Studies on Amphiprotic Compounds. 3.[1] Hydrogen-Bonding Basicity of Oxygen and Sulfur Compounds

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The hydrogen bonding (HB) basicity parameters, β_m, for various "monomeric" alcohols and thiols, as well as for a variety of carbonyl and thiocarbonyl *amphiprotic* bases, have been determined. Also determined were the HB basicity parameters, β, for a series of *aprotic* carbonyl and thiocarbonyl bases ($\beta_m = \beta$ for these materials). The analysis of the data for a set of 62 compounds provides the basis for comparison of structural effects on the HB basicity of oxygen and sulfur bases. In general, the HB basicity of sulfur bases is lower than that of their oxygen homologues. Within families, structural effects on the basicity of oxygen and sulfur bases are proportional. Our results show the contributions from polarizability and field/inductive and resonance effects to the basicity of these compounds. Also some differential contributions from steric hindrance and hybridization changes have been singled out. The relative stability of cyclic 1:1 complexes involving amphiprotic thioamides and 4-chlorophenol has been evaluated.

I. Introduction

Recent studies have shown the usefulness of the empirical parameters π^* (dipolarity–polarizability), α (hydrogen-bonding acidity), and β (hydrogen-bonding basicity) for the quantitative analysis of solvent effects on chemical reactivity,[8] solubility,[9] and spectral (UV–vis, IR, EPR) and biological properties.[9]

We have pointed out[1] that the determination of β values for "monomeric" self-associating compounds, β_m, requires the use of special techniques. This is so because the use of solvatochromic indicators[10a] dissolved in the bulk liquids provides a measure of the "average" basicity of "monomers" and "oligomers".

Consider equilibrium 1, describing the hydrogen-bonding (HB) association between a nonamphiprotic HB base, B, and a proton donor, H–A, in dilute solution in an inert solvent, S. K_c and K_x respectively stand for the equilibrium constants for this reaction expressed in liters/mole and in mole fraction units. It is found[1,10b] that

$$\text{H–A} + \text{B} \underset{\text{S}}{\rightleftharpoons} \text{A–H...B} \qquad (1)$$

$$\log K_x \text{ (or } \log K_c) = a + b\beta + c\mu \qquad (2)$$

where a, b, and c are constants and β and μ respectively stand for the HB basicity parameter and the molecular dipole moment of the base. For nonamphiprotic bases, $\beta_m = \beta$ and the agreement between β values generated through eq 2 and by means of solvatochromic indicators is generally excellent.[10] Indeed, eq 2 has been extensively used as a source of β values for nonamphiprotic bases (the "final" values being an average of these and solvatochromic[10] data). This equation has thus been used for the purpose of determining the β values for amphiprotic compounds under high dilution conditions. As previously shown,[1] it is important that the HB acid, H–A, be strong in order to minimize the self-association of the base.

In this work we have determined the formation constants of HB complexes involving 3,4-dinitrophenol (A–H acid) and several oxygen and sulfur compounds (B), in dilute cyclohexane solutions. These results combined with data taken from the literature or from our own previous studies are intended to provide a general view of structural effects on the HB basicity of oxygen and sulfur compounds.

II. Experimental Results

The use of eq 2 requires the previous determination of the unknowns a, b, and c. This can be achieved by correlating a set of equilibrium constants pertaining to the associations between the appropriate proton donor and a series of non-self-associating bases having well-known β and μ values. We have applied this method to associations involving 3,4-dinitrophenol (1) in c-C_6H_{12} at 23.3 °C as well as phenol (2), 4-fluorophenol (3), and 4-chlorophenol (4) in CCl_4 at 25.0 °C. In all cases, the correlation between β and μ for these data sets is quite small.

The parameters a, b, and c have been used to treat the experimental equilibrium constants, K_x and K_c, given in Table I, to yield the final β_m values collected in the same table.

Other β_m values, taken from various sources, are summarized in Table II. We emphasize again that, for nonamphiprotic HB bases, $\beta_m = \beta$.

III. Discussion

A. Precision and Physical Meaning of the β_m Values. The standard deviation of fit through eq 2 is ca. 0.1 log units. Given the size of coefficient b in this equation, the maximum uncertainty on a single determination of β_m is ca. 0.04 β units. If we compare the β_m values for

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[1] Part 2: Abboud, J.-L. M.; Sraidi, K.; Guihéneuf, G.; Negro, A.; Kamlet, M. J.; Taft, R. W. *J. Org. Chem.* **1985**, *50*, 2870.

