 58-59 °C, was prepared from *tert*-nitrobutane and sodium by the method of Hoffmann et al.,[22] except that tetrahydrofuran was employed as solvent in place of glyme.

4-Amino-2,2,6,6-tetramethylpiperid-1-yloxy (**2**) and 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (**3**) were used as purchased from Aldrich Chemical Co., Milwaukee, Wis. 53233.

Solvents. In each case, except water, the commercial reagent grade solvent was purified, usually by methods described by Wiberg[23] or Riddick and Bunger.[24] Water was purified by distillation.

Spectra. All spectra were run on a Varian E-4(X-band) spectrometer at room temperature. The N^{14} triplet was always scanned at a rate of 5 G/min (1 G = 1 cm on chart) with a microwave power of 20 mW and a modulation frequency of 100 kHz. For each radical in each solvent at least six scans were recorded; the scans were run alternately upfield and downfield. The N^{14} hyperfine splitting was measured between maxima and between minima in the first derivative spectra of the nitrogen triplet; thus this procedure generally afforded a minimum of 24 values for the N^{14} hyperfine splitting of each nitroxide radical in each solvent. In some solvents the N^{14} signals of **2** were further split into partially resolved pentets; also, in some solvents the N^{14} signals of **3** were further split into partially resolved sextets.[25] In these cases $\mathcal{A}_N$ was measured between corresponding positions on the nitrogen triplet.

The spectra were obtained from solutions of the three nitroxides in the various solvents. The solutions were purged from 15 to 20 min with dry nitrogen. The concentration of the nitroxide in solution was ca. 5×10^{-6} M for di-*tert*-butyl nitroxide (**1**) and 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (**3**) and was ca. 5×10^{-5} M for 4-amino-2,2,6,6-tetramethylpiperid-1-yloxy (**2**). Small variations in nitroxide concentration would not be expected to affect the N^{14} hfs at the concentrations employed. In several cases the concentration of the nitroxide in a particular solvent was increased by a factor of 10 without altering the N^{14} hfs significantly. All spectra were run using a flat cell.

Results and Discussion

The results are presented in Tables I-III. Table I shows the N^{14} hyperfine splitting, along with the 95% confidence limit and standard deviation, for the three nitroxides employed in the 31 solvents which were investigated. Table II shows the results of our unweighted linear-least-squares plots of $\mathcal{A}_N$ vs. other solvent polarity parameters (lines 1-34), along with the correlation coefficients, *r*. This table includes data culled from other sources, as well as our own; the source is indicated in the table.

It can be seen that for the three nitroxides employed in this study the correlation between $\mathcal{A}_N$ and μ (dipole moment) is very poor (Table II, lines 1-3) and that between $\mathcal{A}_N$ and ϵ (dielectric constant) is poor (lines 18-20) when all 31 solvents are considered. Furthermore the correlation between $\mathcal{A}_N$ and μ is still poor (lines 4-9) when the solvents are divided into two groups: those with hydroxyl groups (hydrogen bonding) and those without. However, the correlation is better for the nonhydrogen-bonding solvents.

On the other hand the correlation between $\mathcal{A}_N$ and $E_T(30)$ for each of the three nitroxides employed in the 31 solvents is good (lines 21-23 and Figures 1-3). The correlation between $\mathcal{A}_N$ and *Z* is also reasonably good (lines 29-31) for the three nitroxides in the 16 solvents in this study for which the *Z* values have been determined (solvents 5, 11, 13, 14, 17-21, 24, 25, 27-31 in Table I). Furthermore, the correlation between $\mathcal{A}_N$ and Berson's Ω values[26] is good (lines 32-34) for the three nitroxides used. However, Ω values were available for only 10 of the solvents (solvents 11, 13, 16-18, 21, 22, 27-29 in Table I)

Table I. Nitrogen Hyperfine Splitting Constants of Di-*tert*-butyl nitroxide (**1**), 4-Amino-2,2,6,6-tetramethylpiperid-1-yloxy (**2**), and 3-Carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (**3**) Free Radicals in Various Solvents

