

(1.548 Å)<sup>18</sup> show. The lack of conjugation implied by these bond lengths, at least by comparison with the butadienes, is also in accord with the observation that the oxalyl halides (unlike the butadienes) are found to exist as readily interconvertible rotational conformers. On the other hand, carbon-carbon bonds to methyl groups adjacent to double bonds are known to be short, as in acetone (1.515 Å),<sup>19</sup> acetaldehyde (1.515 Å),<sup>19</sup> acetic acid monomer (1.517 Å),<sup>20</sup> propylene (1.502 Å),<sup>21</sup> and others. Our results for the carbon-carbon bonds in biacetyl are completely consistent with the picture provided by these comparisons.

The length of the central bond in biacetyl compared with those from the similar compounds cited above suggests little, if any, conjugation stabilization of the planar form; additional evidence to this effect is seen in the low values of 48<sup>3</sup> and 56<sup>2</sup> reported for the torsional wavenumbers. The absence of detectable amounts of a second conformer such as the gauche form found in the gaseous oxalyl halides thus becomes an interesting question. The answer is not clear, but it seems likely to involve CH<sub>3</sub>...O attractive forces acting in concert with repulsions between like groups. For example, electronegativity differences lead to predictions of small residual positive charges on the hydrogen atoms and negative charges on the oxygens and stabilization of the trans form. Atom-atom steric effects might be imagined to favor a staggered conformation, but bond-bond repulsions should be greatest for a cis and least for the trans form if the double bonds are regarded as formed from the shared edges of a tetrahedral carbon atom as was proposed for the oxalyl halides.<sup>6</sup>

The root mean square amplitudes of the torsional motion permit an estimate of the torsional frequency. Application of the formulas  $\omega = (2\pi c)^{-1}(k_\phi/\mu_1)^{1/2}$  and  $V = V^*\phi^2/4$  with  $k_\phi = V^*/2 = RT/\delta^2$  and where  $\mu_1$  is the reduced moment of inertia for the torsional motion has been described.<sup>6</sup> The results for biacetyl are 52.6 ( $2\sigma = 7.4$ ) cm<sup>-1</sup> at 228 °C and 52.4 ( $2\sigma = 11.9$ ) cm<sup>-1</sup> at 525 °C in excellent agreement with the spectroscopic value reported at 48<sup>3</sup> and 56 cm<sup>-1</sup>.<sup>2</sup>

**Acknowledgment.** We are grateful to Cand. real. Lise Hedberg for much helpful advice about the spectroscopic calculations. This work was supported by Grants CHE74-13527 and CHE78-04258 from the National Science Foundation and a grant from the OSU Computer Center.

**Supplementary Material Available:** Intensity curves for the 525 °C experiment and tables of the total intensity data, final backgrounds, symmetry coordinates, symmetry force constants, observed and calculated wavenumbers, and calculated amplitudes and perpendicular amplitudes (19 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) J. E. LuValle and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 3520 (1939).
- (2) J. R. Durig, S. E. Hannum, and S. C. Brown, *J. Phys. Chem.*, **75**, 1946 (1971).
- (3) W. G. Fateley, R. K. Harris, F. H. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1965).
- (4) R. N. Noack and R. N. Jones, *Z. Elektrochem.*, **64**, 707 (1960).
- (5) T. Miyazawa, *J. Chem. Soc. Jpn.*, **74**, 743 (1953).
- (6) (a) K. Hagen and K. Hedberg, *J. Am. Chem. Soc.*, **95**, 1003 (1973); (b) *ibid.*, **95**, 4796 (1973).
- (7) K. Hagen and K. Hedberg, *J. Am. Chem. Soc.*, **95**, 8266 (1973).
- (8) G. Gundersen and K. Hedberg, *J. Chem. Phys.*, **51**, 2500 (1969).
- (9) L. Hedberg, Abstracts, Fifth Austin Symposium on Gas Phase Molecular Structure, Austin, Texas, March 1974, No. T9.
- (10) L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055 (1971).
- (11) Y. Morino, K. Kuchitsu, and T. Oka, *J. Chem. Phys.*, **36**, 1108 (1962).
- (12) Such refinements of what is already a rather gross approximation are of questionable value. However, they are consistent with the classical model being used.
- (13) K. Hedberg and M. Iwasaki, *Acta Crystallogr.*, **17**, 529 (1964).
- (14) K. J. Hole and M. F. R. Mulcahy, *J. Phys. Chem.*, **73**, 177 (1969).
- (15) H. Knoll, K. Scherzer, and G. Geisler, *Int. J. Chem. Kinet.*, **5**, 271 (1973).
- (16) Program written by L. Hedberg in collaboration with I. M. Mills at the University of Reading, England. See L. Hedberg, Abstracts, Seventh Austin Symposium on Gas Phase Molecular Structures, Austin, Texas, Feb 1978, p 49.
- (17) K. Hagen, T. Borgers, and K. Hedberg, preliminary results.
- (18) Z. Náhlovská, B. Náhlovsky, and T. G. Strand, *Acta Chem. Scand.*, **24**, 2617 (1970).
- (19) C. Kato, S. Konaka, T. Iijima, and M. Kimura, *Bull. Chem. Soc. Jpn.*, **42**, 2148 (1969).
- (20) J. L. Derisson, *J. Mol. Struct.*, **7**, 67 (1971).
- (21) J. Tokue, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, **17**, 207 (1973).

## Linear Solvation Energy Relationships. 5. Correlations between Infrared $\Delta\nu$ Values and the $\beta$ Scale of Hydrogen Bond Acceptor Basicities<sup>1</sup>

Mortimer J. Kamlet,\* Abraham Solomonovici, and R. W. Taft\*

Contribution from the Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910, Scientific Department, Ministry of Defense, Israel, and Department of Chemistry, University of California, Irvine, California 92717.