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[8] (a) Taft, R. W.; Abboud, J.-L. M.; Kamlet, M. J.; Abraham, M. H. *J. Solution Chem.* **1985**, *14*, 153. (b) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

[9] (a) Kamlet, M. J.; Doherty, R. M.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *CHEMTECH* **1986**, 566. (b) Kamlet, M. J.; Doherty, R. M.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Pharm. Sci.* **1986**, *75*, 338. (c) Taft, R. W.; Abraham, M. H.; Doherty, R. M.; Kamlet, M. J. *Nature (London)* **1985**, *313*, 384. (d) Kamlet, M. J.; Abraham, M. H.; Doherty, R. M.; Taft, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 464.

[10] (a) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485 and references therein. (b) Kamlet, M. J.; Dickinson, C.; Gramstad, T.; Taft, R. W. *J. Org. Chem.* **1982**, *47*, 4971.

0022-3263/88/1953-1545$01.50/0

Table I. Equilibrium Constants K_c or K_x Used for the Determination of β_m Values for Oxygen and Sulfur Bases

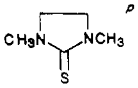
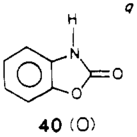
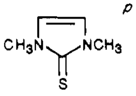
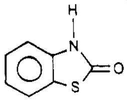
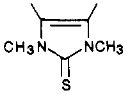
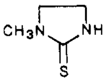
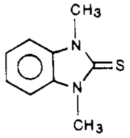
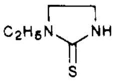
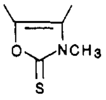
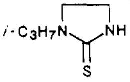
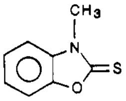
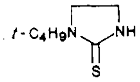
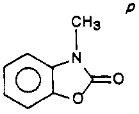
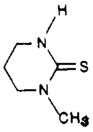
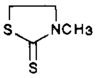
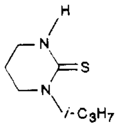
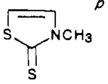
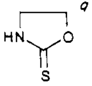
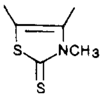
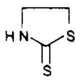
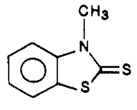
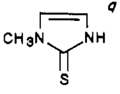
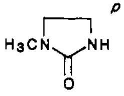
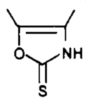
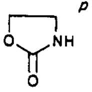
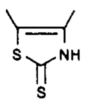
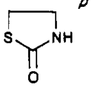
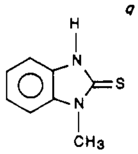
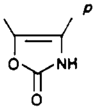
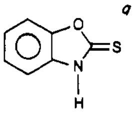
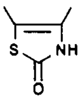
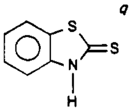
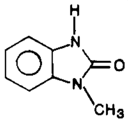
base[a]	K_c[b] or K_x[c,d]	β_m[e,f]	base[a]	K_c[b] or K_x[c,d]	β_m[e,f]
CH_3OH [**1**(O)][d]	$(1.41 \pm 0.11) \times 10^3$	0.43	$CH_3C(S)N(CH_3)_2$ [**14**(S)][i]	10.7	0.41
C_2H_5OH [**2**(O)][g]	$(2.62 \pm 0.21) \times 10^3$	0.48	$SC[N(CH_3)_2]_2$ [**13**(S)][i]	14.7	0.44
n-C_4H_9OH [**3**(O)][g]	$(3.14 \pm 0.25) \times 10^3$	0.49	$CH_3OC(S)N(CH_3)_2$ [**15**(S)][i]	4.61	0.33
i-C_3H_7OH [**4**(O)][g]	$(4.25 \pm 0.21) \times 10^3$	0.52	$CH_3SC(S)N(CH_3)_2$ [**16**(S)][i]	3.44	0.28
t-C_4H_9OH [**5**(O)][g]	$(6.94 \pm 0.35) \times 10^3$	0.56	$(C_2H_5)_3PS$[**17**(S)][j]	4.30	0.33
C_2H_5SH [**6**(S)][h]	21.3 ± 0.3	0.11	$C_2H_5OC(O)N(C_2H_5)_2$ [**18**(O)][k]	63	0.63
n-C_3H_7SH [**7**(S)][h]	27.6 ± 0.4	0.13	$CH_3SC(O)N(C_2H_5)_2$ [**19**(O)][k]	36	0.56
i-C_3H_7SH [**8**(S)][h]	32.6 ± 0.2	0.15	$(C_2H_5)_2S$ [**10**(S)][l]	2.71	0.28
t-C_4H_9SH [**9**(S)][h]	43.5 ± 0.3	0.17	$(n$-$C_4H_9)_2S$ [**20**(S)][l]	2.88	0.29
$(C_2H_5)_2S$ [**10**(S)][h]	153.8 ± 6.1	0.27	$HC(S)N(CH_3)_2$ [**12**(S)][m]	14.6 ± 1.0	0.38
$(CH_2)_4S$ [**11**(S)][h]	463 ± 41	0.33	$SC[N(CH_3)_2]_2$ [**13**(S)][m]	24.3 ± 1.7	0.44
$HC(S)N(CH_3)_2$ [**12**(S)][h]	$(6.52 \pm 0.45) \times 10^3$	0.35	$CH_2SC(S)SCH_2$ [**21**(S)][n]	1.6	0.14
$SC[N(CH_3)_2]_2$ [**13**(S)][h]	$(34.7 \pm 0.6) \times 10^3$	0.47	camphor [**22**(O)][o]	11	0.40
 **23** (S)[p]	32	0.45	 **40** (O)[q]	140	0.66*
 **24** (S)[p]	18	0.39	 **41** (O)[q]	110	0.59*
 **25** (S)[p]	95	0.57	 **42** (S)[q]	120	0.61*
 **26** (S)[p]	22	0.45	 **43** (S)[p]	64	0.54*
 **27** (S)[p]	24	0.45	 **44** (S)[p]	62	0.54*
 **28** (S)[p]	8	0.31	 **45** (S)[p]	50	0.51*
 **29** (O)[p]	29	0.47	 **46** (S)[p]	90	0.58*
 **30** (S)[p]	11	0.35	 **47** (S)[p]	82	0.57*
 **31** (S)[p]	9	0.36	 **48** (S)[q]	35	0.47*
 **32** (S)[p]	19	0.44	 **49** (S)[q]	30	0.46*

