A Generalized Solvent Basicity Scale: The Solvatochromism of 5-Nitroindoline and Its Homomorph 1-Methyl-5-nitroindoline

Javier Catalán*, Cristina Díaz, Vicenta López, Pilar Pérez, José-Luis G. de Paz, and José Gonzalo Rodríguez

Departamentos de Química Física Aplicada y Química Orgánica, Universidad Autónoma de Madrid,
E-28049 Cantoblanco, Spain
Telefax: (internat.) +91-3974-187
E-mail: catalan@VM1.SDI.UAM.ES

Received April 22, 1996

Key Words: Solvent basicity scale / Solvent effects / Solvatochromism

A total of 202 organic solvents and the gas phase were placed on a solvent basicity scale for hydrogen bond acceptor based on parameter SB. The value of such a parameter can readily be determined from the UV/Vis spectrum for an appropriate acid probe (5-nitroindoline) (NI) and its non-acid homomorph (1-methyl-5-nitroindoline) (MNI). The proposed scale can advantageously substitute the more widely used solvent scales such as Gutmann's donor number (DN), the Koppel-Palm $B_{(\mathrm{MeOD})}$ scale, and the Taft-Kamlet β scale. While data for the proposed scale are derived only from electronic transitions, they are accurately descriptive of solvent basicity in both spectroscopy (UV/Vis, IR and NMR) and miscellaneous chemical areas (thermodynamic, kinetics, and electrochemistry).

The solvent in which a physico-chemical process takes place is a non-inert medium that plays a major role in solution chemistry. Hence, chemists have been interested in describing solvent properties since the evidence collected last century by Berthelot and Saint-Gilles[1] and Menschutkin[2] was published. They showed that even some solvents traditionally regarded as inert exert significant effects on the rate of chemical reactions.

The description of the behavior of a given solvent by means of a single empirical parameter is unfit since such a parameter would always be dependent on the nature of the dissolved solute and hence would be of little predictive value. Roughly, the solvent effect can be split into *non-specific* and *specific* solute/solvent interactions[3].

In non-specific interactions, the solvent is assumed to act as a continuous dielectric. The earliest modelling attempts in this area were made by Kirkwood[4] and Onsager[5] and subsequently refined for the electrostatic saturation effect[6,7]. Because of the inherent difficulty of determining the dimensions of the cavity around a solute molecule in the solvent, the need has arisen to develop empirical approximations to a parameter that can be used to characterize solvent dipolarity and polarizability. A variety of scales have been developed in response to this need[8,9,10].

According to Drago et al.[11], specific interactions can be described in terms of localized donor-acceptor interactions involving specific orbitals by using an electrostatic (E) and a covalent parameter (C). On the other hand, Kamlet and Taft[12] use acid-base hydrogen bonding interactions in order to describe specific interactions.

Ever since Lewis unified the acidity and basicity concepts in 1923[13], chemists have been confronted with the challenge to find a single quantifiable property of solvents that can be used as a general basicity indicator. The donor number (DN) of Gutmann et al.[14], the $B_{(\mathrm{MeOD})}$ of Koppel and Palm[15], the ΔH_f of Arnett et al.[16], the β values of Kamlet and Taft[12], and the E_B and C_B parameters of Drago[11b] are noteworthy contributions in this respect.

One serious shortcoming of these basicity scales is that they are family-dependent[16b,17–24]. Even though the dependence may arise from contamination with other interactions such as dipole-dipole, steric, or conformational effects, Drago et al.[17], Panchenco et al.[19], and Maria et al.[25] showed that the most likely sources are the different electrostatic and covalent contributions to the specific solute/solvent interaction. Thus, Taft et al.[23] introduced a coordinate covalence parameter, ξ, to restore family-independent situations in combination with parameter β. More recently, Maria et al.[25] analyzed the difficulty of comparing basicity scales and showed that two basicity-dependent properties (BDP) can only vary linearly (i.e. exhibit a familiy-independent behavior) if the two acids used to define them result in similar electrostatic-to-covalent ratios in the two BDP sets. This type of analysis also revealed that only unsubstituted amines are seemingly appropriate acids for this purpose and that, despite the apparently acceptable spectral features of phenol acids (Nicolet et al.[26]), they should not be used to construct basicity scales[25,27].

In this work, we addressed the solvent basicity issue by using an appropriate probe/homomorph couple (the probe of the N–H type has a single acid site and advantageous structural features relative to previously used probes for building basicity scales). This chromophore couple was studies UV/Vis spectroscopically in a wide range of solvents in order to develop a broad empirically derived solvent basicity scale: the SB scale. Data of this scale were first com-

0947–3440/96/1111–1785 $ 15.00+.25/0

pared with reported evidence ascribed to the effect of the solvent basicity, evidence which was obtained not only from spectroscopy but also from other types of chemical data (kinetic, thermodynamic, and electrochemical). In addition, data were compared with those from some of the more commonly used pure solvent scales [$B_{(\mathrm{MeOD})}$, β, and *Basicity*]. Some dilute solution scales such as the DN and the boron trifluoride scales are also considered.

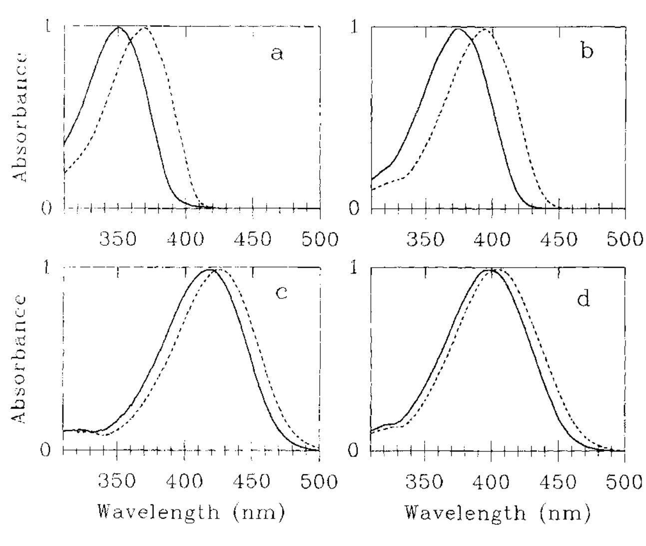
Results and Discussion

Suitability of the 5-Nitroindoline/1-Methyl-5-nitroindoline Couple: Formulation of the SB Scale

For use in UV/Vis spectroscopy, a probe of solvent basicity must have a number of features. One is that it should be acidic enough in its electronic ground state in order to characterize the basicity of the environment. In addition, its acidity should increase on electronic excitation such that its electronic transitions are sensitive to the basicity of the medium. This behavior will result in a bathochromic absorption band shift the magnitude of which will increase with increasing basicity of the environment. The probe should also be free of potential conformational changes that might influence the electronic transition to be evaluated. Finally, its molecular structure should easily be converted into a homomorph lacking the acid site without any side effects that might affect the resulting solvent basicity.

5-Nitroindoline (NI) possesses the above-described electronic and structural features. It is an N−H acid with a single acid site borne by a donor group whose free rotation is hindered by an ethylene bridge on the ring. However, if charge transfer endows the compound with appropriate acid properties that increase with electronic excitation, the basicity of the acceptor group (the nitro group) will also increase and the compound polarity will be altered as a result. Both effects will affect the electronic transition of the probe that is intended to be used for the evaluation of the basicity.

Figure 1. UV/Vis spectra, normalized at the maximum, of NI (–) and MNI (---) in (a) cyclohexane, (b) toluene, (c) DMSO, and (d) ethanol



Replacement of the acid hydrogen (N−H) by a methyl group in this molecular structure has the same side effects; therefore, the compound will be similarly sensitive to the medium polarity and acidity, but not to its basicity because of the absence of the acid site. Consequently, this compound (1-methyl-5-nitroindoline, MNI) has the required properties for the use as a homomorph of 5-nitroindoline in order to construct our solvent basicity scale. This adequacy of the present couple of probe/homomorph molecules agrees well with theoretical MP2-6-31G** results. Thus, both probe and homomorph show the same sensitivity to dipolarity/polarizability of the solvent, because of the similar dipole moments ($\mu_{\mathrm{NI}} = 7.13$, $\mu_{\mathrm{MNI}} = 7.31$ D) and polarizabilities (20.38 and 22.78 $\alpha/\mathrm{J}^{-1}\ \mathrm{C}^2\mathrm{m}^2$, respectively). The sensitivity to the acidity of solvents is also the same for both molecules because the surface electrostatic potential minima have practically the same values [$V_{\mathrm{S,min}}(\mathrm{NI}) = -47.49$ and $V_{\mathrm{S,min}}(\mathrm{MNI}) = -47.58$ $\mathrm{kcal \cdot mol^{-1}}$] which, according to Politzer et al.[28], show the same basicity by hydrogen bond for both molecules. Moreover, the electrostatic potential surface in both molecules indicates that the unique electrophilic centers reside on the oxygen atoms of the nitro group.

