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Ion Pair Basicity of Some Amines in THF: Implications for Ion Pair Acidity Scales[1]

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Abstract: Amines form proton-transfer ion pairs of the type $BH^+\ In^-$ with acidic indicator hydrocarbons InH in THF. Relative equilibrium constants measured for a number of amines in THF differ substantially from ionic pK_a values for BH^+ in acetonitrile or DMSO. The results show that ion pair dissociation constants of the protonated amine ion pairs in THF vary by several orders of magnitude and point out that at the present time amines cannot be placed quantitatively on any of the ion pair acidity scales currently in use for neutral acids in THF.

The pK_a values for many protonated amines have been determined in polar solvents such as water, DMSO, and acetonitrile. Amines are frequently used as base catalysts in nonpolar solvents such as THF in which the corresponding ammonium salts are present entirely as ion pairs. To our knowledge there are no quantitative data available concerning the ion pair basicities of amines in nonpolar solvents. In the present work we give such quantitative data and show that relative *ion pair basicities* can differ substantially from the corresponding *ionic basicities*. The results also have important implications concerning ion pair acidity scales for charged acids.

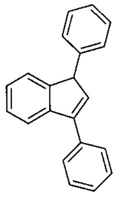
Ion Pair Basicities

We define ion pair basicity in terms of equilibrium 1 in which B is a base such as an amine and InH is a suitable proton donor, generally an indicator of known relative acidity.

$$\mathrm{B} + \mathrm{InH} \overset{K_{\mathrm{ip}}}{\rightleftharpoons} \mathrm{BH^+\ In^-} \overset{K_{\mathrm{diss}}}{\rightleftharpoons} \mathrm{BH^+} + \mathrm{In^-} \tag{1}$$

The product $K_{\mathrm{ip}}K_{\mathrm{diss}} = K_{\mathrm{b}}$ is the ionic equilibrium constant that corresponds to ΔpK_a for BH^+ and InH. A few pK_a values are known in THF but only for some strong acids such as perchloric acid;[2] however, the relative values of K_{b} in THF would be expected to correspond to relative pK_a values of BH^+ in polar aprotic solvents such as DMSO and acetonitrile. If all of the K_{diss} values are about the same, the values of K_{ip} would also be expected to parallel these pK_a values. In the present work we find that relative K_{ip} values for some amines in THF differ substantially from polar pK_a values.

Results and Discussion



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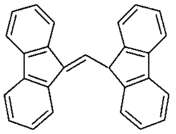
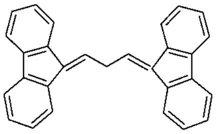
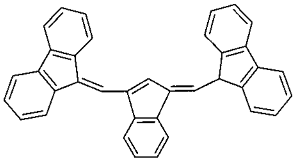


2 BBP



3 BBP-5



4 DFB

We recently determined the ion pair acidity of several acidic carbon indicators **1**−**4** in THF on the lithium and cesium ion pair scales.[3] Ion pair acidity is defined in terms of equilibrium 2 where M^+ is generally either Li^+ solvent-separated ion pairs

$$\mathrm{R^-\ M^+} + \mathrm{R'H} \overset{K}{\rightleftharpoons} \mathrm{RH} + \mathrm{R'^-\ M^+} \tag{2}$$

(SSIP) or Cs^+ contact ion pairs (CIP) in our work and the equilibrium constants are converted to absolute numbers by eq 3 where the standard is taken as 22.90, the ionic pK_a of fluorene

$$\Delta \mathrm{p}K = \mathrm{p}K(\mathrm{R'H}) - \mathrm{p}K(\mathrm{RH}) = -\log K \tag{3}$$

per hydrogen in DMSO.[4] Tables of such pK values have been published previously for the Cs[5] and Li[6] scales. A corresponding list was published recently by the Antipin group for a range of [2.2.1]encryptated lithium ion pairs.[7]

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(1) Carbon Acidity. 114.

(2) Deshmukh, B. K.; Siddiqui, S.; Coetzee, J. F. *J. Electrochem. Soc.* **1991**, *138*, 124−132.

(3) Facchetti, A.; Kim, Y.-J.; Streitwieser, A. *J. Org. Chem.* **2000**, *65*, 4195−7.