Table I (Continued)

base[a]	K_c[b] or K_x[c,d]	β_m[e,f]	base[a]	K_c[b] or K_x[c,d]	β_m[e,f]
 **33** (S)	6	0.30	[q] **50** (S)	245	0.67*
[p] **34** (O)	600	0.81	[q] **51** (S)	100	0.58*
[p] **35** (O)	160	0.65	[q] **52** (S)	100	0.59*
[p] **36** (O)	115	0.63	[q] **53** (S)	50	0.54*
[p] **37** (O)	420	0.76	[q] **54** (S)	25	0.42*
[q] **38** (O)	200	0.68	[q] **55** (S)	20	0.43*
[q] **39** (O)	360	0.79			

[a] The proton donor, solvent, and temperature are as follows: 1, cyclohexane, and 23.3 °C for bases 1(O) to 13(S); 2, carbon tetrachloride, and 25.0 °C for bases 14(S) to 17(S); 3, carbon tetrachloride, and 25.0 °C for bases 18(O) to 19(O); 4, carbon tetrachloride, and 25 °C for all other bases. [b] In liters/mole. [c] In mole fraction units. [d] All the constants involving 1 are K_x values. All others are K_c values. [e] Values with an asterisk pertain to cases wherein $\beta_{tr} < \beta_m$. [f] Calculated through eq 2. [g] From ref 1. [h] This work. [i] Reference 18. [j] Reference 19. [k] Reference 20. [l] Reference 21. [m] Reference 22. [n] Reference 23. [o] Reference 24. [p] Reference 12c. [q] Reference 12a.

Table II. Selected β Values from Other Sources

base	β
thiocamphor [**56**(S)][a]	0.17
CH_3S-n-C_4H_9 [**57**(S)][b]	0.26
$CH_3OC(S)$-n-C_4H_9 [**58**(S)][b]	0.25
$CH_3SC(S)$-n-C_4H_9 [**59**(S)][b]	0.18
$CH_3OC(O)$-n-C_4H_9 [**60**(O)][b]	0.45
$CH_3SC(O)$-n-C_4H_9 [**61**(O)][b]	0.43
CH_3O-n-C_4H_9 [**62**(O)][b]	0.48

[a] Reference 11b. [b] Reference 11a.

compounds **20**(S), **12**(S), and **13**(S) obtained with different HB acids, we see that they nicely agree within these limits. The agreement between the β_m values obtained by means of eq 2 and those obtained by Begtrup, Taft, and Kamlet[11a] using ^{13}C NMR spectroscopy is also very good. Thus, these workers give β_m [**57**(S)] = 0.26, a value that, as expected, is close to, but lower than, β_m [**10**(S)] = 0.27, determined in this work.