While both chromophores (the probe and its homomorph) were tested in a wide range of solvents (about 200), the need remained to determine the position of the first absorption band for both in the gas phase (i.e. in the absence of solvent). The probe and homomorph are solids at room temperature, and they sublimate only to a low extent. For this reason, their gas-phase UV/Vis spectra could not be obtained by means actually available in our laboratory. Instead, a linear relation between the position of the first absorption band in *n*-alkanes and the corresponding Lorenz-Lorentz function, $f_1(n^2) = (n^2 - 1)/(n^2 + 2)$, was established[29]. Extrapolation of this function to zero provided the value for the gas phase with high precision, as recently confirmed by our group[30] for C_{60} and from DMANF and FNF data[10].

Our experimental data for NI in *n*-alkanes yielded equation (1)

$$\tilde{\nu}_{\mathrm{NI}} = (-12.564 \pm 0.661)\,f_1(n^2) + 31659\ (n = 9,\ r = 0.990,\ sd = 0.025) \quad (1)$$

from which $\tilde{\nu}_{\mathrm{NI}}^{\mathrm{gas}} = 31659\ \mathrm{cm^{-1}}$ was obtained.

Also, our data for MNI in *n*-alkanes yielded equation (2)

$$\tilde{\nu}_{\mathrm{MNI}} = (-12.045 \pm 0.703)\,f_1(n^2) + 30089\ (n = 9,\ r = 0.998,\ sd = 0.027) \quad (2)$$

from which $\tilde{\nu}_{\mathrm{MNI}}^{\mathrm{gas}} = 30089\ \mathrm{cm^{-1}}$ was obtained.

Obviously, the difference in solvatochromism between NI and MNI will cancel many spurious effects accompanying the basicity effect of the solvent. In addition, NI and MNI possess several advantageous spectral features; thus, they exhibit a clean first absorption band that overlaps with no higher-energy band in any solvent, and both have the same spectral envelope in such a band (Figure 1), which facilitates comparisons between the two spectra and the precise establishment of the basicity parameter.

Table 1. Wavenumbers of the maximum of the first UV/Vis absorption band of the probe ($\tilde{\nu}_{NI}$) and the homomorph ($\tilde{\nu}_{MNI}$). Differences between $\tilde{\nu}_{NI}$ and $\tilde{\nu}_{MNI}$ ($\Delta\tilde{\nu}$, cm^{-1}) and their normalized values SB[a]

No.	Solvent	$\tilde{\nu}_{NI}$	$\tilde{\nu}_{MNI}$	$\Delta\tilde{\nu}$	SB
0	gas	31659[b]	30089[c]	1570	0.000
1	hexafluoro-2-propanol	23128	21583	1545	0.014
2	1,1,2,2-tetrachloroethane	25347	23806	1541	0.017
3	1,1,2-trichlorotrifluoroethane	28377	26873	1504	0.038
4	petroleum ether	28916	27420	1496	0.043
5	tetrachloromethane	27978	26484	1494	0.044
6	2,2,4-trimethylpentane	28742	27249	1493	0.044
7	3-(trifluoromethyl)-phenol	22876	21395	1481	0.051
8	n-nonane	28570	27092	1478	0.053
9	2-methylbutane	28950	27472	1478	0.053
10	n-hexane	28804	27331	1473	0.056
11	decaline	28335	26862	1473	0.056
12	cis-decaline	28295	26823	1472	0.056
13	perfluorohexane	29921	28451	1470	0.057
14	cyclopentane	28595	27134	1461	0.063
15	n-decane	28544	27088	1456	0.066
16	n-pentadecane	28447	26996	1451	0.068
17	cycloheptane	28431	26980	1451	0.069
18	chloroform	25938	24492	1446	0.071
19	1,4-difluorobenzene	26741	25296	1445	0.072
20	(trifluoromethyl)benzene	26518	25076	1443	0.073
21	cyclohexane	28545	27102	1443	0.073
22	thiophenol	25278	23834	1444	0.073
23	n-pentane	28919	27476	1443	0.073
24	cyclooctane	28378	26942	1436	0.077
25	methylcyclohexane	28537	27103	1434	0.078
26	n-octane	28603	27171	1432	0.079
27	perfluorotriethylamine	29598	28171	1427	0.082
28	n-heptane	28672	27246	1426	0.083
29	1,1,1-trichloroethane	26792	25370	1422	0.085
30	n-hexadecane	28398	26978	1420	0.086
31	n-dodecane	28439	27018	1421	0.086
32	carbon disulfide	26629	25239	1390	0.104
33	furan	26735	25351	1384	0.107
34	2,2,2-trifluoroethanol	24156	22772	1384	0.107
35	fluorobenzene	26387	25014	1373	0.113
36	hexafluorobenzene	27273	25910	1363	0.119
37	benzene	26604	25249	1355	0.124
38	1,2-dichloroethane	25685	24334	1351	0.126
39	toluene	26733	25385	1348	0.128
40	1-chlorobutane	26783	25453	1330	0.138
41	1,2-dichlorobenzene[d]	25705	24384	1321	0.144
42	perfluoropyridine	26621	25300	1321	0.144
43	ethylbenzene	26798	25491	1307	0.152
44	1-methylnaphthalene	25520	24221	1299	0.156
45	o-xylene	26697	25399	1298	0.157
46	iodobenzene[d]	25641	24345	1296	0.158
47	p-xylene	26855	25563	1292	0.160
48	m-xylene	26818	25530	1288	0.162
49	2-methylfuran	26897	25610	1287	0.163
50	dichloromethane	25559	24298	1261	0.178
51	pyrrole	24143	22883	1260	0.179
52	tetraline	26587	25329	1258	0.180
53	chlorobenzene[d]	26060	24806	1354	0.182
54	chloroacetonitrile	24704	23453	1251	0.184
55	2,2,2-trichloroethanol	23848	22600	1248	0.186
56	1,2,3,5-tetramethylbenzene	26786	25539	1247	0.186
57	mesitylene	26878	25637	1241	0.190
58	bromobenzene[d]	25847	24609	1238	0.191
59	m-cresol	23325	22088	1237	0.192
60	thioanisole	25497	24268	1229	0.197
61	N-methylaniline	24580	23378	1202	0.212
62	methyl salicylate	25445	24249	1196	0.216
63	ethyl trifluoroacetate	26580	25408	1172	0.229
64	nitroethane	25340	24176	1164	0.234
65	ethyl salicylate	25619	24458	1161	0.236
66	nitromethane	25068	23907	1161	0.236
67	nitrobenzene	24954	23801	1153	0.240
68	1-methylpyrrole	25374	24227	1147	0.244
69	aniline	23919	22808	1111	0.264
70	benzonitrile	25036	23953	1083	0.281
71	iodoethane	26028	24948	1080	0.282
72	acetonitrile	25274	24200	1074	0.286
73	benzaldehyde	24940	23873	1067	0.290
74	phenetole	25865	24807	1058	0.295
75	anisole	25658	24607	1051	0.299
76	hexanoic acid	26740	25698	1042	0.304
77	N,N-dimethylaniline	25392	24352	1040	0.305
78	glycerol	23977	22943	1034	0.309
79	dibenzyl ether	25409	24412	997	0.330
80	diethyl carbonate	26457	25477	480	0.340
81	veratrole	25143	24163	980	0.340
82	propylene carbonate	24760	23781	979	0.341
83	sulfolane	24541	23604	939	0.365
84	acetophenone	24915	23978	936	0.365
85	propionitrile	25387	24451	936	0.365
86	2-chloroethanol	24233	23318	915	0.377
87	methyl benzoate	25368	24454	914	0.378
88	propioacetophenone	24988	24080	908	0.382
89	butyronitrile	25410	24503	903	0.384
90	acetic acid	25728	24834	894	0.390
91	γ-butyrolactone	24705	23827	878	0.399
92	valeronitrile	25462	24595	867	0.408
93	formamide	23707	22855	852	0.414
94	triacetin	25576	24728	848	0.416
95	ethyl benzoate	25515	24669	846	0.417
96	methyl formate	25684	24846	838	0.422
97	isobutyronitrile	25480	24638	824	0.430
98	dimethyl carbonate	26070	25252	818	0.433
99	tetrahydrothiophene	25692	24878	814	0.436
100	1,4-dioxane	26074	25275	799	0.444
101	1,1-diethoxyethane	26647	25863	784	0.453
102	benzyl alcohol	24244	23474	770	0.461
103	cyclopentanone	25211	24448	763	0.465
104	acetone	25359	24613	746	0.475
105	methyl caproate	26252	25511	741	0.478
106	isoamyl acetate	26244	25508	736	0.481
107	cyclohexanone	25206	24473	733	0.482
108	ethyl 2-methoxy acetate	25596	24866	730	0.484
109	trimethyl phosphite	25858	25130	728	0.485
110	n-butyl methyl ether	26688	25995	693	0.505
111	2-butanone	25440	24773	667	0.520
112	isophorone	25096	24430	666	0.521
113	trimethyl phosphate	24776	24111	665	0.522
114	2-phenylethanol	24430	23768	662	0.523
115	n-butyl acetate	26083	25424	659	0.525
116	quinoline	24251	23594	657	0.526
117	methyl acetate	25860	25205	655	0.527
118	ethylene glycol	24109	23466	643	0.534
119	4-methylpentanone	25580	24947	633	0.540
120	ethyl acetate	25939	25309	630	0.542
121	methanol	24927	24303	624	0.545
122	n-propyl acetate	25993	25374	619	0.548
123	n-propyl formate	25794	25176	618	0.549
124	di-n-butyl oxalate	25721	25104	617	0.549
125	3-pentanone	25456	24853	603	0.557
126	diethyl ether	26774	26180	594	0.562
127	tert-butyl methyl ether	26691	26104	587	0.567