Received August 30, 1978

**Abstract:** Infrared  $\Delta\nu$  values (free minus hydrogen bonded) of X-H bonds are shown to be linear with  $\beta$  values within families of hydrogen bond acceptor (HBA) bases having similar bonding sites, but not between families. Classes of HBA bases considered are (in order of increasing  $\Delta\nu$ 's) double-bonded oxygen, single-bonded oxygen, pyridine bases, and trialkylamines. Reasons suggested for the nonlinearity of  $\Delta\nu$  with  $\beta$  between families involve differing geometries of the hydrogen bonds (angles between axis of vibrating X-H bond and direction of acceptor dipole) and differing hybridizations on the acceptor atoms. Linear relations between  $\Delta\nu$  and  $\beta$  within families are used to amend and expand the scale of HBA basicities.

In earlier papers of these series<sup>1</sup> we described the formulation and some applications of three scales of intrinsic solvent properties: an  $\alpha$  scale of solvent HBD (hydrogen bond donor) acidities,<sup>2-4</sup> a  $\beta$  scale of HBA (hydrogen bond acceptor)

basicities,<sup>5,6</sup> and a  $\pi^*$  scale of solvent polarity-polarizabilities.<sup>7,8</sup> These indexes were intended to serve, singly or in linear combinations with one another, toward rationalization of solvent effects on many free energy proportional properties

through a schematic equation of the form

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (1)$$

where  $XYZ$  may represent a rate or equilibrium constant, a heat or free energy of solution or of transfer between solvents, or a position or intensity of maximal absorption in an IR, UV, NMR, or ESR spectrum.<sup>9</sup> The  $\delta$  term in eq 1 is a polarizability factor (equal to 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents).

A number of workers have suggested that overall solvent effects might better be described in terms of multiple-parameter rather than single-parameter equations.<sup>10,11</sup> Closest in concept to eq 1 was the approach of Koppel and Palm,<sup>12</sup> who proposed a four-parameter equation incorporating nonspecific solvent effects ("polarity" and "polarizability") and specific solute-solvent interactions (nucleophilic and electrophilic solvation):

$$XYZ = XYZ_0 + yY + pP + eE + bB \quad (2)$$

$Y$  and  $P$  in eq 2 are the solvent "polarity" and "polarizability" terms, corresponding in intent to  $\pi^*$  and  $\delta$  (eq 1);  $E$  is the electrophilicity parameter, corresponding in intent to  $\alpha$ ;<sup>13</sup> and  $B$  is the nucleophilicity parameter, corresponding in intent to  $\beta$ .

As their measure of solvent nucleophilicity, Koppel and Palm initially employed a scale of  $B$  values based on solvent shifts of the infrared O-D stretching frequency of monomeric (non-self-associated) [2H]methanol in the pure base media:

$$B = \Delta\nu_{\text{MeOD}} = \nu_{\text{MeOD}}^0 - \nu_{\text{MeOD}\cdots\text{B}} \quad (\text{cm}^{-1}) \quad (3)$$

where  $\nu_{\text{MeOD}}^0$  and  $\nu_{\text{MeOD}\cdots\text{B}}$  refer to the vapor phase and the pure base, respectively. More recently, Koppel and Paju<sup>14</sup> proposed an alternative general hydrogen bond basicity scale, also labeled  $B$ , and based on solvent shifts of the IR stretching frequencies of the free and hydrogen-bonded OH group of phenol in carbon tetrachloride media:

$$B = \Delta\nu_{\text{PhOH}}^{\text{CCl}_4} = \nu_{\text{PhOH}}^{\text{CCl}_4} - \nu_{\text{PhOH}\cdots\text{B}}^{\text{CCl}_4} \quad (\text{cm}^{-1}) \quad (4)$$

Shorter and co-workers<sup>15</sup> have refined and expanded the  $B$  (eq 3) scale on the basis of more accurate  $\nu_{\text{MeOD}}$  measurements, and a similar index of "solvent electron donating power" based on  $\Delta\nu_{\text{MeOD}\cdots\text{B}}$  (relative to  $B = \text{benzene}$ ) has been reported by Kagiya and co-workers.<sup>16</sup> The latter group also demonstrated a monotonic (but not linear) free-energy relationship between  $\log K_{\text{assn}}$  (the formation constant for the hydrogen-bonded complex of MeOD with the base) and  $\Delta\nu_{\text{MeOD}\cdots\text{B}}$ .<sup>17</sup>

Koppel and Palm<sup>12</sup> reported fair success in their use of the  $B$  (eq 3) scale to rationalize solvent effects on a variety of  $XYZ$ 's, and Chapman, Shorter, and their colleagues have had good results with this  $B$  scale in correlating the rate coefficients for the reaction of diphenyldiazomethane with benzoic acid in aprotic solvents.<sup>18</sup> Further, Koppel and Paju have reported excellent linear correlations between  $B$  (eq 3),  $B$  (eq 4) and 14 other sets of  $\Delta\nu_{\text{HX}}$  ( $\text{HX} = t\text{-BuOH}$ , pyrrole, HCl,  $\text{PhC}\equiv\text{CH}$ , HNC=O, etc.) in large numbers of HBA base solvents.

If relative HBA basicities of electron donor solvents were correctly represented by the Koppel-Palm-Paju  $B$  scales on the one hand and the Kamlet-Taft  $\beta$  scale on the other, it would logically follow that solvent  $B$  and  $\beta$  values must be proportional to one another. Unfortunately, however, no such direct correlation is observed. Indeed the nonproportionality between the  $B$  and  $\beta$  indexes is so marked and so readily evident as to indicate that one or the other of these measures of hydrogen bond basicity must be incorrect, as must be, to a greater or lesser extent, the many linear free energy relationships based thereon in the recent chemical literature.