Electrostatic contributions to the overall stability of the HB complexes are reflected by the presence of the μ term in eq 2. Experimentally determined dipole moments for some heterocycles included in this study are not available, and the poor additivity of mesomeric bond moments makes the estimated values rather uncertain. The ratio c/b is always small, so that even an error of 0.5 D will not affect the calculated β_m's by more than 0.01 β units.

Finally, we stress that β_m values for self-associating compounds are intended to provide a "pure" measure of the HB basicity of their basic centers. We know, however, that there are cases wherein favorable steric conditions allow the existence of stable cyclic structures.[12] The as-

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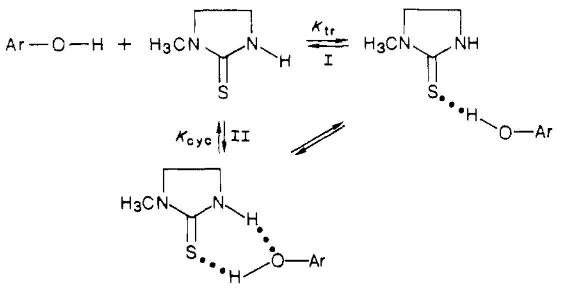
(11) (a) Begtrup, M.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1986**, *51*, 2130. (b) β_m value determined from a limited correlation involving FCH_2CH_2OH complexes (Singh, S.; Murthy, A. S. N.; Rao, C. N. R. *Trans. Faraday Soc.* **1966**, *62*, 1056).

(12) (a) Gentric, E. Thesis, University of Brest. (b) Gentric, E.; Lauransan, J.; Roussel, C.; Metzger, J. *J. Chem. Res., Synop.* **1980**, 48 and references therein. (c) Gentric, E.; Lauransan, J.; Roussel, C.; Metzger, J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1015.

Scheme I



sociation between 4-chlorophenol (Ar–OH) and **42**(S) provides a representative example (Scheme I). It is clear that, in these cases, the β_m values do not reflect the "true" basicity of the molecule. More precisely, let us consider a reference proton donor such as 4-chlorophenol and an amphiprotic base such as **42**(S). Let K_c be the experimentally determined gross equilibrium constant, while K_{tr} and K_{cyc} stand for the equilibrium constants pertaining to the competing equilibria I and II (Scheme I). In any case,

$$K_c = K_{tr}(1 + K_{cyc}/K_{tr}) \qquad (3)$$

and

$$\log K_c = \log K_{tr} + \log (1 + K_{cyc}/K_{tr}) \qquad (4)$$

From eq 2 it follows that

$$\beta_m = \beta_{tr} + \beta_{cyc} \qquad (5)$$

where β_{tr} stands for the value taken by β_m, had eq 2 been applied to K_{tr}. As we shall see in the next section, there is a simple method allowing the estimation of β_{tr} and β_{cyc}.

B. Structural Effects. Some Interesting Features Revealed by Inspection of Tables I and II. 1. Alcohols, Thiols, Ethers, and Thioethers. We have shown in part 2 of this series[1] that the relative HB basicities of "monomeric" aliphatic alcohols, ROH, are largely determined by the polarizabilities of the aliphatic moieties of these compounds. The HB basicity of thiols follows the same pattern. There is a limited linear relationship between β_m (ROH) and β_m (RSH), as shown in Figure 1. The slope of the line is ca. 1.4, indicating that the HB basicity of alcohols is some 40% more sensitive to the polarizability of the alkyl substituents than that of the thiols. This is reasonable, on account of the C–S and S...H bonds being longer than the C–O and O...H ones. Also, the bonding oxygen lone pair is less diffuse, and further, there is a greater relief of lone pair–lone pair repulsion resulting from HB to oxygen than to corresponding sulfur lone pairs.

The HB basicity of aliphatic ethers has long been known.[13] to be very sensitive to the steric contributions from R and R′. The longer bond lengths involved in the assocations of thioethers would explain why the HB basicity of the latter smoothly increases with the chain length and branching of the substituents, while no simple pattern appears in the case of ethers.[13]

Figure 1 also shows that thioethers are appreciably stronger HB bases than thiols, while ethers have HB basicities comparable to, and often smaller than, those of the alcohols. Again, steric effects could explain this behavior, but we cannot rule out other important factors, such as hybridization differences.[14]