Table 1 *(Continued)*

No.	Solvent	$\tilde{\nu}_{NI}$	$\tilde{\nu}_{MNI}$	$\Delta\tilde{\nu}$	SB
128	pyridine	24583	24021	562	0.581
129	2-methyltetrahydrofuran	25912	25356	556	0.584
130	allyl alcohol	24707	24152	555	0.585
131	N-methylformamide	24362	23815	547	0.590
132	tetrahydrofuran	25693	25148	545	0.591
133	tetrahydropyran	25887	25343	544	0.591
134	morpholine	24901	24390	511	0.610
135	1-methylpyrrolidin-2-one	24334	23828	506	0.613
136	N,N-dimethylformamide	24434	23927	507	0.613
137	triethyl phosphate	24958	24453	505	0.614
138	N,N-diethylformamide	24662	24157	505	0.614
139	4-methylmorpholine	25840	25341	499	0.617
140	di-n-hexyl ether	27028	26530	498	0.618
141	diglyme	25365	24876	489	0.623
142	tetramethylurea	24117	24229	488	0.624
143	2,5-dimethyltetrahydrofuran	26091	25606	485	0.625
144	2-methylpyridine	24906	24428	478	0.629
145	di-n-pentyl ether	26961	26482	479	0.629
146	monoglyme	25554	25087	467	0.636
147	di-n-butyl ether	26991	26527	464	0.637
148	dimethyl sulfoxide	23988	23541	447	0.647
149	N,N-dimethylacetamide	24421	23978	443	0.650
150	diisopropyl ether	26885	26455	430	0.657
151	ethanol	25191	24763	428	0.658
152	N-methylimidazole	23887	23458	429	0.658
153	N,N-diethylacetamide	24715	24291	424	0.660
154	di-n-propyl ether	26837	26422	415	0.666
155	2,6-dimethylpyridine	25248	24907	341	0.708
156	n-propanol	24952	24643	309	0.727
157	N-methylacetamide	24603	24308	295	0.735
158	cineole	25985	25693	292	0.737
159	triethyl phosphite	25557	25277	280	0.743
160	N,N′-dimethylpropyleneurea	24092	23826	266	0.752
161	2-propanol	24872	24625	247	0.762
162	n-butanol	24931	24764	167	0.809
163	HMPA	24234	24074	160	0.813
164	1,4-dimethylpiperazine	25863	25736	127	0.832
165	cyclopentanol	24669	24549	120	0.836
166	1-methylpiperidine	26508	26389	119	0.836
167	ethylenediamine	23934	23826	108	0.843
168	tri-n-propylamine	26924	26818	106	0.844
169	cyclohexanol	24878	24789	89	0.854
170	tri-n-butylamine	26952	26864	88	0.854
171	3-methyl-1-butanol	25021	24939	82	0.858
172	n-pentanol	25073	24996	77	0.860
173	n-hexanol	25160	25115	45	0.879
174	triethylamine	26805	26771	34	0.885
175	2-butanol	24847	24819	28	0.888
176	3-methyl-2-butanol	24871	24851	20	0.893
177	2-methyl-1-butanol	24809	24800	9	0.900
178	n-nonanol	25357	25359	-2	0.906
179	n-undecanol	25454	25461	-7	0.909
180	cycloheptanol	24195	24205	-10	0.911
181	n-heptanol	25199	25211	-12	0.912
182	n-decanol	25369	25381	-12	0.912
183	2-pentanol	24895	24915	-20	0.916
184	2-methylpentanol	24907	24928	-21	0.917
185	1-methylpyrrolidine	25817	25840	-23	0.918
186	cyclooctanol	24817	24841	-24	0.919
187	n-octanol	25247	25279	-32	0.923
188	N-methylcyclohexylamine	25555	25590	-35	0.925
189	*tert*-butyl alcohol	24938	24978	-40	0.928
190	piperidine	25377	25425	-48	0.933
191	2-methyl-2-butanol	25223	25285	-62	0.941
192	n-butylamine	25329	25397	-68	0.944

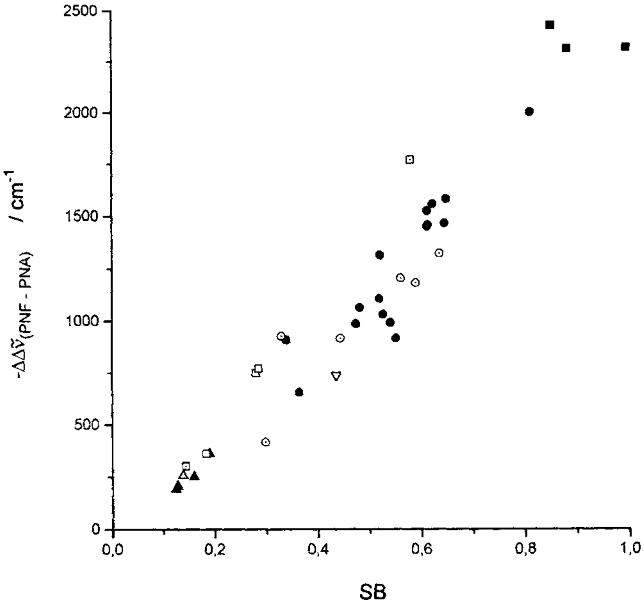
Table 1 *(Continued)*

No.	Solvent	$\tilde{\nu}_{NI}$	$\tilde{\nu}_{MNI}$	$\Delta\tilde{\nu}$	SB
193	3-pentanol	24785	24864	-79	0.950
194	cyclohexylamine	25190	25284	-94	0.959
195	n-butyl methyl amine	25634	25729	-95	0.960
196	2-octanol	25219	25320	-101	0.963
197	2-hexanol	24952	25058	-108	0.966
198	3-hexanol	24917	25046	-129	0.979
199	pyrrolidine	24874	25022	-148	0.990
200	di-n-butylamine	26024	26174	-150	0.991
201	N,N-dimethylcyclohexylamine	26212	26374	-162	0.998
202	tetramethylguanidine	24381	24546	-165	1.000

[a] SB = [$\Delta\tilde{\nu}$(solvent) − $\Delta\tilde{\nu}$ (solvent 0)]/[$\Delta\tilde{\nu}$ (solvent 202) − $\Delta\tilde{\nu}$ (solvent 0)]. — [b] Calculated from eq. (3). — [c] Calculated from eq. (4). — [d] According to the criticism of a referee concerning the unusual basicity sequence of the solvent pairs bromobenzene/benzene, chlorobenzene/xylenes, iodobenzene/toluene, 1,2-dichlorobenzene/toluene, we note that the halogen substituents in aromatic solvents do not decrease the SB value as can be expected by electron-withdrawing effects.