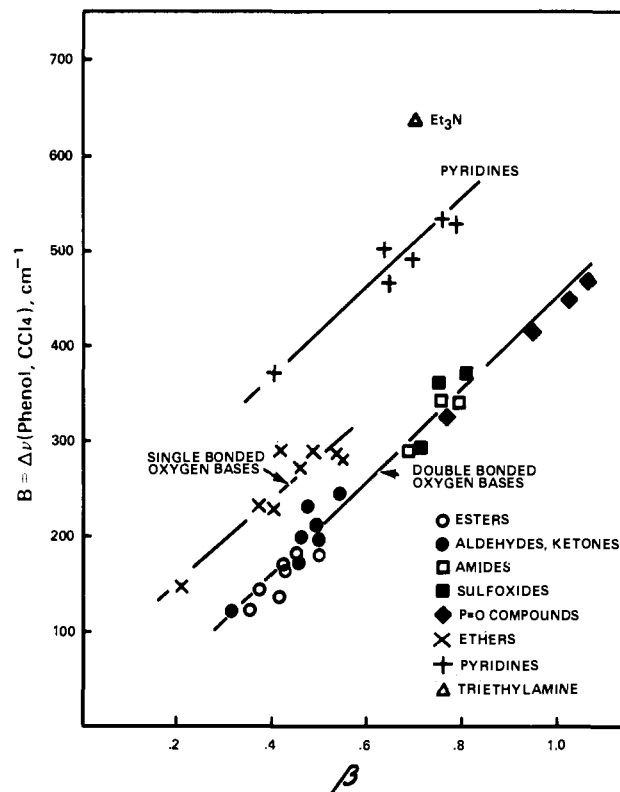


Figure 1. Relationships between  $B$  (eq 4) and  $\beta$ .

## Results

$B$  (eq 3) values of Koppel and Palm,<sup>12</sup> Shorter and co-workers,<sup>15</sup> and Kagiya and co-workers<sup>16</sup> and  $B$  (eq 4) values of Koppel and Paju<sup>14</sup> are compared with Kamlet-Taft  $\beta$  values for corresponding hydrogen bond acceptor bases in Table I. Also included in the table are  $\Delta\nu_{\text{HX}}$  values reported by Arnett and co-workers<sup>19,20</sup> for 4-fluorophenol (4-FP) and methanol with many of the same HBA bases in  $\text{CCl}_4$ . In addition to the  $\beta$  values reported earlier,<sup>5,6</sup> the table contains a number of tentative  $\beta$  values (in brackets and parentheses) estimated from previously reported correlations between  $\beta$  and (a)  $\log K_{\text{assn}}$  of the 4-FP:HBA complexes in  $\text{CCl}_4$  ( $pK_{\text{HB}}$ );<sup>21</sup> (b) limiting  $^{19}\text{F}$  NMR shifts of the same 4-FP:HBA complexes ( $^{19}\text{F}$  NMR  $\Delta$ ).<sup>5,22</sup>

The relationships between  $B$  (eq 4) and  $\beta$  are shown in Figure 1. It is seen that  $B$  (eq 4) values exhibit good linear regression with corresponding  $\beta$  values (but not passing through the origin) if the comparisons are restricted to families of bases with similar hydrogen bond acceptor sites, i.e., single-bonded oxygen bases, double-bonded oxygen bases, pyridine bases, and single-bonded nitrogen bases. It is also seen, however, that correlation would be significantly poorer if solvents from the different families should be considered together. Separations into families of straight lines are similarly evident in comparisons of  $\beta$  with  $B$  (eq 3),  $\Delta\nu_{4\text{-FP}}^{\text{CCl}_4}$ , and  $\Delta\nu_{\text{MeOH}}^{\text{CCl}_4}$ . The individual regression equations are assembled in Table II together with the  $r$  and SD measures of the goodness of the statistical fits.

## Discussion

The phenomenology shown in Figure 1 and Table II was not really unexpected, as it is a direct and necessary consequence of a series of cogent and pertinent observations reported by Gramstad beginning more than 15 years ago,<sup>23-25</sup> but largely ignored by later workers in the field. Gramstad measured  $K_{\text{assn}}$ ,  $\Delta H$ ,  $\Delta F$ ,  $\Delta S$ , and  $\Delta\nu_{\text{HA}}^{\text{CCl}_4}$  for 1:1 hydrogen-bonded complexes of phenol, pentachlorophenol, and chloroform with large

Table I. Infrared Shifts Due to Hydrogen Bonding,  $\Delta\nu$  (cm<sup>-1</sup>)