(4) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−63.

(5) Streitwieser, A.; Ciula, J. C.; Krom, J. A.; Thiele, G. *J. Org. Chem.* **1991**, *56*, 1074−6.

(6) Streitwieser, A.; Wang, D. Z.; Stratakis, M.; Facchetti, A.; Gareyev, R.; Abbotto, A.; Krom, J. A.; Kilway, K. V. *Can. J. Chem.* **1998**, *76*, 765−9.

(7) Antipin, I. S.; Gareyev, R. F.; Vedernikov, A. N.; Konovalov, A. I. *J. Phys. Org. Chem.* **1994**, *7*, 181−91.

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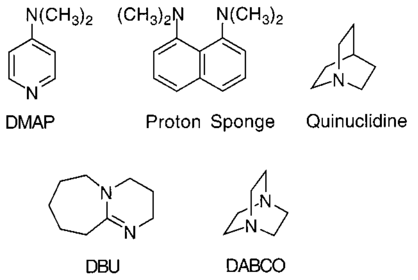

The hydrocarbons **1**−**4** are sufficiently acidic that they give colors with some amines in THF corresponding to the formation of the ion pairs $BH^+ In^-$. The equilibrium constants, K_{ip}, were determined by assuming that the extinction coefficients are the same as the corresponding lithium ion pairs, whose λ_{max} are similar to the protonated amine salts. This procedure was also justified by the behavior of DBU, the most basic of the amines studied. DBU reacts completely with DBF to form the ion pair with λ_{max} 696.5 nm (ϵ, 73600), values that are close to those of the lithium SSIP, λ_{max} 699 nm (ϵ, 79600). Most experiments were done with the most acidic indicator **4** (DFB) but because the K_{ip} of DBU could not be measured directly with this indicator, it was estimated from other amines and BBP-5; DMAP and quinuclidine are 22 and 24 times as basic, respectively, toward DBF compared to BBP-5 and the average was used for DBU. The results of all of the experiments are summarized in Table 1.

pK_{ip} is defined as $-\log K_{ip}$; thus, smaller or more negative values correspond to greater basicity. The values obtained are also summarized in Table 1 corrected for statistical effects; for example, imidazole has one basic nitrogen but the protonated structure has two equivalent protons that can be lost giving a statistical correction of −0.3. pK_{ip} values for DBU are available for four carbon acids. A plot of these values vs the corresponding p*K* values of the indicators on the lithium scale is linear but with a slope of 0.75 (Figure 1). This result has some important implications.

Equation 2 is converted to eq 4 by incorporating the dissociation constants of the ion pairs, K_{diss} in eq 5.

$$R^- + R'H \overset{\Delta K_a}{\rightleftharpoons} RH + R'^- \qquad (4)$$

$$-\log \Delta K_a = pK_a(R'H) - pK_a(RH) = -\log K - \log [K_{diss}(R'^-\ M^+)/K_{diss}(R^-\ M^+)] \qquad (5)$$

Table 1. Spectroscopic Data and Ion Pair Basicities of Amines in THF at 25 °C

indicator RH	amine	λ_{max} nm	K_{ip} (THF) M^{-1}	$pK_{ip}{}^a$
DBF[b]	DMAP	699	0.25 ± 0.03	0.61
	benzimidazole	699	0.33 ± 0.06	0.19
	imidazole	699	0.050 ± 0.004	1.01
	quinuclidine	692.5	0.72 ± 0.08	0.15
	triethylamine	693−693.5	0.0077 ± 0.0014	2.11
	tribenzylamine	687.5	0.0039	2.41
	proton sponge	693.5	0.0071	2.15
	tributylamine	691.5	0.00040	3.40
	DABCO	690	0.32	0.80
	DBU	696.5	6000[c]	−3.78
BBP-5[d]	DMAP	638	0.012	1.91
	quinuclidine	634.5−635.5	0.030 ± 0.007	1.53
	DBU	634.0−634.5	261 ± 3	−2.42
BBP[e]	DBU	558	1.04	−0.02
DPI[f]	DBU	437	0.094	1.03