Table 1 lists the positions of the maxima for the first absorption band of the probe and its homomorph, and the difference between the two in each of the solvents studied and in the gas phase. Solvents are arranged in descending order according to such a difference, which we propose as the parameter for measuring the solvent hydrogen-bond acceptor basicity. It should be noted that this index varies from 1570 cm^{-1} for the gas phase (solvent 0) to -165 cm^{-1} for tetramethylguanidine (TMG) (solvent 202). In order to standardize the scale to values from 0 to 1, the right-most column in Table 1 contains the converted values, which vary from 0 for the gas phase to 1 for the most basic solvent studied, i.e. TMG.

Figure 2. Solvatochromic shifts $-\Delta\Delta\tilde{\nu}$ attributable to hydrogen bonding between 4-nitrophenol and solvent[26,34] vs. the SB of the solvents



A brief analysis of the SB data allows us to draw several interesting conclusions from structural effects on solvent basicity. Thus:

(a) Appropriate substitution in compound families such as amines and alcohols allows the whole range of the solvent basicity scale to be encompassed with compounds from such families. For example, perfluorotriethylamine can be considered as non-basic (SB = 0.082), whereas *N,N*-dimethylcyclohexylamine is at the top of the scale (SB = 0.998). Also, hexafluoro-2-propanol is non-basic (SB = 0.014), whereas 2-octanol is very near the top (SB = 0.963).

(b) The basicity of *n*-alkanols increases significantly with increasing chain length and then levels off above octanol.

(c) Cyclization hardly influences the solvent basicity; for example, there is little difference in SB between *n*-pentane (0.073) and cyclopentane (0.063) or between *n*-pentanol (0.860) and cyclopentanol (0.836).

(d) Aromatization decreases the solvent basicity by a factor of 3.5–5.5, as illustrated by the following couples: pyrrolidine/pyrrole (0.99/0.18), *N*-methylpyrrolidine/*N*-methylpyrrole (0.92/0.22), tetrahydrofuran/furan (0.59/0.11), 2-methyltetrahydrofuran/2-methylfuran (0.58/0.16), cyclohexylamine/aniline (0.96/0.26), *N*-methylcyclohexylamine/*N*-methylaniline (0.92/0.21), *N,N*-dimethylcyclohexylamine/*N,N*-dimethylaniline (0.99/0.30), and a structurally less similar couple such as piperidine/pyridine (0.93/0.58).

It is also remarkable that the SB values of *n*-alkanes are small but never zero and, on the other hand, that the halogen substituents in aromatic solvents do not decrease the SB value as can be expected by their electron-withdrawing effect.

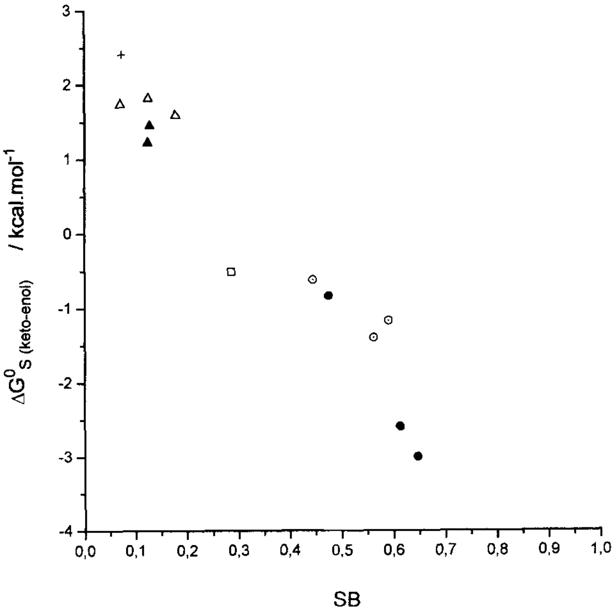
Correlation of Experimental Data with the SB Scale

Having a scale that describes solvent hydrogen-bond acceptor basicity without contaminating effects, we can analyze experimental behavior patterns assigned to this type of specific interaction and explain any deviations from the dependence on solvent basicity. Let us analyze the applicability of our scale to data obtained from other spectroscopic techniques and alternative chemical areas. The cases analyzed below and the data used were produced by the same laboratory whenever possible. For simplicity and in order to facilitate detection of family-dependent trends, solvents were labeled as follows: alcohol-like bases (○); ether-like bases (⊙); carbonyl-, thionyl-, and phosphoryl-containing bases (•); sp nitrogen-containing bases (□); sp^2 nitrogen-containing bases (⊡); sp^3 nitrogen-containing bases (■); S-containing bases (▽); halogen-containing bases (△); aromatic bases (▲); hydrocarbons (+); and the gas phase (◆). The evidence gathered below was obtained from bulk solvents in every case.

IR Data: Recently, Laurence et al.[31] used an IR method to compare the frequencies of the carbonyl stretching vibrations of trichloroacetic acid and methyl trichloroacetate dissolved in pure solvents in order to determine the basicity of a series of solvents; their Δν(C=O) data are consistent with the corresponding SB values (r = 0.956, n = 11) taking into account that they include aromatic bases, ether, carbonyl and phosphoryl bases, sp^2 and sp^3 nitrogen-containing bases, and sulfur-containing bases.

UV/Vis Absorption Data: Laurence et al.[26,32] carried out a thorough spectroscopic analysis of chromophore couples previously used by Kamlet and Taft[12a] to develop their β scale and contributed evidence that allowed a substantially improved application of their solvatochromic method. They also demonstrated the spectroscopic advantages of 4-nitrophenol over 4-nitroaniline. A comparison of the basicity data of Laurence et al.[3], obtained from solvatochromic data using the 4-nitrophenol/4-nitroanisole couple, with our SB values (Figure 2), reveals an acceptable correlation (r = 0.966, n = 35). It should be noted that the solvent set used by Laurence et al. included aromatic bases, ether-like and carbonyl bases, nitrogen-containing bases of the three types, and halogen- and sulfur-containing bases.

Figure 3. Free energies of the keto-enol equilibrium of 5,5-dimethyl-1,3-cyclohexane dione[37] in various solvents vs. its SB values



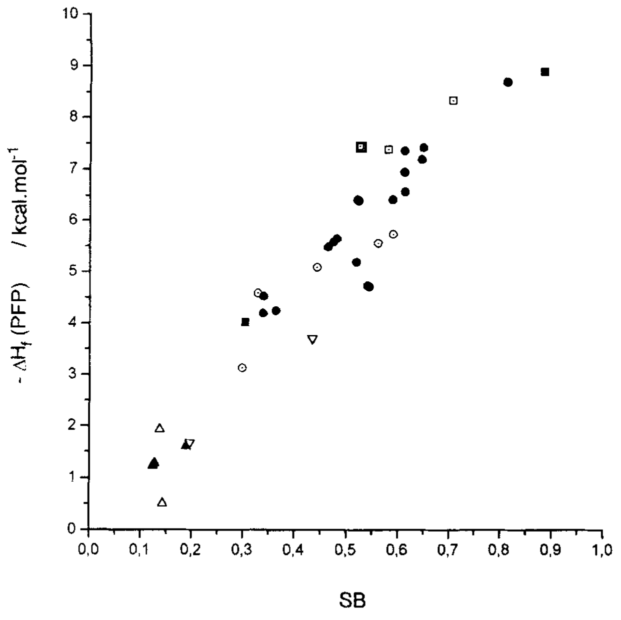
NMR Data: Popov et al.[33–35] carried out a comprehensive NMR analysis of sodium salts in various non-aqueous solvents and stressed the significance of the nature and concentration of the dissolved sodium salt to the chemical shift undergone by ^{23}Na. They found the chemical shifts for all the salts studied to converge to the same infinite dilution value and proposed to use such a limiting value as the chemical shift for free sodium ion in each solvent. The structural significance of these data lies in their high sensitivity to the environment (it changes by 22 ppm from nitromethane to TMG) and may be useful as a measure of solvent donicity. The ^{23}Na-NMR chemical shifts measured in a 3 M solution of $NaClO_4$ at infinite dilution against the SB values for the solvents are fairly proportional (r = 0.956, n = 14). However, the deviations in the case of formamide and pyridine (r = 0.911, n = 16) are remarkable.