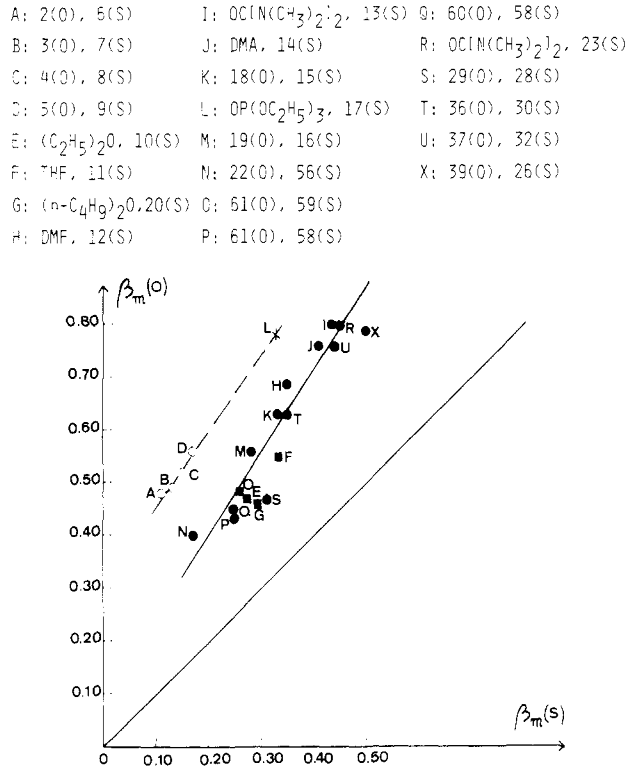


Figure 1. β_m values for sulfur HB bases vs β_m values for HB oxygen bases having the same or closely related structures. Open circles: alcohols and thiols. Closed circles: carbonyl and thiocarbonyl compounds. Squares: ethers and thioethers.

2. Carbonyl and Thiocarbonyl Compounds. Taft, Gramstad, and Kamlet[15] have discussed the influence of structural effects on the β values of nonamphiprotic carbonyl compounds, XC(O)Y. These workers have found that, for a constant X, these parameters follow expressions of the form of eq 6 where σ_I and σ_R^+ are parameters

$$\beta = \rho_I\sigma_I + \rho_R\sigma_R^+ + \text{constant} \qquad (6)$$

measuring the field/inductive and resonance contributions of substituent Y.[16] The corresponding equations for Y = CH_3, OC_2H_5, and $N(CH_3)_2$ are as follows:

$$\beta\ [CH_3C(O)Y] = 0.40 - 0.56\sigma_I - 0.20\sigma_R^+ \qquad (7a)$$

$$\beta\ [C_2H_5OC(O)Y] = 0.30 - 0.46\sigma_I - 0.14\sigma_R^+ \qquad (7b)$$

$$\beta\ [(CH_3)_2NC(O)Y] = 0.70 - 0.74\sigma_I - 0.072\sigma_R^+ \qquad (7c)$$

These equations show that, as the π-donor ability increases from CH_3 to C_2H_5O to $N(CH_3)_2$, i.e., as given by its σ_R^+ value, the magnitude of the ρ_R value, as well as the ratio ρ_R/ρ_I, decreases; that is, electronic saturation reduces the π donation to the carbonyl group. Saturation effects of this sort have been reported in the case of the charge-transfer complexes between carbonyl bases and iodine.[17]

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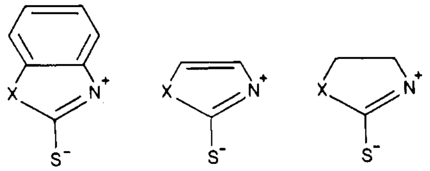
[13] (a) West, R.; Powell, D. L.; Lee, M. K. T.; Whatley, L. S. *J. Am. Chem. Soc.* **1959**, *81*, 6141. (b) Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223. (c) Abboud, J.-L. M.; Bellon, L. *Ann. Chim. (Paris)* **1970**, *5*, 63. (d) Bellon, L.; Taft, R. W.; Abboud, J.-L. M. *J. Org. Chem.* **1980**, *45*, 1166.

[14] The lone pairs on the oxygen atoms of alcohols and ethers are likely to have an appreciably higher s character than those on the sulfur atoms of thiols and thiothers, as indicated by the following bond angles: in CH_3CH_2SH, CSH = 96° (Hargittai, I.; Schultz, G. *J. Chem. Soc., Chem. Commun.* **1972**, 323), and in CH_3SCH_3, CSC = 98.9° (Pierce, L.; Hayashi, M. *J. Chem. Phys.* **1961**, *35*, 479), while in CH_3OH, COH = 108° 32′ (*J. Chem. Phys.* **1968**, *48*, 5299) and in $(C_2H_5)_2O$, COC = 112° 02′ (André, D.; Fourme, R.; Zechmeister, K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, B*28*, 2389).