no. <sup>a</sup>	HBA base	$\beta$ <sup>f,i</sup>	PhOH, <sup>b</sup> CCl <sub>4</sub>		MeOD <sup>c</sup> pure base		4-FC <sub>6</sub> H <sub>4</sub> OH, <sup>d</sup> CCl <sub>4</sub>		MeOH, <sup>e</sup> CCl <sub>4</sub>	
			$\Delta\nu$	$\beta_i$	$\Delta\nu$	$\beta_i$	$\Delta\nu$	$\beta_i$	$\Delta\nu$	$\beta_i$
Double Bonded Oxygen Bases										
11	ethyl acetate	0.446	181		91			199		102
25	dimethylformamide	0.689	291		166			305		157
23	dimethylacetamide	0.756	343		178			356		203
26	hexamethylphosphoramide	1.056	471		234			479		269
18	acetone	0.478	224		123			232		
16	2-butanone	0.481	209		109			221		113
51	cyclopentanone	0.524			124			246		
41	cyclohexanone	0.534	242		133			229		147
29	dimethyl sulfoxide	0.764	362		192			367		199
39	ethyl chloroacetate	0.348	125		79					
47	ethyl benzoate	0.412	142							
19	triethyl phosphate	0.774 <sup>h</sup>	0.767	331	0.756			341	0.748	
27	butyrolactone	0.489	190		118					
28	<i>N</i> -methylpyrrolidone	0.774	330					339		
64	ethyl propionate	[0.459]	0.424	174	0.434	84	0.376			
58	acetophenone	(0.493)	0.488	202	0.491	108	0.476			
65	methyl <i>tert</i> -butyl ketone	[0.463]	0.446			97	0.430			
66	benzaldehyde	(0.431)	0.443	180	0.446	105	0.463			
52	methyl acetate	0.454 <sup>h</sup>	0.424	170	0.426	88	0.393			
67	diphenyl sulfoxide	(0.698)	0.681	294	0.680			311	0.685	160 0.646
68	triphenylphosphine oxide	(0.942)	0.935	420	0.939			422	0.918	237 0.935
69	dimethyltrifluoroacetamide	[0.496]	0.463					190	0.430	
70	trimethyl phosphate	(0.745)	0.733					323	0.710	
71	dimethyl- $\gamma$ -pyrone	(0.788)	0.815					400	0.871	
72	dimethylchloroacetamide	(0.620)	0.620					280	0.620	
73	trimethylphosphine oxide	[1.021]	1.020	450	1.001			480	1.039	
74	di- <i>n</i> -butyl sulfoxide	[0.818]	0.833	373	0.842			384	0.838	
75	tetramethylurea	(0.781)	0.775	340	0.775			350	0.766	
76	benzophenone	[0.447]	0.458	192	0.470					
77	biacetyl	[0.302]	0.313	121	0.324					
85	diethyl carbonate	—	0.377	145	0.374	85	0.380			
Single Bonded Oxygen Bases										
7	diethyl ether	0.466	280		129			285		139
4	diisopropyl ether	[0.466]	0.487	293	0.518	134	0.477			
5	di- <i>n</i> -butyl ether	0.453 <sup>h</sup>	0.460	285	0.499	129	0.454			
13	tetrahydrofuran	0.550	287		145			292		150
17	anisole	0.223	155		75			169		75
9	dioxane	0.369	237		128			252		122
40	tetrahydropyran	0.544	290		145					
46	dibenzyl ether	0.410 <sup>h</sup>	0.405	233	0.380			249	0.403	126 0.417
61	1,2-dimethoxyethane		0.405	238	0.393	123	0.423	248	0.400	
59	diphenyl ether		0.128	123	0.128			132	0.100	66 0.157
86	di- <i>n</i> -propyl ether		0.459	279	0.485	125	0.433			
87	phenetole		0.204	158	0.208	77	0.199			
Pyridine Bases										
24	pyridine	0.642	472					485		
78	4-methylpyridine	(0.697)	0.667	497	0.665			495	0.610	
79	2,6-dimethylpyridine	[0.711]	0.757	535	0.750			614	0.793	
80	2,4,6-trimethylpyridine	[0.750]	0.777	531	0.742			644	0.839	
81	quinoline	(0.637)	0.636	494	0.663			498	0.615	
82	3,5-dichloropyridine	(0.410)	0.418	374	0.410			385	0.441	
83	3-bromopyridine	(0.517)	0.510					421	0.496	
84	4-dimethylaminopyridine	(0.874)	0.865					650	0.848	
Trialkylamines										
3	triethylamine	0.705	650			314		756		410
48	tri- <i>n</i> -butylamine	0.618				290				

<sup>a</sup> Compound numbering is the same in all papers of this series. <sup>b</sup> References 14, 24, 25, and 26. <sup>c</sup> References 12 and 15. <sup>d</sup> References 19 and 20. <sup>e</sup> References 16 and 20. <sup>f</sup> Values in brackets estimated from  $pK_{HB}$ ; values in parentheses estimated from  $pK_{HB}$  and 4-fluorophenol <sup>19</sup>F NMR  $\Delta$ . <sup>g</sup> Amended  $\beta$  values obtained by averaging the  $\beta_i$  values estimated as in footnote *f* with  $\beta_i$  values back-calculated from the correlation equations in Table II. <sup>h</sup> Secondary value, still subject to change; see ref 6. <sup>i</sup> Unless otherwise noted,  $\beta$  values are from ref 6.

numbers of various types of HBA bases, and found excellent linear correlations between  $\Delta\nu$  and  $\log K_{assn}$  within families of bases, but not between families of bases.<sup>26</sup> Most importantly also, Gramstad and Sandstrom<sup>25</sup> showed similar separations into families in plots of  $\Delta H$  vs.  $\Delta\nu$ .

In a similar vein, Gramstad and Vikane<sup>24</sup> plotted infrared  $\Delta\nu$ (phenol, CCl<sub>4</sub>) results against limiting <sup>19</sup>F NMR shifts of 4-fluorophenol complexes with the same hydrogen bond acceptors (Gurka and Taft's data),<sup>21</sup> and showed separate, easily distinguishable regression lines for the same families of HBA

**Table II.** Correlation Equations between  $\Delta\nu$  ( $\text{cm}^{-1}$ ) and  $\beta$ 

indicator	class of HBA bases	correlation eq	$r$	SD	$n$
phenol, $\text{CCl}_4$	double-bonded oxygen	$\Delta\nu = -37.1 + 487\beta$	0.991	13.8	23
	single-bonded oxygen	$= 67.1 + 436\beta$	0.933	18.5	8
	pyridine bases	$= 180.2 + 473\beta$	0.974	14.8	6
[ $^2\text{H}$ ]methanol, pure base	double-bonded oxygen	$\Delta\nu = -6.4 + 240\beta$	0.970	11.0	16
	single-bonded oxygen	$= 36.3 + 205\beta$	0.943	8.7	7
4-fluorophenol, $\text{CCl}_4$	double-bonded oxygen	$\Delta\nu = -14.9 + 476\beta$	0.982	16.4	20
	single-bonded oxygen	$= 93.3 + 387\beta$	0.962	15.3	5
	pyridine bases	$= 97.9 + 651\beta$	0.916	43.8	8
methanol, $\text{CCl}_4$	double-bonded oxygen	$\Delta\nu = -12.1 + 266\beta$	0.980	11.7	9
	single-bonded oxygen	$= 29.7 + 231\beta$	0.980	6.8	5

bases as in Figure 1, i.e., double-bonded oxygen, single-bonded oxygen, substituted pyridines, and triethylamine. Inasmuch as the phenol  $\log K_{\text{assn}}$  results and the 4-FP  $^{19}\text{F}$  NMR  $\Delta$  results have been shown to be linear with  $\beta$ ,<sup>5</sup> the phenomenology in Figure 1 and Table II follows logically from Gramstad and co-workers' findings.