Solvent							Free radical **1**		Free radical **2**		Free radical **3**	
No.	Name	$E_T(30)$,[a] kcal/mol	Z,[b] kcal/mol	Ω[c]	ϵ[d]	μ,[e] D	$\mathcal{A}_N$ ± CL(95),[f] G	SD, G	$\mathcal{A}_N$ ± CL(95),[f] G	SD, G	$\mathcal{A}_N$ ± CL(95),[f] G	SD, G
1	*n*-Hexane	30.9			1.88	0	15.134 ± 0.012	0.029	15.219 ± 0.013	0.030	14.016 ± 0.014	0.042
2	Carbon tetrachloride	32.5			2.24	0.0	15.331 ± 0.017	0.040	15.404 ± 0.010	0.033	14.240 ± 0.013	0.031
3	Carbon disulfide	32.6			2.64	0.00	15.289 ± 0.013	0.030	15.374 ± 0.017	0.040	14.176 ± 0.010	0.025
4	Toluene	33.9			2.38	0.36	15.347 ± 0.011	0.025	15.461 ± 0.010	0.023	14.292 ± 0.014	0.032
5	Benzene	34.5	54		2.28	0	15.404 ± 0.009	0.021	15.532 ± 0.013	0.030	14.291 ± 0.011	0.025
6	Diethyl ether	34.6			4.34	1.15	15.334 ± 0.010	0.025	15.421 ± 0.018	0.043	14.255 ± 0.011	0.026
7	1,4-Dioxane	36.0			2.21	0	15.452 ± 0.010	0.025	15.539 ± 0.012	0.028	14.379 ± 0.010	0.025
8	Tetrahydrofuran	37.4			7.58	1.63	15.373 ± 0.014	0.034	15.474 ± 0.015	0.034	14.308 ± 0.008	0.019
9	Chlorobenzene	37.5			5.62	1.69	15.472 ± 0.011	0.025	15.563 ± 0.009	0.021	14.369 ± 0.010	0.025
10	Bromobenzene	37.5			5.40	1.70	15.479 ± 0.012	0.027	15.565 ± 0.012	0.027	14.373 ± 0.009	0.021
11	1,2-Dimethoxyethane	38.2	62.1	0.543	7.20	1.71[d]	15.424 ± 0.011	0.025	15.525 ± 0.020	0.047	14.356 ± 0.008	0.019
12	Chloroform	39.1			4.81	1.01	15.863 ± 0.014	0.032	15.775 ± 0.020	0.046	14.709 ± 0.008	0.018
13	Pyridine	40.2	64.0	0.595	12.4	2.19	15.608 ± 0.016	0.042	15.663 ± 0.010	0.024	14.535 ± 0.009	0.021
14	Methylene chloride	41.1	64.2		8.93	1.60	15.752 ± 0.014	0.033	15.775 ± 0.028	0.044	14.623 ± 0.011	0.026
15	Acetophenone	41.3			17.39	3.02	15.562 ± 0.013	0.031	15.639 ± 0.013	0.031	14.477 ± 0.007	0.017
16	1,2-Dichloroethane	41.9		0.600	10.36	1.20	15.655 ± 0.010	0.024	15.709 ± 0.014	0.031	14.552 ± 0.008	0.018
17	Acetone	42.2	65.7	0.619	20.70	2.88	15.527 ± 0.011	0.029	15.621 ± 0.012	0.026	14.467 ± 0.011	0.025
18	*N,N*-Dimethylformamide	43.8	68.5	0.620	36.71	3.82	15.635 ± 0.018	0.041	15.672 ± 0.020	0.048	14.516 ± 0.011	0.025
19	*tert*-Butyl alcohol	43.9	71.3		12.47	1.66[d]	15.860 ± 0.011	0.026	15.912 ± 0.032	0.075	14.813 ± 0.017	0.039
20	Dimethyl sulfoxide	45.0	71.1		46.68	3.96	15.692 ± 0.012	0.028	15.771 ± 0.011	0.026	14.616 ± 0.008	0.020
21	Acetonitrile	46.0	71.3	0.692	37.5	3.92	15.666 ± 0.010	0.022	15.761 ± 0.028	0.062	14.634 ± 0.006	0.014
22	Nitromethane	46.3		0.680	35.87	3.46	15.759 ± 0.009	0.022	15.858 ± 0.010	0.024	14.714 ± 0.011	0.024
23	Isopentyl alcohol	47.0			14.7	1.82[d]	16.004 ± 0.012	0.029	15.961 ± 0.031	0.073	14.939 ± 0.017	0.039
24	Isopropyl alcohol	48.6	76.3		19.92	1.66	15.973 ± 0.010	0.022	16.044 ± 0.016	0.036	14.911 ± 0.028	0.065
25	*n*-Butyl alcohol	50.2	77.7		17.51	1.66	16.018 ± 0.013	0.035	16.038 ± 0.018	0.029	14.934 ± 0.018	0.043
26	Benzyl alcohol	50.8			13.1	1.71	16.266 ± 0.022	0.049	16.286 ± 0.032	0.109	15.168 ± 0.018	0.043
27	Acetic acid	51.9	79.2	0.823	6.15	1.74	16.420 ± 0.012	0.028	16.189 ± 0.031	0.073	15.210 ± 0.016	0.038
28	Ethyl alcohol	51.9	79.6	0.718	24.55	1.69	16.030 ± 0.013	0.031	16.075 ± 0.011	0.026	14.978 ± 0.012	0.027
29	Methyl alcohol	55.5	83.6	0.845	32.7	1.70	16.210 ± 0.011	0.027	16.199 ± 0.022	0.051	15.118 ± 0.014	0.033
30	Ethylene glycol	56.3	85.1		37.7	2.28	16.364 ± 0.013	0.030	16.298 ± 0.042	0.099	15.211 ± 0.026	0.062
31	Water	63.1	94.6		78.4	1.85	17.175 ± 0.009	0.021	16.990 ± 0.018	0.057	15.974 ± 0.012	0.028