[15] Taft, R. W.; Gramstad, T.; Kamlet, M. J. *J. Org. Chem.* **1982** *47*, 4557.

[16] (a) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1. (b) Taagepera, M.; Summerhays, K. D.; Hehre, W. J.; Topsom, R. D.; Pross, A.; Taft, R. W. *J. Org. Chem.* **1981**, *46*, 891.

Scheme II



In general, β values for cyclic HB bases are somewhat higher than those for acyclic compounds having closely related structures. The fact that β (Me_2CO) = 0.48, while for 3-pentanone, β = 0.45, suggests that, at least, a part of the difference between the β values for this compound and for cyclopentanone has a steric origin. Other couples show smaller cyclization effects. At this point we cannot exclude the existence of minor electronic contributions arising from small hybridization changes, but in any case, the smaller steric hindrance, alone, should lead to larger β values for cyclic compounds. For our present purposes we shall consider the "normal" difference between the β (or β_m) values for a cyclic compound and an acyclic one of closely related structure to range between 0.0 and 0.04 β units. If we compare *N*-methylimidazolidinone [**34**(O)] and tetramethylurea, we find that their respective β values are 0.81 and 0.80. This difference is quite reasonable. The same holds for the carbamate 18(O) and the oxazolidine **35**(O): both compounds have very close β_m values. The azolidines **34**(O) and **35**(O) are amphiprotic, but these comparisons suggest that their β_m values reflect their "intrinsic" basicities, that is, process II (Scheme I) does not seem to significantly contribute to the experimental K_c values. For the thiocarbamate **19**(O), β = 0.56, while for the thiazolidine **36**(O), β_m = 0.63. We consider that this case shows the onset of effects originating in the competing process II. As we shall see, these contributions can be quite large. Let us next reexamine Figure 1: we observe the existence of a rather good linear relationship between the β (or β_m) values of carbonyl and thiocarbonyl bases, of closely related structures, whenever process I is the sole (or the main) association mechanism. The regression equation is

$$\beta\ (\mathrm{C{=}S}) = -0.04 + 0.607\beta\ (\mathrm{C{=}O}) \qquad (8)$$

with n = 12 (excluding the **29**(O), **28**(S) couple), r = 0.979, and SD = 0.02 β units.

This shows a *general proportionality of structural effects on the HB basicities of carbonyl and thiocarbonyl compounds.* The slope of eq 8, ca. 0.60, indicates the attenuation of structural effects on the basicity of thiocarbonyl compounds, relative to carbonyl bases. Both a distance effect *and* a reduced conjugation of the C=S group can explain this fact. The couple **29**(O), **28**(S) (point S in Figure 1) is well below the regression line. We also notice that point X (that is, the couple **39**(O), **26**(S)) is also below this line, albeit to a much lesser extent. These facts suggest that the proportionality of substituent effects on the HB basicities of the carbonyl and thiocarbonyl groups might well break down whenever these groups strongly compete with the aromatic ring for the lone pairs of the substituent(s). Indeed, the better conjugated, less electronically saturated carbonyl should be more strongly affected than the thiocarbonyl.

Next we compare the β values for the thiazolidine **30**(S), the thiazoline **31**(S), and the benzothiazoline **33**(S). We find β [**30**(S)] = 0.35, β [**31**(S)] = 0.36, and β [**33**(S)] = 0.30. This ranking indicates that mesomeric structures such as those shown in Scheme II become increasingly important in the order benzothiazoline < thiazoline $\lesssim$ thiazolidine.

Field/inductive effects should also tend to reduce the electronic density on the thiocarbonyl group of **33**(S) relative to that of **30**(S). We also find that β [**32**(S)] = 0.44. This value is even larger than that for **30**(S), implying that field/inductive and hyperconjugative contributions from the methyl groups can overcome the effects discussed above. Analogous behavior appears in the series **23**(S), **24**(S), and **26**(S) as well as in the couple **27**(S), **28**(S). We also confirm[12] (see Table I) that, *for each of the series azolidine, azoline, benzazoline, the relative HB basicity ranks as follows: imidazole > oxazole > thiazole.*

In a future paper we shall discuss the HB acidities of "monomeric" carbonyl and thiocarbonyl compounds containing the $\overline{\mathrm{XC(O)NHY}}$ and $\overline{\mathrm{XC(S)NHY}}$ moieties. At this point, however, we devote our attention to the β_{cyc} values for these compounds. For the purpose of estimating β_{cyc} for an amphiprotic heterocycle, $\overline{\mathrm{XC(O)NHY}}$ or $\overline{\mathrm{XC(S)NHY}}$, we take its β_{tr} to be equal to the β value pertaining to its N-methylated derivative. If such a value is not available, β_{tr} is taken to be equal to the β value for an open-chain compound of closely related structure. Finally, the β values for some N-methylated compounds can be estimated by means of eq 8. Although admittedly crude, these "ground rules" seem reasonable.