By way of contrast, the same workers<sup>24</sup> reported excellent colinearity of all families of HBA bases in plots comparing  $^1\text{H}$  NMR  $\Delta(\text{CHCl}_3:\text{HBA}, \text{CCl}_4)$  and  $^{19}\text{F}$  NMR  $\Delta(4\text{-FP}:\text{HBA}, \text{CCl}_4)$  with  $\log K_{\text{assn}}(\text{phenol}:\text{HBA}, \text{CCl}_4)$  and  $\log K_{\text{assn}}(\text{CHCl}_3:\text{HBA}, \text{CCl}_4)$ . These findings also conform with the very good linear regressions between these properties and  $\beta$  values and with the concept of linear solvation energy relationships.

Thus we must rationalize two bodies of correlational information which are self-consistent and mutually supporting within themselves, but seriously inconsistent with one another. On the one hand, we have the Kamlet-Taft  $\beta$  scale, shown to be (a) proportional to large numbers of electronic spectral  $\Delta\Delta\nu$  results (enhanced solvatochromic shifts attributable to hydrogen bonding);<sup>5,6,27</sup> (b) proportional to  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR  $\Delta$  results and linear with coupling constants for a variety of HBD and Lewis acid indicators;<sup>5,27</sup> (c) linear with  $\log K_{\text{assn}}$  for a variety of HBD:HBA complexes;<sup>5,27</sup> (d) linear with "catalytic rate constants" of HBA additives in several nucleophile-assisted reactions; (e) used with good success in combination with  $\pi^*$  values (giving  $r$  values  $> 0.98$ ) in a number of multiparameter correlations of aprotic solvent effects on reaction rates,<sup>27</sup> including the much-studied reaction of diphenyldiazomethane with benzoic acid;<sup>18</sup> (f) linear with heats of solution of a number of HBD solutes in HBA solvents; (a-f) numbering in toto over 100 correlations with  $\beta$  or with  $\pi^*$  and  $\beta$ .

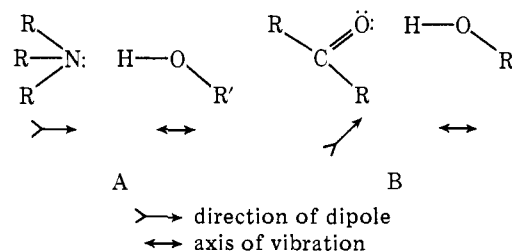
On the other hand, we have the Koppel-Palm-Paju  $B$  indexes, linear with ( $r > 0.975$ ) and very nearly proportional to one another and to  $\Delta\nu_{\text{HX}}$  results for more than 12 HBD acids with up to 89 HBA bases, and also used with good success in multiple parameter correlations (through eq 2) of solvent effects on a number of rate constants, electronic spectra, and proton chemical shifts.<sup>12,14</sup> We are faced with the unresolved inconsistency: if one of these scales is correct in concept as a measure of HBA basicity, the other is necessarily incorrect.

**Extrathermodynamic Relationships.** The incompatibility of the  $B$  and  $\beta$  indexes as measures of HBA basicity is the most recent manifestation of a long-standing controversy regarding extrathermodynamic relationships between  $-\Delta H_f$ ,  $\log K_{\text{assn}}$ , and  $\Delta\nu$  for HBA:HBD complexes. In 1937, Badger and Bauer<sup>28</sup> proposed that a linear correlation existed between  $-\Delta H_f$ 's of hydrogen-bonded complexes and their infrared  $\Delta\nu$ 's; several years later, Badger<sup>29</sup> conceded that there were fairly strong indications that the relationships might not, after all, be linear. In a 1960 review, Pimentel and McClellan<sup>30</sup> concluded that the then available data did not substantiate the Badger-Bauer relationship, and more recent workers with more and better data to draw on have been similarly critical.<sup>31</sup>

Arnett and co-workers<sup>19</sup> seem to have laid the  $-\Delta H_f$  vs.  $\Delta\nu$  question to rest in a benchmark 1974 paper comparing the various measures of "basicity". They pointed out that, "although high quality  $\Delta\nu$  values have been available for several decades, an extensive data base of reliable  $\Delta H_f$  values has only been developed during the last 10 years", and that "there is now nearly unanimous agreement that no general linear correlation exists." They also stated that, "for closely related compounds (such as those of a single functional group) interacting with the same A-H . . . good correlations (standard deviation of  $\Delta H_f \approx 0.1$  kcal/mol) are found"; i.e., similar separations into families are observed as in the  $B$  vs.  $\beta$  comparisons.