[a] References 1 and 4. [b] Reference 6, p 301. [c] Reference 25. [d] Reference 23. [e] R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 10** (1967). [f] Confidence limit, 95%.

Table II. Linear Relationships Among the Various Solvent Polarity Parameters, Calculated Using a Linear-Unweighted Least-Squares Program

	Ordinate	Abscissa	Radical	Slope Value	Slope SD	Intercept Value	Intercept SD	Overall SD	*r*, corr coef	Data source	Comments
1	$\mathcal{A}_N$	μ	**1**	0.100	0.067	15.572	0.138	0.419	0.267	This paper	31 solvents
2	$\mathcal{A}_N$	μ	**2**	0.059	0.0563	15.620	0.115	0.350	0.302	This paper	31 solvents
3	$\mathcal{A}_N$	μ	**3**	0.107	0.064	14.466	0.130	0.396	0.299	This paper	31 solvents
4	$\mathcal{A}_N$	μ	**1**	0.0831	0.0238	15.373	0.051	0.147	0.626	This paper	21 non OH solvents
5	$\mathcal{A}_N$	μ	**1**	0.731	0.660	14.933	1.178	0.374	0.365	This paper	10 OH solvents
6	$\mathcal{A}_N$	μ	**2**	0.0819	0.0190	15.449	0.041	0.118	0.703	This paper	21 non OH solvents
7	$\mathcal{A}_N$	μ	**2**	0.537	0.541	15.246	0.966	0.306	0.331	This paper	10 OH solvents
8	$\mathcal{A}_N$	μ	**3**	0.0916	0.0222	14.270	0.048	0.137	0.668	This paper	21 non OH solvents
9	$\mathcal{A}_N$	μ	**3**	0.588	0.580	14.081	1.036	0.328	0.337	This paper	10 OH solvents
10	$\mathcal{A}_N$	μ	DPNO	0.242	0.123	9.695	0.225	0.535	0.403	Ref 9	Solvents 1–22 in ref 9
11	$\mathcal{A}_N$	μ	DPNO	0.212	0.049	9.371	0.107	0.210	0.852	Ref 9	Solvents 1–9 in ref 9, non H bonding
12	$\mathcal{A}_N$	μ	DPNO	0.410	2.070	9.851	3.477	0.544	0.075	Ref 9	Solvents 10–18 in ref 9, alcohols and water
13	$\mathcal{A}_N$	μ	DPNO	1.218	0.770	8.363	0.942	0.264	0.746	Ref 9	Solvents 19–22 in ref 9, amines
14	$\mathcal{A}_N$	μ	DPANO	0.247	0.102	10.058	0.181	0.463	0.487	Ref 9	Solvents 1–21 in ref 9
15	$\mathcal{A}_N$	μ	DPANO	0.181	0.017	9.856	0.036	0.076	0.970	Ref 9	Solvents 1–9 in ref 9, non H bonding
16	$\mathcal{A}_N$	μ	DPANO	3.599	1.252	4.949	2.138	0.189	0.856	Ref 9	Solvents 10–14 in ref 9, alcohols and water
17	$\mathcal{A}_N$	μ	DPANO	1.380	0.365	8.534	0.484	0.248	0.861	Ref 9	Solvents 15–21 in ref 9, amines
18	$\mathcal{A}_N$	ϵ	**1**	0.0167	0.0034	15.457	0.082	0.320	0.676	This paper	31 solvents