It is remarkable that *the β_{cyc} values for most carbonyl compounds are either nil or very small, while those for the thiocarbonyl derivatives are often quite large.* The larger lone pairs on the sulfur atom likely reduce the geometric constraints regarding bond angles, thus favoring the formation of cyclic complexes. Compounds **40**(O) and **41**(O) have sizable β_{cyc} values. This is likely a consequence of the acidity of the NH group being enhanced through conjugation with the aromatic ring.

IV. Conclusion

Without exception, sulfur HB bases have been found to be weaker than their oxygen homologues.

We have shown the existence of a family-dependent proportionality between the HB basicities of these two series of bases. Also, some significant differential factors have been singled out. The stability of cyclic 1:1 complexes involving amphiprotic thioamides and 4-chlorophenol has been estimated.

Experimental Section

Thiols, thioethers, and *N*,*N*-dimethylthioformamide were Aldrich products dried over 3-Å molecular sieves (Merck) and fractionally distilled. Tetramethylthiourea (Aldrich) was recrystallized twice. The origin and purification of cyclohexane and 3,4-dinitrophenol as well as the working conditions used in the determination of the equilibrium constants are given in ref 1.

In all cases, the purity of the reagents was checked by GLC or TLC. The structures were confirmed by IR and NMR techniques.

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(17) Rafik, C.; Abboud, J.-L. M.; Guihéneuf, G. *J. Org. Chem.* **1983**, *48*, 4761.

(18) Gramstad, T.; Sandström, J. *Spectrochim. Acta, Part A* **1969**, *25A*, 31.

(19) Reyntjens-Van Damme, D.; Zeegers-Huyskens, Th. *J. Phys. Chem.* **1980**, *84*, 282.

(20) Joris, L.; Mitsky, J.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 3438.

(21) Ginzburg, I. *Opt. Spektrosk.* **1964**, *17*, 57.

(22) Reyntjens-Van Damme, D.; Zeegers-Huyskens, Th. *Spectrosc. Lett.* **1976**, *9*, 765.

(23) Mukherjee, S.; Palit, S. R.; De, S. K. *J. Phys. Chem.* **1970**, *74*, 1389.

(24) Leicknam, J. P. Thesis, University of Paris, 1966.

to Prof. Louis Bellon on his 70th birthday.

Registry No. **1**(O), 67-56-1; **2**(O), 64-17-5; **3**(O), 71-36-3; **4**(O), 67-63-0; **5**(O), 75-65-0; **6**(S), 75-08-1; **7**(S), 107-03-9; **8**(S), 75-33-2; **9**(S), 75-66-1; **10**(S), 352-93-2; **11**(S), 110-01-0; **12**(S), 758-16-7; **13**(S), 2782-91-4; **14**(S), 631-67-4; **15**(S), 16703-45-0; **16**(S), 3735-92-0; **17**(S), 597-51-3; **18**(O), 3553-80-8; **19**(O), 37174-63-3; **20**(S), 544-40-1; **21**(S), 822-38-8; **22**(O), 76-22-2; **23**(S), 13461-16-0; **24**(S), 6596-81-2; **25**(S), 25433-07-2; **26**(S), 3418-46-0; **27**(S), 25444-93-3; **28**(S), 13673-63-7; **29**(O), 21892-80-8; **30**(S), 1908-87-8; **31**(S), 5685-07-4; **32**(S), 21364-38-5; **33**(S), 2254-94-6; **34**(O), 694-32-6; **35**(O), 497-25-6; **36**(O), 2682-49-7; **37**(O), 59167-68-9; **38**(O), 25444-99-9; **39**(O), 1849-01-0; **40**(O), 59-49-4; **41**(O), 934-34-9; **42**(S), 13431-10-2; **43**(S), 29704-02-7; **44**(S), 20406-60-4; **45**(S), 61406-12-0; **46**(S), 24421-05-4; **47**(S), 29228-88-4; **48**(S), 5840-81-3; **49**(S), 96-53-7; **50**(S), 25433-05-0; **51**(S), 6670-14-0; **52**(S), 5351-51-9; **53**(S), 2360-22-7; **54**(S), 2382-96-9; **55**(S), 149-30-4.