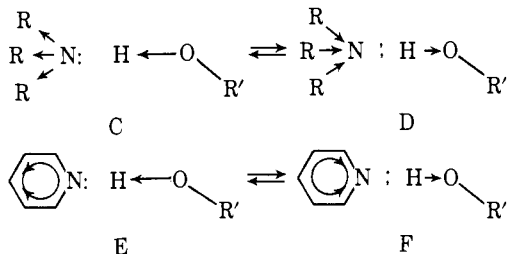
As concerns  $\Delta\nu$  vs.  $\Delta G_f$ , the evidence of Gramstad and co-workers, discussed above, leaves no doubt regarding the non-generality of frequency shift vs.  $\log K_{\text{assn}}$  linear correlations. However, there seems currently to be less consensus of opinion as to whether  $\Delta\nu$  or solution phase  $\log K_{\text{assn}}$  is a more appropriate measure of hydrogen bond acceptor strength. Koppel and Paju<sup>14</sup> suggested in 1974 that "one should pay attention to the approximate linear relationship between the  $\Delta\nu_{\text{PHOH}}$  parameter and the gas phase proton affinities." Also, Chapman and Shorter and their co-workers<sup>32</sup> have recently commented that 4-FP  $\log K_f$  ( $= \text{p}K_{\text{HBD}}$ ) appeared to have no advantage over  $B$  as a measure of solvent basicity in the correlation analysis of the reaction of diphenyldiazomethane with benzoic acid (however, we shall offer contradictory evidence regarding this reaction in a future paper).

**A Rationale for the Separation into Families.** We believe that the differing viewpoints can be reconciled and the separation into families rationalized if one considers the geometry of the hydrogen bond and the nature of the orbital hybridization on the hydrogen bond acceptor atom. It is instructive, for example, to compare the geometric relationship between the axis of the X-H vibration whose  $\Delta\nu$  is being measured and the direction of the molecular or group dipole of the HBA base in the cases of a trialkylamine (A) and a dialkyl ketone (B).



It is seen that in the first instance the X-H bond vibrates head-on into the molecular dipole of the trialkylamine, i.e., at an angle of  $0^\circ$ , while in the second instance the axis of the bond vibration is at a  $60^\circ$  angle from the direction of the dialkyl ketone molecular dipole. It is not unreasonable, therefore, that the energetics of expansion and contraction of the X-H bonds should differ significantly on hydrogen bonding to these two types of HBA bases. We consider that this effect accounts in part for the separation into families in the  $B$ - $\beta$  correlation.

The above rationale does not explain the separation into families between trialkylamine and pyridine bases, however, since in both instances the axis of the donor X-H vibration is at a 0° angle with the direction of the acceptor dipole. A second effect, suggested by Arnett and co-workers,<sup>19</sup> may provide the explanation here. The effect relates to how the differing orbital hybridization of the acceptor atom influences the energetics of the donor X-H vibration. The vibrations may be represented as follows for a trialkylamine ( $C \rightleftharpoons D$ ) and a pyridine base ( $E \rightleftharpoons F$ ).



As the X-H bonds expand and contract, they induce back and forth displacements of the nitrogen electron pairs involved in the hydrogen bonds, resulting in fluctuations of the net electron densities on the nitrogen atoms. To minimize free energies of the total systems, this leads in turn to synchronous back and forth displacements of the electrons in the other bonds to the HBA nitrogen atoms [represented by the directions of the arrows in ( $C \rightleftharpoons D$ ) and ( $E \rightleftharpoons F$ )]. In effect, as the hydrogen on the HBD acid vibrates back and forth, it pulls and pushes the total electron system of the HBA base with it. Again, it is not unreasonable that the energetics of the X-H vibration should depend on the mobility of the electron pair on nitrogen which, in turn, should depend strongly on whether only  $\sigma$  or  $\pi$  bonds are affixed to this atom.

Taking into account the above effects (whose theoretical basis we plan to explore in greater detail in a future paper), we consider that there should be no difficulty in accepting that  $\Delta\nu$  should vary with HBA basicity within families of bases having similar geometries and hybridizations on the acceptor atoms. We see no reason, however, to expect that such relationships should apply between families, as is required by the Koppel-Palm-Paju treatment and the Badger-Bauer relationship.

**The Amended and Expanded  $\beta$  Scale.** The correlations between  $\Delta\nu$  and  $\beta$  within families seemed to us to be sufficiently precise to warrant using the wealth of experimental information in Table I to amend and expand the data base for our scale of hydrogen bond acceptor basicities. We have mentioned that Table I includes a number of tentative or preliminary  $\beta$  values which were obtained by averaging  $\beta_i$ 's estimated from relationships of  $\beta$  with  $pK_{HB}$  and 4-FP <sup>19</sup>F NMR  $\Delta$ . We have, in addition, back-calculated further  $\beta_i$ 's for these bases from the  $\Delta\nu$  data in Table I and the reciprocals of the regression equations in Table II [e.g., based on the correlation equation involving phenol and double-bonded oxygen bases,  $\beta_i = (\Delta\nu + 37.1)/487$ ]. All the  $\beta_i$ 's from both sources were then averaged to yield the 32  $\beta_{cor}$  values which, with the 21 unchanged  $\beta$  values in Table I and additional values reported earlier,<sup>5,6</sup> comprise the amended and expanded scale of HBA basicities.

The table contains no surprises. The  $\beta$  value for tetramethylurea confirms that hydrogen bonding is to oxygen rather than nitrogen, and that for 4-dimethylaminopyridine confirms that bonding is to the pyridine rather than the dimethylamine nitrogen. *N,N*-Dimethyltrifluoroacetamide and dimethylchloroacetamide bear the expected relationship to dimethylacetamide and dimethylformamide [indeed, the correlation coefficient between  $\beta$  of  $RCON(CH_3)_2$  and  $\sigma^*$  of R is 0.992]. As pointed out earlier,<sup>21</sup> hydrogen-bonding basicities also

parallel proton transfer basicities within families, but not between families.

**Concluding Remarks.** It remains only to explain why earlier workers have obtained seemingly acceptable correlations of solvent effects with the  $B$  parameter. The reason becomes evident when we compare  $B$  with  $\beta$  for limited numbers of HBA bases. As an illustration, we use the 24 more common solvents in Table I for which the  $\beta$  values had been reported earlier.