19	$\mathcal{A}_N$	ϵ	**2**	0.0149	0.0027	15.528	0.066	0.258	0.713	This paper	31 solvents
20	$\mathcal{A}_N$	ϵ	**3**	0.0163	0.0032	14.372	0.076	0.298	0.692	This paper	31 solvents
21	$\mathcal{A}_N$	$E_T(30)$	**1**	0.0509	0.0034	13.559	0.150	0.148	0.940	This paper	31 solvents
22	$\mathcal{A}_N$	$E_T(30)$	**2**	0.0438	0.0025	13.901	0.109	0.108	0.956	This paper	31 solvents
23	$\mathcal{A}_N$	$E_T(30)$	**3**	0.0494	0.0028	12.529	0.124	0.123	0.955	This paper	31 solvents
24	$\mathcal{A}_N$	$E_T(30)$	**1**	0.0571	0.0093	13.342	0.482	0.211	0.951	Ref 11, 4	6 solvents
25	$\mathcal{A}_N$	Z	**1**	0.0528	0.0049	12.073	0.392	0.125	0.983	Ref 11	6 solvents Z(benzene) = 62.3
26	$\mathcal{A}_N$	Z	**1**	0.0411	0.0072	13.059	0.570	0.227	0.943	Ref 11, 6	6 solvents Z(benzene) = 54.0
27	$\mathcal{A}_N$	$E_T(30)$	**1**	0.0569	0.0105	13.251	0.545	0.239	0.938	This paper	6 solvents in ref 11
28	$\mathcal{A}_N$	Z	**1**	0.0411	0.0079	12.957	0.619	0.246	0.934	This paper	6 solvents in ref 11, Z(benzene) = 54.0
29	$\mathcal{A}_N$	Z	**1**	0.0414	0.0045	12.901	0.334	0.179	0.925	This paper	16 solvents
30	$\mathcal{A}_N$	Z	**2**	0.0341	0.0034	13.447	0.249	0.134	0.938	This paper	16 solvents
31	$\mathcal{A}_N$	Z	**3**	0.0392	0.0036	11.963	0.265	0.142	0.946	This paper	16 solvents
32	$\mathcal{A}_N$	Ω	**1**	3.036	0.390	13.748	0.266	0.116	0.940	This paper	10 solvents
33	$\mathcal{A}_N$	Ω	**2**	2.353	0.250	14.242	0.170	0.074	0.958	This paper	10 solvents
34	$\mathcal{A}_N$	Ω	**3**	2.828	0.299	12.803	0.203	0.089	0.958	This paper	10 solvents
35	$\mathcal{A}_N$(**1**)	$\mathcal{A}_N$(**2**)		1.173	0.028	−2.773	0.451	0.056	0.992	This paper	31 solvents
36	$\mathcal{A}_N$(**1**)	$\mathcal{A}_N$(**3**)		1.043	0.017	0.468	0.256	0.039	0.996	This paper	31 solvents
37	$\mathcal{A}_N$(**3**)	$\mathcal{A}_N$(**2**)		1.123	0.019	−3.070	0.300	0.038	0.996	This paper	31 solvents
38	Z	$E_T(30)$		1.325	0.038	10.663	1.838	1.211	0.993	Ref 6	18 solvents
39	$\mathcal{A}_N/\mathcal{A}_{NH}$	$E_T(30)$	TBNO	−0.00735	0.00038	1.468	0.018	0.011	−0.988	Ref 15	11 solvents
40	$\mathcal{A}_N$	$E_T(30)$	TBNO	0.0281	0.0063	11.881	0.294	0.178	0.829	Ref 15	11 solvents