Another excellent candidate to probe the donicity of a solvent in NMR spectroscopy is trifluoroiodomethane, which forms a complex with the solvent via its iodine atom and induces a change in the charges of the fluorine atoms in the compound that results in altered ^{19}F signals. The ^{19}F data for various solvents measured by Spaziante and Gutmann[36] against the corresponding SB values show an acceptable agreement (r = 0.923, n = 19) except again for pyridine.

Thermodynamic Data. – Equilibrium Data: In order to compare shifts in the equilibrium position with solvent basicity, one should select an equilibrium in which one of the species interacts with the solvent in such a way that the interaction is the dominant contribution to the equilibrium displacement. However, by use of a non-selected group of solvents additional equilibrium driving forces will clearly be introduced. One pertinent example is the keto-enol equilibrium.

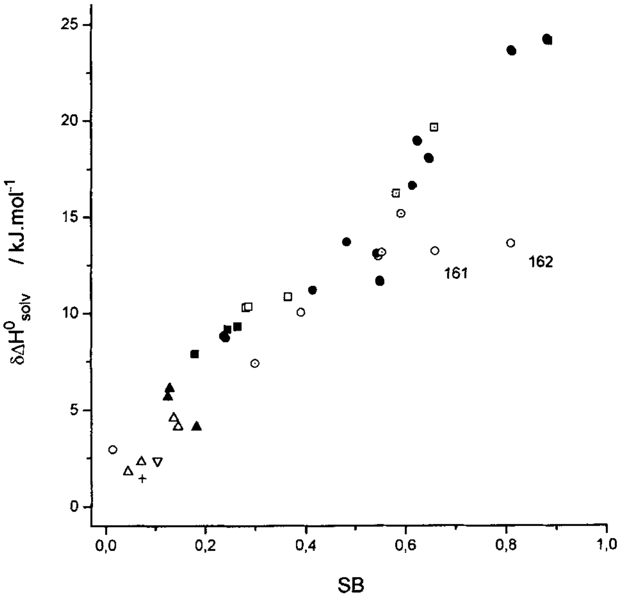
Mills and Beak[37] studied the effect of the solvent on the equilibrium constant for selected pairs of keto–enol isomers and concluded that the equilibrium position of 5,5-dimethyl-1,3-cyclohexanedione is largely controlled by the solvent basicity. Figure 3 shows the variation of the standard free energy for this equilibrium against the SB for the solvents; this plot clearly reflects the anticipated dependence (r = 0.963, n = 13).

Figure 4. Enthalpy of formation for the hydrogen bonding of the 4-fluorophenol[16] for the pure solvent method vs. the SB values of the solvents



Solution Enthalpy Data: In 1970, Arnett et al.[16a] developed a new calorimetric method for determining the enthalpy of hydrogen bond formation in order to circumvent the shortcomings faced in the determination of K_f values at high dilutions. This "pure-base method" involves injection of a small amount of an acid probe into the base (a pure solvent). The resulting heat obviously consists of two different contributions, namely, that from the hydrogen bond interaction between the acid and base (solvent) and that from the remaining heat exchanged. The latter contribution is subsequently subtracted as the measured dissolution heat for an appropriate homomorph of the acid probe used. Specifically, Figure 4 shows the enthalphies of hydrogen bond formation measured by Arnett et al.[16] for a series of non-protic solvents in 4-fluorophenol (PFP) and its homomorph 4-fluoroanisole (PFA). As can be seen, the correlation is quite good for the type of bases considered (r = 0.957, n = 33).

Figure 5. Variation of the enthalpy of the solvation of the couples pyrrole/N-methylpyrrole and toluene/benzene[38] vs. the SB values of the solvents



Recently, our group[38] applied the pure-solvent method to a group of probes (pyrrole, N-methylpyrrole, benzene, and toluene) in order to avoid as far as possible effects other than those from hydrogen bond formation (e.g. small cavity and dipolarity/polarizability effects). In addition, the acid probe used was of the N–H type rather than the O–H type employed by Arnett et al., and our study included protic solvents. Figure 5 compares the results obtained with the corresponding SB values. The correlation is quite good except for 2-propanol (solvent 161) and n-butanol (solvent 162) (r = 0.963, n = 35).

Electrochemical Data: If a cation such as K^+ is assumed to behave as a Lewis acid in interacting with basic solvents, then its polarographic half-wave potential should also be sensitive to the solvent basicity. Figure 6 shows the half-wave potentials for K^+[39] relative to bis(biphenyl)chromium(I)/(0)/against the corresponding SB values for the solvents considered. As can be seen, this plot clearly reflects the anticipated dependence (r = 0.944, n = 16).

Kinetic Data: If the equilibrium position is primarily determined by the complexation with the solvent molecules, the rate of cleavage of the complex should also be dependent on the solvent basicity. One interesting kinetics for analysis is that of $SbCl_5{\cdot}S$ (eq. 3). Thus, the plot of lg k_{12}

Figure 6. Half-wave potentials of K^+ ($E_{1/2(BCr)}$ K^+)[39] vs. the SB values of the solvents

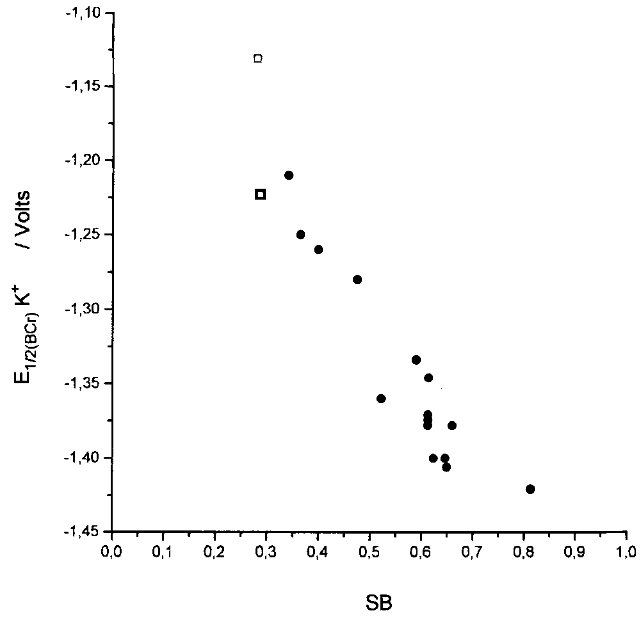
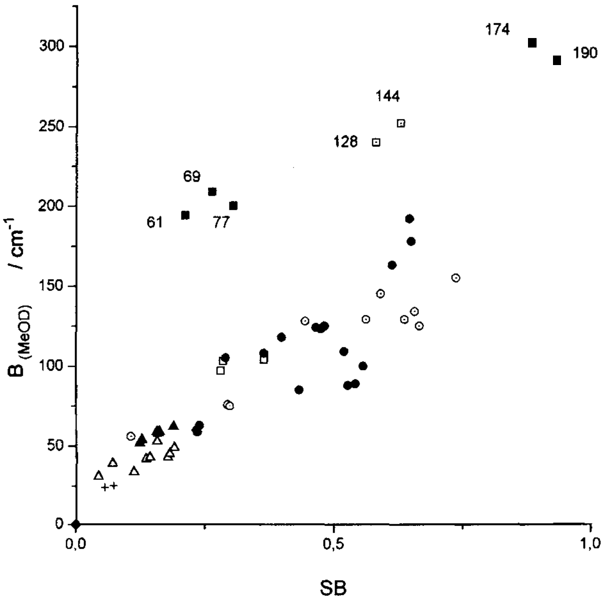


Figure 7. Plot of $B_{(MeOD)}$[15] vs. the SB values of the solvents



against SB reveals an excellent correlation (r = 0.976, n = 6). Moreover, the rate constant varies over a range of 5 orders of magnitude for the solvents studied[40].

