

actions were run in the dark. The reactions with the naphthalene compounds gave only good first-order plots and quantitative yields when run under a nitrogen atmosphere. The reaction of 1-fluoro-4-nitronaphthalene with *n*-butylamine was extremely slow at low amine concentrations and the determination of an infinity value or even an evaluation by the Guggenheim method became impractical. In these runs the reaction was only followed during the first few percent and the infinity value calculated under the assumption of a quantitative yield. The stopped-flow experiments for the reaction of 1-fluoro-2,4-dinitrobenzene with piperidine were carried out on a Durrum²² stopped-flow spectrophotometer.²³

The evaluation of the curvilinear plot of k_A vs. amine concentration, to provide k_1 , k_2/k_{-1} , and k_3^B/k_{-1} , was according to standard procedures^{4,16} in the reaction of piperidine with 1-fluoro-2,4-dinitrobenzene.

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Registry No.—1-Fluoro-2,4-dinitrobenzene, 70-34-8; 1-fluoro-4-nitronaphthalene, 341-92-4; 1-fluoro-4,5-dinitronaphthalene, 52385-37-2; *N*-(4-nitronaphthyl)piperidine, 34599-45-6; *N*-(4-nitronaphthyl)-*n*-butylamine, 57091-55-1; *N*-(4,5-dinitronaphthyl)piperidine, 57091-56-2; *N*-(4,5-dinitronaphthyl)-*n*-butylamine, 57091-57-3; piperidine, 110-89-4; *n*-butylamine, 109-73-9.

References and Notes

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- (a) Alfred P. Sloan Fellow, 1971–1973; (b) Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina; part of this work was carried out at Córdoba.
- For recent reviews see (a) C. F. Bernasconi, *MTP Int. Rev. Sci., Org. Chem. Ser. One*, 1973, 3, 33 (1973); (b) F. Pietra, *Q. Rev., Chem. Soc.*, 23, 504 (1969); (c) J. Miller, "Aromatic Nucleophilic Substitution", American Elsevier, New York, N.Y., 1968; (d) T. J. de Boer and I. P. Dirix in "The Chemistry of the Nitro and Nitroso Groups", Part I, H. Feuer, Ed., Interscience, New York, N.Y., 1969, p 487; (e) S. D. Ross, *Prog. Phys. Org. Chem.*, 1, 31 (1963).
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Electronegativity, Hybridization, and Properties of the Carbonyl Group. I. Lewis Basicity

Carlos A. L. Filgueiras^{1a} and James E. Huheey^{*1b}

Department of Chemistry, University of Maryland, College Park, Maryland 20742

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The basicity of a series of lactams, $C(O)N(CH_2)_n$, lactones, $C(O)O(CH_2)_n$, cyclic ureas, $CH_3NC(O)N(CH_2)_n$, and cyclic carbonates, $OC(O)O(CH_2)_n$, $n = 2$ to $n = 5$, was studied with respect to the acids phenol and 1,1,1,3,3,3-hexafluoro-2-propanol. The enthalpies of reaction (measured by infrared spectroscopy, $\Delta\nu_{CO}$) increased in every case: four-membered rings < five-membered rings < six-membered rings \leq seven-membered rings. The results are explained in terms of the charge capacity of the methylene groups (inductive effect), the effect of ring size upon hybridization and electronegativity, and steric inhibition of resonance from ring strain in small rings.

Although the Lewis basicity of the carbonyl group has been widely studied,²⁻⁵ the factors contributing to the base strength have never been adequately clarified. In this paper we report experiments which indicate that previous workers may have overemphasized certain contributions and minimized other, equally important ones.

It has long been known that the carbonyl group in amides is more basic than that in ketones^{2f,6} when measured in nonpolar solvents. Furthermore, the basicity of esters is only slightly less than that of ketones^{2f} despite the inductive effect of the electronegative amido and alkoxy groups in the carboxylic acid derivatives. More recently, a limited number of gas-phase proton affinities have been determined. The proton affinity of acetamide is about 37 kcal/mol more exothermic than that of acetone and esters are at least as basic as acetone.⁷

We have undertaken the study of the basicity of a series of cyclic bases in nonpolar solvents. We here report the basicities of several lactones, cyclic carbonates, lactams, and cyclic ureas toward phenol and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as measured by infrared spectroscopy ($\Delta\nu$ of the OH band⁴). We use the term *basicity* in its broadest sense, the ability of an electron donor to donate electron density to an electron acceptor,^{8a} which is conveniently measured operationally by the enthalpy of reaction. Ideally, of course, the gas-phase proton affinities are desirable,^{8b} but in view of the interesting effects and some controversy arising from hard-soft interactions^{8c,9} or, alternatively, electrostatic-covalent effects,^{8d,10} we feel that restricting the definition of basicity to proton affinities is undesirable and will simply require that a neologism be invented to replace the old term.

Experimental Section

Reagents. All solvents were Eastman spectrograde. All bases were of the highest purity commercially available and used without further purification (liquids were kept over molecular sieves) except for the following.

1-Acetylpiperidine, γ -butyrolactone, ϵ -hexanolactone, 1-methyl- δ -valerolactam, and tetramethylurea were purchased as practical or technical grades from Aldrich and Eastman and distilled under reduced pressure (9–15 mm).