included in this study. It is interesting to note that the model process on which Ω values are based, the Diels-Alder reaction between cyclopentadiene and methyl acrylate, is considerably different from those on which Z and $E_T(30)$ are based.

It might also be noted that while the three nitroxides employed are of somewhat similar structure,[20] being aliphatic and having no β hydrogens which would render them unstable, they are not identical and yet the correlations among the values of $\mathcal{A}_N$ are excellent (lines 35–37).

The value $r^2 \times 100$ is frequently taken as a measure of the percentage of correlation between two parameters.[27] Table III gives the average values of $r^2 \times 100$ for the correlations indicated, the average being taken over nitroxides **1**, **2**, and **3**. It can be seen from this table that the correlations between $\mathcal{A}_N$ and the nonmodel, noncybotactic parameters μ and ϵ are poor.

Table III. Average Percent Correlation between $\mathcal{A}_N$ and Other Solvent Polarity Parameters[a]

Solvent polarity parameter	$r^2 \times 100$, %	Comments
μ	8.39	31 solvents
μ	45.3	21 non OH solvents
μ	11.9	10 OH solvents
ϵ	48.1	31 solvents
$E_T(30)$	90.3	31 solvents
Z	87.7	16 solvents
Ω	90.6	10 solvents

[a] The percent correlations for nitroxides **1**, **2**, and **3** being averaged.