$$S \cdot SbCl_5 + Ph_3C{-}Cl \rightarrow PhC^+SbCl_6^- + S \qquad (3)$$

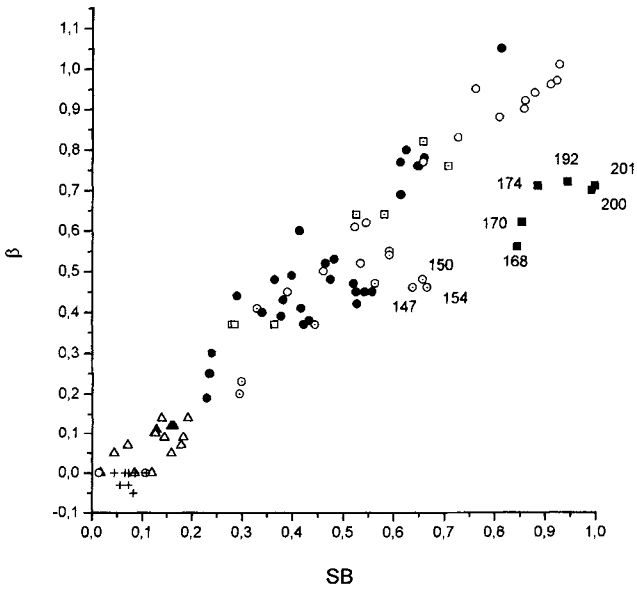
Comparison of the SB Scale with Other Basicity Scales

For consistency, let us consider those basicity scales derived by using the acid probe in pure solvents [viz. the $B_{(MeOD)}$, β, and basicity scales] and then those obtained from dilute solutions of the acid and various bases in an inert solvent [the DN and ΔH (BF_3) scales].

The Koppel-Palm $B_{(MeOD)}$ Scale: This scale was first conceived in 1939–1941, when Gordy and Stanford[41] measured the O–D stretching frequency of monomeric methan[^{2}H]ol in a variety of non-protic media and recommended the use of the solvent-induced shift as an approximately quantitative measure of the Brönsted basicity. In 1968, Kagiya et al.[42] extended the study to other solvents and proposed a quantification of the shift with reference to that for benzene as a measure of the Lewis basicity. However, it was Koppel and Palm[15] in 1972 who developed the $B_{(MeOD)}$ scale, which uses the difference in the frequency for MeOD in this solvent and that in the gas phase (i.e. in the absence of solvent) as a measure of solvent basicity. Subsequently, Shorter et al.[43] revised some of the measurements of Kagiya et al.[42] and contributed to new types of solvents, thus extending the $B_{(MeOD)}$ scale.

Figure 7 shows a plot of $B_{(MeOD)}$ against the corresponding SB values. With the exception of amines and pyridines, the two are linearly related (r = 0.918, n = 46). The exceptional behavior of amines and pyridines may be attributed to in the fact exposed by Shorter et al.[43] that the $\tilde{\nu}_{OD}$ band in these solvents is unusually complex with a doublet structure. (Moreover, the band is extremely weak in some cases.) These authors found no plausible explanation for these unusual findings and revealed marked discrepancies with the results of Kagiya et al.[42].

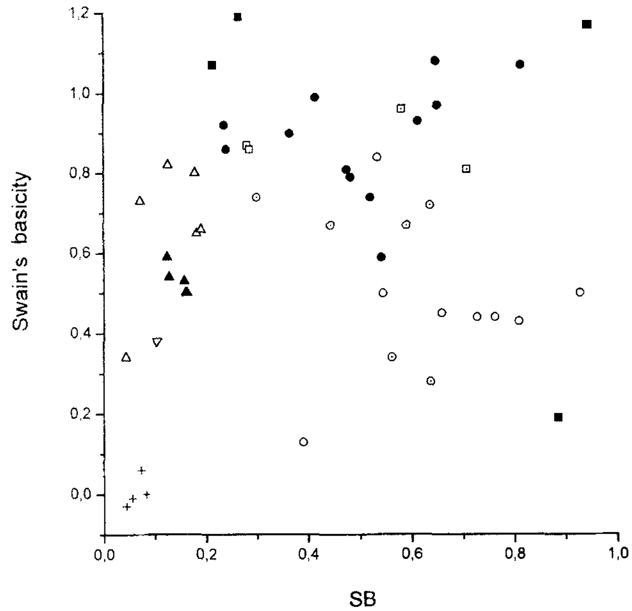
Figure 8. Plot of β[22] vs. the SB values of the solvents



The Kamlet-Taft β Scale: In 1976, Kamlet and Taft[12a] used the solvatochromic method to develop their β solvent scale. However, it should be noted that of the five properties used to establish the β scale, only two are for pure solvents (the other three are measured in dilute solutions of bases in tetrachloromethane).

Figure 8 shows a plot of β values against the SB for the solvents which reveals: (a) the two are linearly related (r = 0.928, n = 98), (b) aliphatic amines and some ethers (specifically non-cyclic aliphatic ethers with long hydrocarbon chains) deviate from general variation pattern. These deviations may be attributed to conformational aspects (the donor group in the probes used to develop the β scale may undergo some bending). From Figure 8 it seems unnecessary to introduce the parameter ξ in order to correct values on the β scale[23].

Figure 9. Plot of Swain's basicity[44] vs. the SB values of the solvents



Swain's Basicity Scale: In 1983, Swain et al.[44] used statistical computations from 1080 reported data sets for 61 solvents and 77 reactions and physico-chemical properties (e.g. rate constants, product ratios, equilibrium constants, UV/Vis, IR, ESR and NMR spectra) and concluded that every solvent effect can be described on the basis of two complementary scales. One such scale, A_j, describes the tendency to solvate anions and is called the "acidity scale"; the other, B_j, characterizes the tendency to solvate anions and is designated as the "basicity scale".

Figure 9 is a plot of basicity against the SB values for the solvents considered. Since there is no linear correlation between the two data sets ($r = 0.232$, $n = 50$) the basicity scale can hardly describe solvent basicity. In Figure 10 the previous basicity data are plotted against the SPP values for the solvents; in contrast to the assumptions of Swain et al.[44], their basicity scale actually describes mostly solvent dipolarity/polarizability ($r = 0.785$, $n = 49$).

Gutmann's Donor Number: Gutmann[14,45] uses the term "donicity" to designate a measure of the ability to donate an electron pair and proposed the so-called "donor number" (DN) to express, in at least a semi-quantitative manner, the donor strength of a solvent. DN is defined as the inverse of the enthalpy change involved in the formation of a 1:1 adduct between antimony pentachloride and an electron donor in a dilute solution of an assumed non-coordinating solvent such as 1,2-dichloroethane.

Figure 11 shows a plot of DN vs SB for the solvents studied. As can be seen, the two parameters are proportional to each other ($r = 0.930$, $n = 24$).

Figure 10. Plot of Swain's basicity[44] vs. the SPP values of the solvents

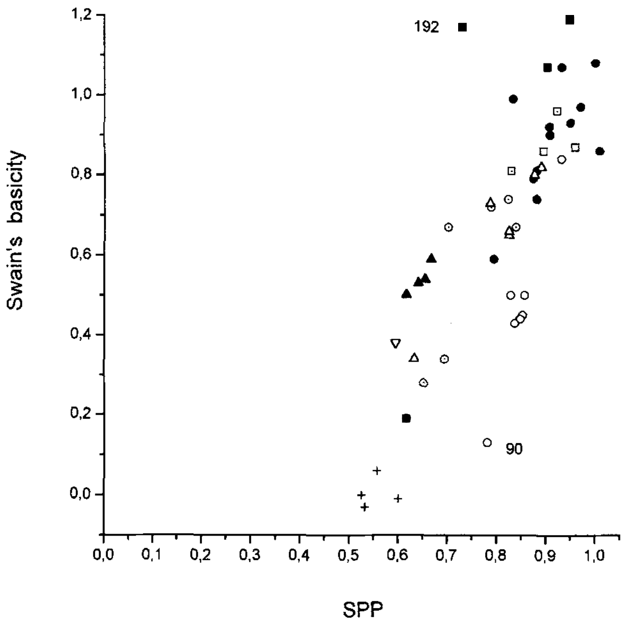
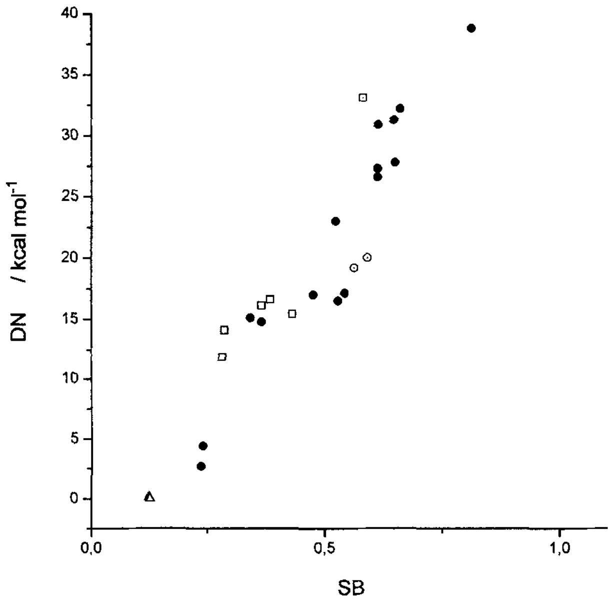