If we consider only the 14 double-bonded oxygen bases, the correlation coefficient between  $\beta$  and  $B$  is 0.985. Including also the 7 single bonded oxygen bases,  $r$  is still almost 0.90, and adding pyridine and triethyl- and tributylamine,  $r$  goes to 0.83. Choosing at random some smaller number of the common solvents for the comparison, it is not unlikely that one would obtain misleadingly higher  $r$  values. Further, in multiple linear regression correlations of solvent effects with  $B$  and additional polarity-polarizability parameters (e.g., Koppel and Palm's  $Y$  and  $P$ ), and where the polarity-polarizability terms contributed fair portions of the total solvent effects, it should not be too surprising to see overall correlation coefficients of 0.95 and higher.

**Acknowledgments.** The work by A.S. was done while a Visiting Scientist at the University of Maryland. The work by M.J.K. was done under Naval Surface Weapons Center Foundational Research Task IR-144. The work by R.W.T. was supported in part by a grant from the Public Health Service.

## References and Notes

- (1) Part 13 of Solvatochromic Comparison Method Series.
- (2) R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, **98**, 2886 (1976).
- (3) Part 3: M. J. Kamlet and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 349 (1979).
- (4) Part 4: R. W. Taft and M. J. Kamlet, *J. Chem. Soc., Perkin Trans. 2*, in press.
- (5) M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976).
- (6) Part 2: M. J. Kamlet, J. L. Abboud, M. E. Jones, and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 342 (1979).
- (7) M. J. Kamlet, J. L. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977).
- (8) Part 1: M. J. Kamlet and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 337 (1979).
- (9) In most of the correlations which we have described till now, we have used equations of the form  $XYZ = XYZ_0 + s\pi^* + a\alpha$  and  $XYZ = XYZ_0 + s\pi^* + b\beta$ . The full equation incorporating the  $a\alpha$ ,  $b\beta$ , and  $d\delta$  terms has been applicable only in a few instances.
- (10) U. Mayer, V. Gutmann, and W. Gerger, *Monatsh. Chem.*, **106**, 1235 (1975); U. Mayer, *Pure Appl. Chem.*, **41**, 291 (1975); V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions", Plenum Press, New York, 1978.
- (11) T. M. Krygowski and W. R. Fawcett, *J. Am. Chem. Soc.*, **97**, 2143 (1975).
- (12) I. A. Koppel and V. A. Palm, "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Eds., Plenum Press, New York, 1972, Chapter 5.
- (13) We have shown, however, that the  $E$  term corresponds in fact to a linear combination of  $\pi^*$  and  $\alpha$ .<sup>3</sup>
- (14) I. A. Koppel and A. I. Paju, *Org. React. (USSR)*, **11**, 121 (1974).
- (15) A. G. Burden, G. Collier, and J. Shorter, *J. Chem. Soc., Perkin Trans. 2*, 1627 (1976).
- (16) T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Jpn.*, **41**, 767 (1968).
- (17) T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Jpn.*, **41**, 773 (1968).
- (18) N. B. Chapman, M. R. J. Dack, and J. Shorter, *J. Chem. Soc. B*, 834 (1971); N. B. Chapman, M. R. J. Dack, D. J. Newman, J. Shorter, and R. Winkinson, *J. Chem. Soc., Perkin Trans. 2*, 962 (1974).
- (19) E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, *J. Am. Chem. Soc.*, **96**, 3875 (1974).
- (20) E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2365 (1970).
- (21) R. W. Taft, D. Gurka, L. Joris, P. v. R. Schleyer, and J. W. Rakshys, *J. Am. Chem. Soc.*, **91**, 4801 (1969); D. Gurka and R. W. Taft, *ibid.*, **91**, 4794 (1969).
- (22) The correlation equations are  $\beta_i = (pK_{HB} + 1.00)/4.399$  and  $\beta_i = {}^{19}\text{F NMR } \Delta/4.578$ .
- (23) T. Gramstad, *Spectrochim. Acta*, **19**, 497, 829, 1363 (1963).
- (24) T. Gramstad and O. Mundheim, *Spectrochim. Acta, Part A*, **28**, 1405 (1972).
- (25) T. Gramstad and J. Sandstrom, *Spectrochim. Acta, Part A*, **25**, 31 (1969).
- (26) Gramstad's results apparently distinguished esters, ketones, amides, S=O, and P=O compounds from one another, whereas we class them together

as double-bonded oxygen bases. From the rationale which we advance for the separation into families, we consider that Gramstad is probably correct and that our  $\beta$  values (which average  $\beta_i$ 's from many diverse properties and from experimental information of variable precision) are insufficiently precise for the distinctions to become evident.

- (27) Many of these correlations will be reported in future papers of this series.  
 (28) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).  
 (29) R. M. Badger, *J. Chem. Phys.*, **8**, 288 (1940).

- (30) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman, San Francisco, 1960.  
 (31) E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961); S. Wada, *Bull. Chem. Soc. Jpn.*, **35**, 707 (1962); R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3221 (1962); R. West, D. L. Powell, M. K. T. Lee, and L. S. Whatley, *ibid.*, **86**, 3227 (1964); D. L. Powell and R. West, *Spectrochim. Acta*, **20**, 883 (1964).  
 (32) A. G. Burden, N. B. Chapman, H. F. Duggua, and J. Shorter, *J. Chem. Soc., Perkin Trans. 2*, 296 (1978).