[a] Statistically corrected. Protonated DBU and proton sponge are treated as having one basic position. [b] **4**, 3-(dibenzofulvenyl)-6-(9-fluorenyl)-1,2-benzofulvene; Li salt, λ_{max} 699 nm (ϵ, 79600), p*K* 5.6; Cs salt, λ_{max} 670 nm (ϵ, 53300), p*K* 7.4. [c] Extrapolated from BBP-5; see text. [d] **3**, 1,5-bis(biphenylene)-1,4-pentadiene; Li salt, λ_{max} 635 nm (ϵ, 193000), p*K* 8.2; Cs salt, λ_{max} 629 nm (ϵ, 169000), p*K* 10.5. [e] **2**, 1,3-bis(biphenylene)propene; Li salt, λ_{max} 557 nm (ϵ, 112500), p*K* 10.4; Cs salt, λ_{max} 554 nm (ϵ, 107600), p*K* 12.3. [f] **1**, 1,3-diphenylindene; Li salt, λ_{max} 450 nm (ϵ, 32900), p*K* 12.3; Cs salt, λ_{max} 422 nm (ϵ, 23300), p*K* 12.7.

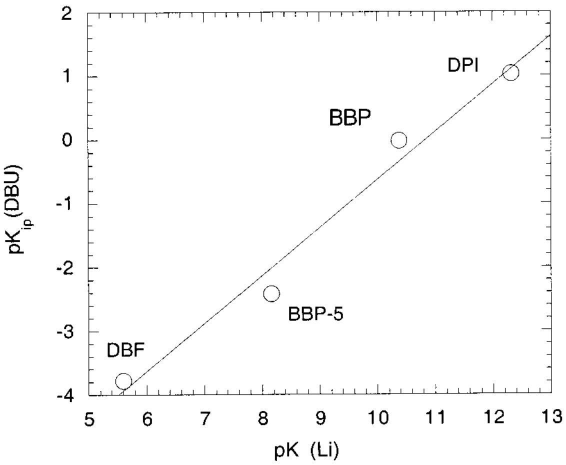

Figure 1. Plot of pK_{ip} of DBU with p*K*(Li) of four indicators. The regression line shown is $-8.14 + 0.75x$; $R^2 = 0.98$.

For lithium SSIP of delocalized carbanions, $K_{diss}(R^-\ Li^+)$ are relatively constant at 10^{-5} M,[8] and thus the ion pair ΔK values of eqs 2 and 3 actually correspond to ΔpK_a values even though the actual pK_a values are not known. Accordingly, the ion pair p*K* values of such SSIP lithium salts give an excellent linear correlation with the DMSO pK_a values[4] with a slope close to unity.[6] The same generalization holds for the [2.2.1]encryptated lithium ion pairs.[7] Similarly, if the protonated amine ion pairs, $R^-\ BH^+$, have the same K_{diss} as the lithium SSIP, the K_{ip} values of eq 1 would actually correspond to ΔpK_a for RH and BH^+. If they differ from $K_{diss}(R^-\ Li^+)$ by a constant value, the ΔpK values of eq 2 would differ from ΔpK_a by a constant value but *the slope of Figure 1 would be unity*. The experimental results show that even over a relatively short ΔpK range of 7 units, $K_{diss}(R^-\ BH^+)$ varies by 2 orders of magnitude. In other words, eq 6, in which BH^+ is a protonated amine, differs substantially from eq 2 in which M^+ is SSIP Li^+, CIP Cs^+, or cryptated Li^+.

$$R^-\ BH^+ + R'H \rightleftharpoons RH + R'^-\ BH^+ \qquad (6)$$

Consequently, no reasonable estimate can be made for $K_{diss}(BH^+\ In^-)$ and it is not possible to assign p*K* values to BH^+ on any of the ion pair acidity scales now in use for RH in THF. To do so will require the actual measurement of the K_{diss} values by, for example, conductivity measurements. The present work provides a good system for such conductivity measurements and we hope to provide these in the future.