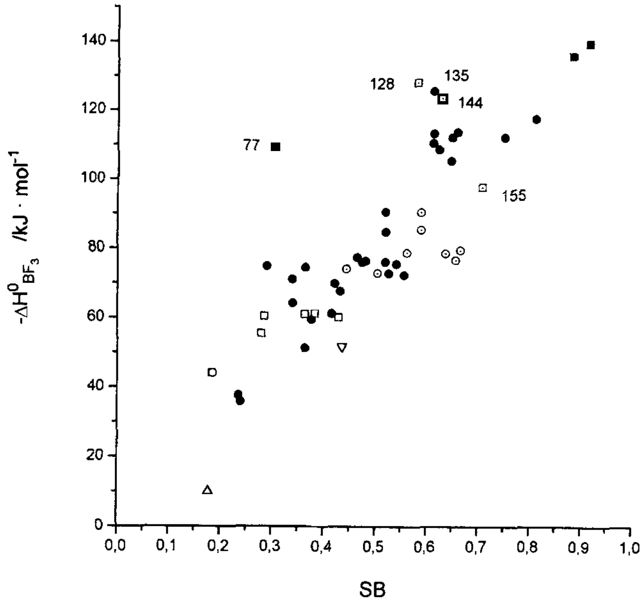
Figure 11. Plot of DN[45] vs. the SB values of the solvents



Notwithstanding the potential of this parameter, which has turned it into one of the most widely used basicity measures, its actual value was questioned in both conceptual[46] and experimental terms[20,47]. The criticism led to the development of alternative Lewis basicity scales such as that based on the formation of BF_3 adducts.

The ΔH(BF₃) Scale: Maria and Gal[20] used boron trifluoride dissolved in dichloromethane as the Lewis acid and the enthalpy change for the formation of a 1:1 adduct between BF_3 and the dissolved basic adduct to develop their scale. The scale was established by using a more suitable experimental technique than the previous one and, es-

Figure 12. Plot of $-\Delta H_{\mathrm{BF_3}}$[20,48] vs. the SB values of the solvents



pecially, with a probe (BF_3) that offers substantial advantages over the $SbCl_5$ employed by Gutmann et al.

Figure 12 shows a plot of $\Delta H(BF_3)$ vs SB data for the solvents considered. The two parameters are linearly related (r = 0.832, n = 52). Yet *N,N*-dimethylaniline (solvent 77), which becomes highly basic by complexation with BF_3, deviates markedly from the general trend. Also, while 2,6-dimethylpyridine (solvent 155) fits the general trend quite well, 2-methylpyridine (solvent 144) and pyridine (solvent 128) are extremely basic against BF_3.

A comparison of the proposed SB scale with previously reported alternatives allows us to draw several interesting conclusions. Thus, the other scales are roughly proportional to the SB scale. The relationships between the two are not close enough to assign them a mutually predictive value, however. In any case, the above plots exhibit no family-dependence effects.

It should be noted that 5-nitroindoline is not an unsubstituted amine probe but provides results consistent with those obtained by using a phenol compound as the acid probe (see Figures 2 and 4) and exhibits no family dependence. These results raise several questions concerning the previously assumed features for a compound to be a suitable probe for the development of a basicity scale[25,27].

Conclusions

The results presented in this work allow us to conclude that the probe 5-nitroindoline and its homomorph 1-methyl-5-nitroindoline can be used to construct a general solvent hydrogen-bond acceptor basicity scale from precise, readily measured UV/Vis spectroscopic data affordable by any laboratory. The SB scale can in principle be used to assess the basicity of any medium provided it can dissolve the probe and its homomorph.

It should be noted that a single family of appropriately substituted compounds can be used to encompass the whole basicity range (see, for example, the data obtained for alcohols or amines).

The results refute the current assumption that two basicity scales constructed from acid probes of a different nature (N–H or O–H) cannot be compared.

The SB scale effectively describes solvent basicity effects based on experimental evidence gathered not only from spectroscopic but also from other types of chemical data.

We are greatly indebted to *CICYT* of Spain for financial support (Project no. PB93-0280).

Experimental

5-Nitroindoline (NI) was purchased from Aldrich and carefully purified by silica gel column chromatography using dichloromethane/hexane (6:4) as eluent.

1-Methyl-5-nitroindoline (MNI): To a solution of 6.0 g (0.037 mol) of 5-nitroindoline and 3.9 g (0.037 mol) of sodium carbonate in 20 ml of tetrahydrofuran, 2.9 ml (0.047 mol) of iodomethane was added dropwise with stirring and boiling at reflux for 24 h. Then the reaction medium was made basic with an 20% aqueous sodium carbonate solution and extracted with chloroform. The extract was dried with magnesium sulfate, filtered, and the solvent was removed. The resulting brown residue was purified by silica gel column chromatography (eluent: hexane/dichloromethane/ethyl acetate, 55:30:15) yielding 5.8 g (89%) of 1-methyl-5-nitroindoline as an orange solid of m.p. 113–114°C. – IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1610, 1600 (sh.) (C–C, Ar), 1530 and 1330 (NO_2), 1430 (CH_2), 1360 (CH_3), 900 and 820 (1,2,4-trisubst.). – ^{1}H NMR ($CDCl_3$): δ = 7.96 (dd, 1H, J_1 = 8.8, J_2 = 2.3 Hz, 6-H), 7.77 (d, 1H, J = 2.3 Hz, 4-H), 6.20 (d, 1H, J = 8.8 Hz, 7-H), 3.60 (t, 2H, J = 8.4 Hz, 2-H), 3.00 (t, 2H, J = 8.4 Hz, 3-H), 2.87 (s, 3H). – MS (70 eV); *m/z*: 178 (100) [M$^+$], 148 (37), 132 (72), 131 (51), 130 (33), 117 (11), 103 (9), 89 (15), 84 (17), 77 (14). – $C_9H_{10}N_2O_2$ (178.2): calcd. C 60.66, H 5.66, N 15.72; found C 60.53, H 5.45, N 15.50.

All solvents used were of the highest available purity and supplied by Aldrich, Fluka or Merck. Some were redistilled in an inert atmosphere prior to use. Solvent purity considerations were the same as for the SPP scale in order to make them fully comparable.

UV/Vis: Shimadzu 2100. The monochromator was calibrated by using the 486.0- and 656.1-nm lines from a deuterium lamp. In those cases where the probe was scarcely soluble in a given solvent, the Shimadzu instrument was replaced by a Cary 5 spectrophotometer and a cell of 10 cm path length was employed. Both instruments were routinely checked for wavelength accuracy by using holmium oxide and didymium filters. All spectral measurements were performed at 25°C by using a matched pair of quartz cells of 0.2, 1, or 10 cm path length. A cell of 0.05 cm path length was used in those cases where solvent cut-off was inadequate. The maximum absorption wavelength was determined from the derivative function. The results are the arithmetic means of at least eight spectra whose maxima were shifted by less than 0.2 nm. Tabulated wavenumbers are direct conversions of λ_{max} values.

Theoretical Calculations: All Computations were carried out by using a standard version of the GAUSSIAN 92 program[49]. The calculations were carried out at the MP2-6-31G** and 6-31G** levels. The geometry was fully optimized at both levels by using Berny's algorithm[50]. The polarizability of both compounds was determined at the 6-31G** level. The molecular electrostatic potentials were calculated at MP2-6-31G** level.