Supplementary Material Available: A more detailed version of this paper, containing a discussion of β_{cyc} values, tables of the experimental dipole moments and equilibrium constants used for the calculation of the coefficients *a*, *b*, and *c*, as well as tables of these parameters, the dipole moments and equilibrium constants used for the determination of the β_m values for the bases studied in this work, β values for cyclic and acyclic bases of closely related structures, and β_{cyc} values for amphiprotic oxygen and sulfur bases (37 pages). Ordering information is given on any current masthead page.

Reaction of Diphenylcarbene with Diphenyldiazomethane[†]

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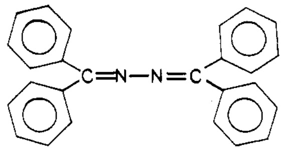
The reaction of diphenylcarbene with diphenyldiazomethane, which leads to the corresponding azine, has been examined by a combination of laser flash photolysis techniques and product studies. In acetonitrile at room temperature, the apparent rate constants for carbene plus diazo compound are 2.3×10^{10} and 3.4×10^7 M^{-1} s^{-1} for the singlet and triplet species, respectively.

A wealth of kinetic data now exists on the reactions of singlet and triplet arylcarbenes with various substrates.[1,2] However, there appears to be virtually no data concerning one of their most common reactions, that of the carbene with its parent diazo compound. Product studies on the thermolysis of diphenyldiazomethane in hydrocarbon solvents show that substantial amounts of benzophenone azine (I)[3,4] are formed.


(1)

I

Experimentally, the reaction belongs to a general class where a triplet ground-state species appears to react with a singlet substrate to yield molecular products in apparent contravention of the Skell–Woodworth rules.[5] Thus, alcohols,[3,6-8] nitriles,[9,10] ketones,[11] and thioketones[12] all quench the optical absorption spectra of the triplet carbene. The usual explanation for this type of observation has been the proposal, originally advanced by Bethell,[4] that the singlet and triplet states of the carbene are in equilibrium; the reactivity is then attributed to the singlet population present. An alternative explanation, which we have suggested for the reactions of alcohols,[6] amines,[13] and carbon tetrachloride[14] with diphenylcarbene is that the triplet may not simply function as a reservoir for the singlet carbene through an equilibrium mechanism but may be directly involved in the above reactions. The direct reaction of the triplet carbene with the substrate has been definitely established in some cases of carbene addition to thioketones.[12] For example triplet fluorenylidene reacts with adamanthanethione with a rate constant of 6.4×10^9 M^{-1} s^{-1} in Freon 113 at room temperature. Since the reaction is essentially diffusion controlled, it cannot be explained in terms of a small population of an upper (i.e., singlet) state.

In this paper we report the results of product and laser flash photolysis studies which lead to rate constants for the reactions of singlet and triplet diphenylcarbene with diphenyldiazomethane in acetonitrile solution.

Experimental Section

Materials. Diphenyldiazomethane was prepared by the literature method[15] and purified by vacuum sublimation. Methanol and acetonitrile (Aldrich) were spectroscopic grade and were purified by distillation from calcium hydride. Authentic samples

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[†] Issued as NRCC-28638.

(1) For a review, see: Griller, D.; Nazran, A. S.; Scaiano, J. C. *Acc. Chem. Res.* **1984**, *17*, 283.

(2) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Tetrahedron* **1985**, *41*, 1525.

(3) Miller, R. J.; Schechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7920.

(4) Bethell, D.; Stevens, G.; Tickle, P. J. *J. Chem. Soc. D* **1970**, 792. Bethell, D.; Hayes, J.; Newall, A. R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1307.

(5) Woodworth, R. C.; Skell, P. S. *J. Am. Chem. Soc.* **1959**, *81*, 3383.

(6) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198.

(7) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

(8) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543.

(9) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813. Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227.

(10) Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833. Barcus, R. L.; Wright, B. B.; Platz, M. S.; Scaiano, J. C. *Tetrahedron Lett.* **1983**, *24*, 3955.

(11) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6631.

(12) McGimpsey, W. G.; Scaiano, J. C. *Tetrahedron Lett.* **1986**, *27*, 547.

(13) Nazran, A. S.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 4613.

(14) Barcus, R. L.; Platz, M. S.; Scaiano, J. C. *J. Phys. Chem.* **1987**, *91*, 695.

(15) Smith, L. I.; Howard, K. L. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 351.

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