Available data are summarized in Table 2 for the pK_a values of protonated amines in DMSO and in acetonitrile. As expected they correlate mutually with a slope close to unity. A comparable plot is shown as Figure 2 comparing pK_{ip} for amines toward DBF in THF compared to the pK_a of the protonated amines in acetonitrile. Although there is a rough trend that more basic amines are more basic in both solvents, there is substantial scatter. The comparison of quinuclidine and tributylamine is

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(8) Kaufman, M. J.; Gronert, S.; Streitwieser, A., Jr. *J. Am. Chem. Soc* **1988**, *110*, 2829−35.

Table 2. pK_a of Protonated Amines in DMSO and Acetonitrile

amine	pK_a DMSO	pK_a acetonitrile
DMAP		18.18[a]
benzimidazole		
imidazole		14.2[b]
quinuclidine	9.8[c]	19.51[d]
triethylamine	9.0[e]	18.70[f]
tribenzylamine	3.65[g]	12.85[h]
proton sponge	7.47[c]	17.28[i]
tributylamine		18.09[f]
DABCO	8.93[c]	18.29[f]
DBU		23.9[k]

[a] Reference 16. [b] Reference 17. [c] Reference 18. [d] Reference 19. [e] Reference 20. [f] Reference 21. [g] Reference 22. [h] Reference 9. [i] Reference 23. [j] Reference 24. [k] Reference 25.

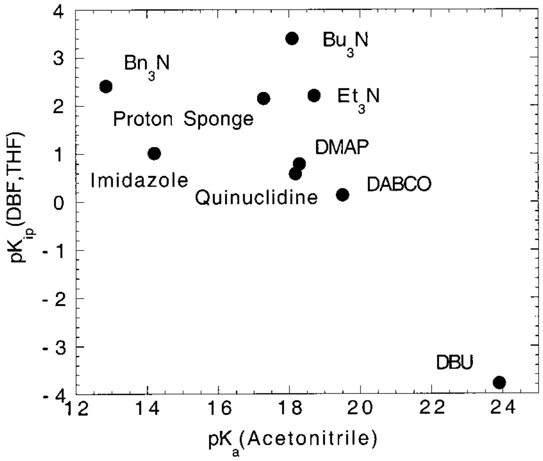

Figure 2. Ion pair basicities of amines in THF compared to ionic basicities in acetonitrile.

particularly noteworthy. They have comparable basicities in acetonitrile but differ by 3 orders of magnitude in THF; the direction is such that the BH^+In^- ion pair is much tighter for quinuclidine with its exposed proton than is that of tributylamine in which the butyl groups undoubtedly increase the effective cation−anion distance. On the other hand, triethylamine and tribenzylamine have comparable basicities toward DBF in THF but differ by almost 6 pK_a units in acetonitrile, consistent with the inductive effect of the benzyl groups;[9] that is, for tribenzylamine BH^+In^- is a tighter ion pair than expected in THF. This comparison further emphasizes the important role of relative ion pair stability and the difficulty at present in trying to put neutral bases and neutral acids on the same quantitative ion pair scale.[10] DBU, however, is a strong base in both solvents consistent with its use as a base catalyst in organic reactions in nonpolar solvents.

Other proton transfers between neutral bases and neutral acids have been reported previously. The competition of several fluorinated carbon acids for a phosphazene in heptane was used to put these acids on an ion pair pK scale.[11] It was assumed by comparison with lithium cryptates in THF[7] that K_{diss} would be similar for all of the large phosphazene ion pairs studied and that the ΔpK measurements are therefore ΔpK_a. Morris et al.[12] have reported a number of proton transfers from transition metal hydrides to phosphines and have used the Fuoss eq 7[13] to estimate K_{diss} and convert the ΔpK values to ΔpK_a.

$$K_{diss} = 3000e^b/(4\pi Na^3) \qquad (7)$$

where $b = -e^2/(a\epsilon kT)$, N = Avogadro's number, a = interionic distance in cm, $e = 4.80E-10$ esu, ϵ = dielectric constant, and k = Boltzmann constant.