## Conformation of 3'-Nucleotides. Crystal Structure of Uncharged 3'-Uridine Monophosphate Monohydrate and Hydrogen Bonding to the Furanose Ring Oxygen

T. Srikrishnan, Susan M. Fridey, and R. Parthasarathy\*

Contribution from the Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, New York 14263. Received September 20, 1978

**Abstract:** An accurate X-ray crystallographic investigation of the structure of 3'-UMP in the free acid form has been carried out. 3'-UMP in the solid state exists as an uncharged molecule, unlike AMP, CMP, and GMP, which are zwitterions in the solid state. The uncharged phosphate group exhibits shorter P-O distances (P-O(ester), 1.567 Å; P-OH, 1.502, 1.521 Å) compared to anionic phosphate groups, indicating that a distinction between the individual P-O<sup>-</sup> and P-OH based purely on the basis of bond distances alone without considering the phosphate group as a whole is not valid. The ribose has the C(2')-endo conformation; the pseudorotation parameters are  $P = 165^\circ$  and  $\tau_m = -38.9^\circ$ . The anti conformation ( $\chi_{CN} = 55.8^\circ$ ) of the molecule and the  $g^+$  orientation of O(5') across C(4')-C(5') are stabilized by an intramolecular C(6)-H...O(5') hydrogen bond. The phosphate group assumes the characteristic staggered conformation across the P-O bonds. The torsion angles  $\psi'$  (C(5')-C(4')-C(3')-O(3')) and  $\phi'$  (C(4')-C(3')-O(3')-P) are respectively 150.1 and 226.3°. The molecular conformation derived from NMR and energy calculations is in broad agreement with the X-ray results. The molecules related by the  $a$  translation are on top of each other at 6.3 Å apart; facing this stack is another related by the  $2_1$  screw. The two stacks interleave such that the O(2) from one and H(C5) from the other project into each other. Hydration is promoted by cation coordination; when the ions form an "inner-sphere" complex, as in most crystals of nucleotides with metal ions, the basic features of the "rigid nucleotide" are conserved. However, deviations from the "rigid nucleotide", though not favored, are possible under appropriate conditions such as the formation of "outer-sphere" complexes or coordination of metal ions through the phosphate groups. The furanose ring oxygen participates in a hydrogen bond (O(2')-H...O(1'), 2.912 Å; H...O(1'), 1.80 Å; O(2')-H...O(1'), 168°), an uncommon occurrence in the usual nucleosides, and the first example in a nucleotide. It is suggested that a similar, but an intramolecular hydrogen bond from O(2')-H of one residue to the O(1') of the next residue on the 5' side is possible for RNAs and might indicate one of the important functions of 2'-OH in RNA compared to DNA. The crystals of 3'-UMP·H<sub>2</sub>O are orthorhombic,  $a = 6.133$  (1),  $b = 7.465$  (2),  $c = 30.256$  (4) Å, space group  $P2_12_12_1$ ; final  $R$  value is 0.051 for 1512 reflections  $> 2\sigma$ .

The conformation analysis of nucleic acid polymers has been greatly facilitated by the availability of conformational data on mononucleotides and by the recognition of the preferred conformations of these monomers.<sup>1</sup> Stereochemical information on mononucleotides have been gathered mainly by using X-ray and NMR techniques. Though extensive studies by NMR on 3'-nucleotides have been carried out, very few X-ray diffraction studies have been carried out on 3'-nucleotides compared to 5'-nucleotides. It has been demonstrated that the 3'- and 5'-phosphate bonds in mononucleotides behave differently with respect to radiation-induced breakage<sup>2</sup> and radiation sensitization.<sup>3</sup> This paper describes the result of our crystallographic studies on 3'-UMP. All the mononucleotides AMP, CMP, and GMP (see discussion later) exist in the solid state as zwitterions, but UMP does not, thereby affording an opportunity to study the conformation of an uncharged nucleotide.

### Experimental Section

Transparent, plate-like crystals of 3'-UMP (Nutritional Biochemical) were obtained by slow evaporation of an aqueous solution (crystals kindly supplied to us by Dr. H. C. Box of our department). The unit cell dimensions were obtained by a least-squares refinement of 45 high-angle reflections ( $\theta \geq 45^\circ$ ) and are given in Table I along with other pertinent crystallographic data. Complete intensity data

were collected to the limit of  $2\theta = 165^\circ$  for Cu K $\alpha$  radiation. The stationary crystal-stationary counter techniques<sup>4</sup> were employed for obtaining the intensities with a 5° takeoff angle on a GE XRD-6 diffractometer; 1743 reflections were measured out of which 231 had their intensities less than twice the background in that  $\sin \theta/\lambda$  range, and were given zero weight during the refinement. The crystal was mounted with the  $b^*$  along the  $\phi$  axis of the goniostat and the difference in absorption as a function of  $\phi^5$  was measured for the axial reflections and was used for correcting approximately the anisotropy of absorption. The data were processed in the usual way.

**Solution and Refinement of the Structure.** The position of the phosphorus atom (P) was found from a sharpened Patterson synthesis but the P-phased electron density maps did not reveal the structure completely. A model consisting of P and 10 atoms was used as a starting structure. The other nonhydrogen atoms were found by a successive least-squares refinement combined with difference electron density maps. The  $R$  factor  $[(\sum ||F_o| - |F_c||)/(\sum |F_o|)]$  at the end of the isotropic refinement was 0.11. Further refinements were continued with anisotropic temperature factors for the nonhydrogen atoms and the  $R$  value converged to 0.073. A difference electron density synthesis at this stage revealed all the hydrogen atoms. The final cycles of refinement were calculated using a full-matrix least-squares refinement<sup>6</sup> with individual isotropic and anisotropic temperature factors for the hydrogen and nonhydrogen atoms, respectively. The final  $R$  value was 0.051. The quantity minimized was  $\sum w(|F_o|^2 - (1/k^2)|F_c|^2)^2$  where the weight  $w = 1/\sigma^2(|F_o|^2)$  and  $k$  is the scale factor. Atomic scattering factors and the anomalous