[1] M. Berthelot, L. Péan de Saint-Gilles, *Ann. Chim. Phys.* **1862**, *65*, 385–422; **1862**, *66*, 5–110, and **1863**, *68*, 225–359.

[2] N. A. Menschutkin, *Z. Phys. Chem.* **1890**, *5*, 589–600.

[3] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed., VCH Publishers, Weinheim, **1988**, and references therein.

[4] J. G. Kirkwood, *J. Chem. Phys.* **1934**, *2*, 351–361; **1939**, *7*, 911–919.

[5] L. Onsager, *J. Am. Chem. Soc.* **1936**, *58*, 1486–1493.

[6] H. Block, S. M. Walter, *Chem. Phys. Lett.* **1973**, *19*, 363–364.

[7] J. E. Brady, P. W. Carr, *J. Phys. Chem.* **1985**, *89*, 5759–5766, and references therein.

[8] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358.

[9] R. S. Drago, *J. Chem. Soc., Perkin Trans. 2*, **1992**, 1827–1838.

[10] J. Catalán, V. López, P. Pérez, R. Martín-Villamil, J. G. Rodríguez, *Liebigs Ann.* **1995**, 241–252; J. Catalán, V. López, P. Pérez, *ibid.* **1995**, 793–795.

[11] [11a] T. D. Epley, R. S. Drago, *J. Am. Chem. Soc.* **1967**, *89*, 5770–5773; R. S. Drago, T. D. Epley, *ibid.* **1969**, *91*, 2883–2890; G. C. Vogel, R. S. Drago, *ibid.* **1970**, *92*, 3924–3929; R. S. Drago, L. B. Parr, C. S. Chanberlain, *ibid.* **1977**, *99*, 3203–3209; R. S. Drago, K. F. Purcell, *Prog. Inorg. Chem.* **1964**, *6*, 271–322. –[11b] R. S. Drago, *Coord. Chem. Rev.* **1980**, *33*, 251–277; R. S. Drago, G. C. Vogel, *J. Am. Chem. Soc.* **1992**, *114*, 9527–9532; R. S. Drago, *Inorg. Chem.* **1993**, *32*, 2473–2479.

[12] [12a] M. J. Kamlet, R. W. Taft, *J. Am. Chem. Soc.* **1976**, *98*, 377–383. – [12b] R. W. Taft, M. J. Kamlet, *J. Am. Chem. Soc.* **1976**, *98*, 2886–2894.

[13] G. N. Lewis, *Valence and Structure of Atoms and Molecules*, The Chemical Catalog Co., New York, **1923**, p. 142.

[14] V. Gutmann, E. Wychera, *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 257–260.

[15] I. A. Koppel, V. A. Palm in *Advances in Linear Free Energy Relationships* (Eds.; N. B. Chapman, J. Shorter), chapter 5, Plenum Press, London, **1972**, p. 204–280.

[16] [16a] E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1970**, *92*, 2365–2377. – [16b] E. M. Arnett, E. J. Mitchell, T. S. S. R. Murty, *J. Am. Chem. Soc.* **1974**, *96*, 3875–3891.

[17] M. P. Li, R. S. Drago, A. J. Pribula, *J. Am. Chem. Soc.* **1977**, *99*, 6900–6905; R. S. Drago, *Inorg. Chem.* **1990**, *29*, 1379–1382.

[18] M. J. Kamlet, A. Solomonovici, R. W. Taft, *J. Am. Chem. Soc.* **1979**, *101*, 3734–3739.

[19] B. Panchenko, N. Oleinik, Yu. Sadovsky, V. Dadali, L. Litvinenko, *Org. React. (Tartu)* **1980**, *17*, 65–87.

[20] P. C. Maria, J. F. Gal, *J. Phys. Chem.* **1985**, *89*, 1296–1304.

[21] R. W. Taft, T. Gramstad, M. J. Kamlet, *J. Org. Chem. 1982*, *47*, 4557–4563.

[22] M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **1983**, *48*, 2877–2887.

[23] M. J. Kamlet, J. F. Gal, P. C. Maria, R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, **1985**, 1583–1589.

[24] M. J. Kamlet, R. M. Doherty, J.-L. M. Abboud, M. H. Abraham, R. W. Taft, *Chemtech.* **1986**, 566–569.

[25] P. C. Maria, J. F. Gal, J. Franceschi, E. Fargin, *J. Am. Chem. Soc.* **1987**, *109*, 483–492.

[26] P. Nicolet, C. Laurence, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 1071–1079.

[27] M. H. Abraham, G. J. Buist, P. L. Grellier, R. A. McGill, D. V. Prior, S. Oliver, E. Turner, J. J. Morris, P. J. Taylor, P. Nicolet, P. C. Maria, J. F. Gal, J.-L. M. Abboud, R. H. Doherty, M. J. Kamlet, W. J. Shuely, R. W. Taft, *J. Phys. Org. Chem.* **1989**, *2*, 540–552.

[28] J. S. Murray, S. Rauganathan, P. Politzer, *J. Org. Chem.* **1991**, *56*, 3734–3737.

[29] I. Renge, *J. Photohcem. Photobiol. A: Chem.* **1992**, *69*, 135–141.

[30] J. Catalán, *Chem. Phys. Lett.* **1994**, *223*, 159–161.

[31] P. Nicolet, C. Laurence, M. Luçon, *J. Chem. Soc., Perkin Trans. 2*, **1987**, 483–485.

[32] C. Laurence, P. Nicolet, M. Helbert, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 1081–1090.

[33] R. H. Erlich, A. I. Popov, *J. Am. Chem. Soc.* **1971**, *93*, 5620–5623.

[34] M. S. Greenberg, R. L. Bodner, A. I. Popov, *J. Phys. Chem.* **1973**, *77*, 2449–2454.

[35] A. I. Popov, *Pure Appl. Chem.* **1975**, *41*, 275–289.

[36] P. Spaziante, V. Gutmann, *Inorg. Chim. Acta.* **1971**, *5*, 273–275.

[37] S. G. Mills, P. Beak, *J. Org. Chem.* **1985**, *50*, 1216–1224.

[38] J. Catalán, J. Gómez, A. Couto, J. Laynez, *J. Am. Chem. Soc.* **1990**, *112*, 1678–1681, and unpublished results.

[39] G. Gritzner, *J. Phys. Chem.* **1986**, *90*, 5478–5485.

[40] V. Gutmann, R. Schmid, *Monatsh. Chem.* **1971**, *102*, 1217–1225.

[41] W. Gordy, *J. Chem. Phys.* **1939**, *7*, 93–99; **1941**, *9*, 215–223; W. Gordy, S. C. Stanford, *ibid.* **1940**, *8*, 170–177; **1941**, *9*, 204–214.

[42] T. Kagiya, Y. Sumida, T. Inoue, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 767–773.

[43] A. G. Burden, G. Collier, J. Shorter, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 1627–1632.

[44] C. G. Swain, M. S. Swain, A. L. Powell, A. Alunni, *J. Am. Chem. Soc.* **1983**, *105*, 502–513.

[45] V. Gutmann, *Coord. Chem. Rev.* **1976**, *19*, 225–255.

[46] R. S. Drago, *Coord. Chem. Rev.* **1980**, *33*, 251–277, and *Pure Appl. Chem.* **1980**, *52*, 2261–2274.

[47] Y. Y. Lim, R. S. Drago, *Inorg. Chem.* **1972**, *11*, 202; G. Olofsson, I. Olofsson, *J. Am. Chem. Soc.* **1973**, *95*, 7231–7233; R. W. Taft, N. J. Pienta, M. J. Kamlet, E. M. Arnett, *J. Org. Chem.* **1981**, *46*, 661–667; O. W. Kolling, *Anal. Chem.* **1982**, *54*, 260–264; J. C. Bollinger, G. Yvernault, T. Yvernault, *Thermochim. Acta.* **1983**, *60*, 137–147.

[48] J. F. Gal, P. C. Maria, *Progr. Phys. Org. Chem.* **1990**, *17*, 159–238; P. C. Maria, J. F. Gal, R. W. Taft, *N. J. Chem.* **1987**, *11*, 617–621.

[49] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Repogle, R. Gomperts, J. L. André, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, *Gaussian 92*, Revision C, Gaussian Inc., Pittsburg PA, **1992**.

[50] H. B. Schlegel, *J. Compt. Chem.* **1982**, *3*, 214–218.

[96109]