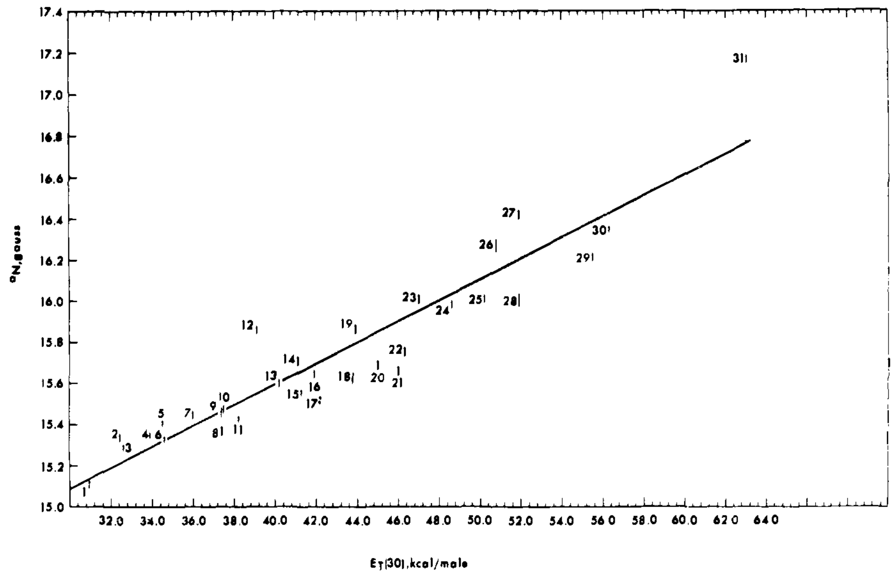

Figure 1. Relationship between the nitrogen hyperfine splitting, $\mathcal{A}_N$, in di-*tert*-butyl nitroxide (**1**) and the Dimroth–Reichardt solvent polarity parameter, $E_T(30)$.

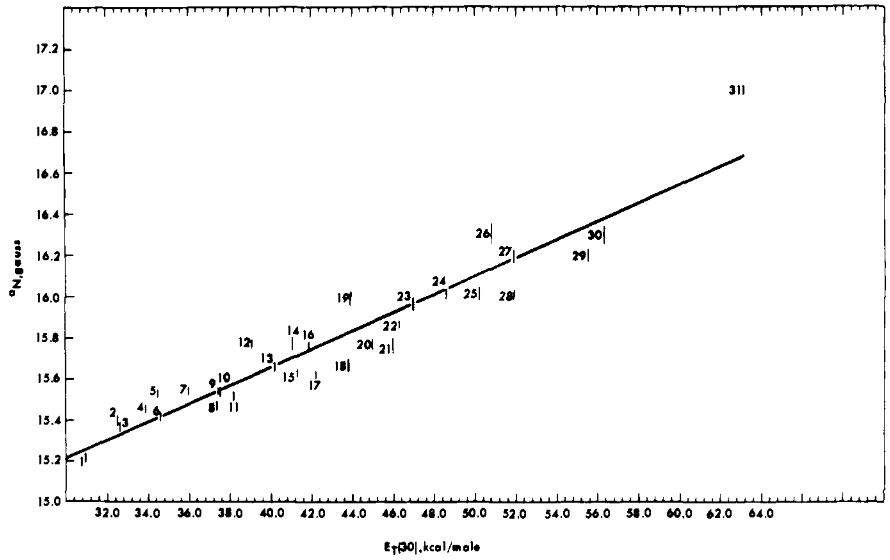

Figure 2. Relationship between the nitrogen hyperfine splitting, $\mathcal{A}_N$, in 4-amino-2,2,6,6-tetramethylpiperid-1-yloxy (**2**) and the Dimroth–Reichardt solvent polarity parameter, $E_T(30)$.