In the absence of direct data for K_{diss}, this is probably as reasonable an approach as any. The problem in all of these studies is in estimating the interionic distance a. The cation contains a proton that can be more or less exposed with a corresponding change in a. Since a enters the Fuoss equation primarily as the cube, the resulting K_{diss} is highly dependent on the choice of a. To our knowledge, the Fuoss equation has never been tested with proton-containing cations in the ion pair. The present work indicates that the assigned ΔpK_a values can easily be in error by several pK units. Figure 2 suggests that part of the lower basicities of triethylamine, tributylamine, and proton sponge might be associated with their more buried protons in the ion pairs making the ion pairs less tightly held.[14] We had hoped that λ_{max} for the ion pairs might be a measure of the effective anion−cation distance in these ion pairs but the results do not show any simple correlation. For example, the λ_{max} of the DBF (**4**) salts are all similar to that of the solvent-separated lithium ion pair (699 nm) and at longer wavelength than for the cesium salt (670 nm) indicating an effective a similar to that of the long anion−Li^+ distance of the lithium salt. Consistent with this thought is the fact that λ_{max} for the quinuclidine salt, with its localized and relatively exposed proton, is at shorter wavelength than those for the more delocalized protonated amines, DMAP, inidazole, and benzimidazole, indicative of an effectively shorter a for the quinuclidine salt. Unfortunately, λ_{max} for the triethylammonium and tributylammonium salts are also at comparable shorter wavelengths even though one might have expected their protons to be more hindered corresponding to a longer effective a value. We reluctantly conclude that further speculation is unwarranted until more diverse data are in hand.[25]

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(9) Peips, M.; Koppel, Y.; Pihl, V.; Koppel, I. *Org. React.* (*Tartu*) **1976**, *13*, 203-219.

(10) Ion pairing is frequently totally neglected in acid−base studies in nonpolar solvents. A few recent examples are the following: Jia, G.; Lee, H. M.; Williams, I. D.; Lau, C. P.; Chen, Y. *Organometallics* **1997**, *16*, 3941−9. Ng, W. S.; Jia, G.; Hung, M. Y.; Lau, C. P.; Wong, K. Y.; Wen, L. *Organometallics* **1998**, *17*, 4556−61. Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Zotto, A. D.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711−720. Cappellani, E. P.; Droulin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375−88.

(11) Leito, I.; Rodima, T.; Koppel, I. A.; Schwesinger, R.; Vlasov, V. M. *J. Org. Chem.* **1997**, *62*, 8479−83.

(12) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155.

(13) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059−61.

(14) A reviewer suggested the possibility in some cases of hydrogen bonding between the protonated base and the free base. Such hydrogen bonding is known in polar solvents but is unlikely in the present case where the cation is associated closely with an anion.

(15) Krom, J. A.; Petty, J. T.; Streitwieser, A. *J. Am. Chem. Soc.* **1993**, *115*, 8024−30.

(16) Augustin-Nowacka, D.; Chmurzyñski, L. *Anal. Chim. Acta* **1999**, *181*, 215−220.

(17) Pawlak, Z.; Urbanczyk, G. *J. Mol. Struct.* **1988**, *177*, 401−6.

(18) Benoit, R. L.; Lefebvre, D.; Frechette, M. *Can. J. Chem.* **1987**, *65*, 996−1001.

(19) Bectrame, P.; Gelli, G.; Loi, A. *Gazz. Chim. Ital.* **1980**, *110*, 491.

(20) Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23−28.

(21) Coetzee, J. F.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005−10.

(22) Kreevoy, M. M.; Wang, Y. *J. Phys. Chem.* **1977**, *81*, 1924.

(23) Brzezinski, B.; Schroeder, G.; Grech, E.; Malarski, Z.; Sobczyk, L. *J. Mol. Struct.* **1992**, *274*, 75−82.

(24) Liu, W. Z.; Bordwell, F. G. *J. Org. Chem.* **1996**, *61*, 4778−83.

(25) Galezowski, W.; Jarczewski, A.; Stanczyk, M.; Brzezinski, B.; Bartl, F.; Zundel, G. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2515−8.

Experimental Section

The indicators were available from previous work. The amines are commercial materials purified by crystallization or distillation and monitored spectroscopically before use. Solutions of the indicator and amine were prepared in a glovebox and spectroscopic measurements were made at 25 °C using the glovebox−spectrometer system described previously.[15] The experimental data are summarized in Table S1 (Supporting Information).

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Supporting Information Available: Table of experimental results for equilibria of amines and indicator acids (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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