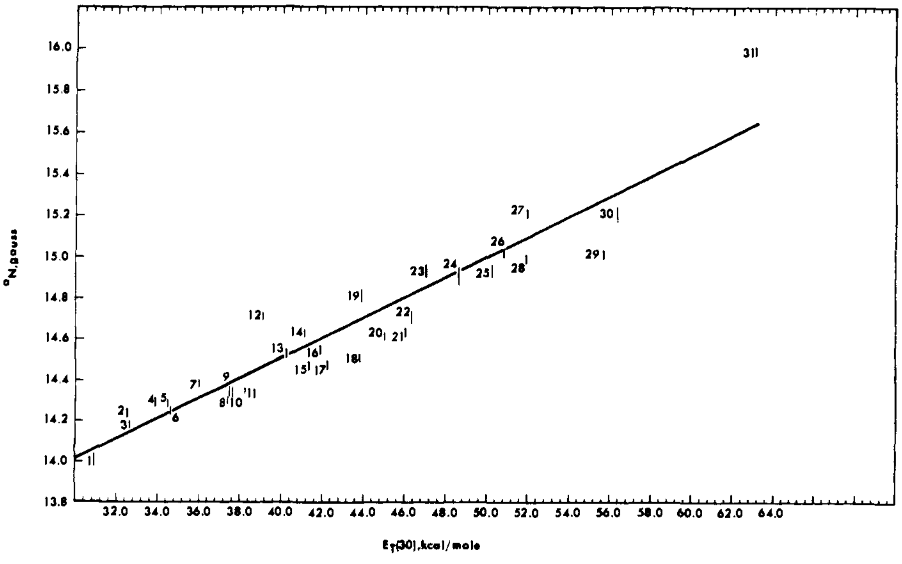

Figure 3. Relationship between the nitrogen hyperfine splitting, $\mathcal{A}_N$, in 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (**3**) and the Dimroth–Reichardt solvent polarity parameter, $E_T(30)$.

In contrast, the correlations between $\mathcal{A}_N$ and the model, cybotactic parameters $E_T(30)$, Z, and Ω are good.

Conclusions

Since the nonmodel, cybotactic solvent polarity parameter $\mathcal{A}_N$ correlates closely (ca. 90%) with the model, cybotactic solvent polarity parameters and only poorly with the nonmodel, noncybotactic solvent polarity parameters, it seems reasonable to infer that the cybotactic probe nature of a solvent polarity parameter is considerably more important than whether it involves a model chemical transformation.

Since there is a good correlation between $\mathcal{A}_N$ and $E_T(30)$, Z, and Ω, $\mathcal{A}_N$ would make a useful solvent polarity parameter, especially in cases where values for the other parameters cannot be obtained because of solubility limitations, spectral interference, etc.

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Origin of Alkyl Substituent Effect in the Proton Affinity of Amines, Alcohols, and Ethers

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Abstract: An energy decomposition analysis within ab initio SCF-MO theory has been carried out for the proton affinity of a series of amines NH_3, CH_3NH_2, $CH_3CH_2NH_2$, $(CH_3)_2NH$, and $(CH_3)_3N$, and of H_2O, CH_3OH, and CH_3OCH_3. The electrostatic energy and the charge transfer energy are found to provide the dominant stabilizing contribution to protonation. The polarization energy contributes less. On the other hand, the alkyl substituent effect, i.e., the order of proton affinity $NH_3 < CH_3NH_2 < CH_3CH_2NH_2 < (CH_3)_2NH < (CH_3)_3N$ and $H_2O < CH_3OH < CH_3OCH_3$, is found to be controlled predominantly by the polarization energy. Methyl groups make amines more polarizable by an approaching proton.

The alkyl substituent effects on the basicity of amines have been studied extensively both experimentally[1-7] and quantum chemically.[8-12] In aqueous solution the order of basicity of simple aliphatic amines is NH_3 < primary < secondary < tertiary. Recent gas-phase measurements of both proton affinities and basicities of amines by Aue et al.[1] have established the following order: $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$. Henderson et al.[2] analyzed the gas phase basicity data of alkylamines and attributed the trend to inductive and polarization stabilization effects of the CH_3 group on protonated amines.

An ab initio SCF calculation by Hehre and Pople[8] with a minimal (STO-3G) basis set showed for methylamines that the calculated order of proton affinity is in agreement with experiment, even though the nitrogen atomic charge *decreases* as the number of the CH_3 groups is increased. The same trend was also found for H_2O, CH_3OH, and CH_3OCH_3. Johansson et al.,[9] employing ab initio calculations, showed that methyl and amino groups bonded to the proton acceptor increase its proton affinity, while hydroxyl and fluoro groups decrease the proton affinity relative to the simple hydrides NH_3, H_2O, and HF. The polarization effect was suggested to be responsible for the CH_3 substituent effect.[8,9] No theoretical evidence, however, has yet been presented on the origin of such an effect.

The energy and charge distribution decomposition analysis of Morokuma and co-workers[13-15] decomposes the intermolecular interaction energy ΔE into the electrostatic E_{ES}, exchange repulsion E_{EX}, polarization (or induction) E_{PL}, and charge transfer (or delocalization) E_{CT} energies and their coupling term E_{MIX}. The method has been a powerful tool for