Ethylene Carbonate. Eastman practical grade was recrystallized from a mixture of equal parts of benzene and chloroform (mp 38–40°).

***N,N*-Dimethylaminoacetone.** Aldrich technical grade was distilled at reduced pressure [bp 27° (9 mm)]. The colorless pure compound becomes yellow and then brown after a few hours; a freshly distilled sample was used each time.

Pyridine. This was distilled at atmospheric pressure (bp 115.5°).

δ -Valerolactone. This compound shows a marked tendency to polymerize even at room temperature. The method of Saotome and Kodaira¹¹ was used to convert the partially polymerized material into the monomer. The mixture was treated above 200° and distilled under reduced pressure [bp 130° (19 mm), n_{20}^D 1.4500]. The pure lactone was used immediately and also kept over phosphorus pentoxide, remaining unpolymerized for several weeks.

***N,N*-Dimethylethyleneurea** was prepared by the Eschweiler-Clarke reaction^{12,13} from a mixture of 43.0 g (0.50 mol) of ethyleneurea, 90.8 ml (1.21 mol) of 3 aqueous formaldehyde, and 187.2 ml (1.50 mol) of 99% formic acid refluxed on a steam bath for 48 hr. The solution was evaporated to approximately one-half of its original volume, 140 ml of 6 M NaOH was added, and the mixture was extracted with eight 200-ml portions of ether. The ether was evaporated and the residue was distilled under reduced pressure (15 mm). The fraction (14.6 g) boiling at 106–108° was collected. It was neutralized with 10 ml of 1 M HCl and extracted with six 15-ml portions of ether. The evaporation and distillation were repeated, yielding 10.62 g (18.2% yield) of a pale yellow oil [bp = 107–108° (15 mm)]. Other physical constants: mol wt (by mass spectroscopy), 114.073 (calcd, 114.079); n_{20}^D 1.4690; nuclear magnetic resonance spectrum, δ_{CH_2} 3.24 ppm from Me₄Si (reported²⁹ 3.24), δ_{CH_3} 2.74 ppm from Me₄Si (reported¹⁴ 2.75).

***N,N*-Dimethyltrimethyleneurea.** The Eschweiler-Clarke reaction was used as above on a mixture of 50 g (0.5 mol) of trimethyleneurea, 100 ml (3.61 mol) of 3 aqueous formaldehyde, and 187.2 ml (5 mol) of 99% formic acid. The fraction of extracted product boiling at 114–115° (10 mm) was collected, proved to be neutral to litmus, and was redistilled, yielding 29.42 g (43.1%) of product. Since the compound is light sensitive and hygroscopic it was kept over phosphorus pentoxide in the dark. Other physical constants: mol wt (by mass spectroscopy) 128.096 (calcd, 128.095); n_{20}^D 1.4852; nuclear magnetic resonance spectrum, δ_{CH_2} 1.98, 3.26 ppm from Me₄Si (reported²⁹ 1.98, 3.25); δ_{CH_3} 2.88 ppm from Me₄Si (reported¹⁴ 2.92).

The reference Lewis acids were Eastman 1,1,1,3,3,3-hexafluoro-2-propanol, used as received and kept over molecular sieves, and phenol. The latter was purified according to the procedure of Draper and Pollard:¹⁵ 88 g of phenol, 12 g of water, 0.1 g of aluminum turnings, and 0.05 g of sodium bicarbonate were distilled until all the azeotrope was driven off (bp \leq 99°). Then the pure phenol was distilled at reduced pressure [bp 114–115° (10 mm)]. The 66.19 g (0.703 mol) of phenol that was recovered was dissolved in 100.00 ml of spectrograde CCl₄, giving 170.9 ml of a 4.114 M solution that was kept over phosphorus pentoxide in the dark. The dilute solutions used were prepared from this stock solution. In the absence of light this solution stayed unaltered for several weeks. Periodic purity checks were made by nuclear magnetic resonance.

Equipment. All the infrared spectroscopy was carried out using a Digilab FTS-14 Fourier transform spectrophotometer and the cells used had sodium chloride windows with 0.1- or 1.0-mm spacers. The number of scans for each sample varied according to need and ranged from 80 to 300.¹⁶ Two parallel investigations were undertaken, viz., the interaction of several bases with phenol and with 1,1,1,3,3,3-hexafluoroacetone.

Procedure. Pure phenol was prepared as described above. Dilutions of the stock solutions to concentrations of 0.055 and 0.563 M were made. Several dilute solutions of each base were prepared using the phenol solution as the solvent.¹⁶ The infrared spectra of these solutions show a band due to the phenol-base interaction. Triangulation of this band yielded the frequency shift between the free OH group and the hydrogen-bonded OH group. Each spec-

Table I

Base	$-\Delta H_{\text{calorim}}$, kcal/mol	$\Delta\nu_{\text{OH}}$, cm ⁻¹ (this work)	$\Delta\nu_{\text{OH}}$, cm ⁻¹ (lit. values)
Acid: Phenol			
CH ₃ CN	4.6 ^a	155	178, ^b 150 ^c
CH ₃ COOCH ₃	4.8 ^d	160	171, ^e 164 ^f
CH ₃ COCH ₃	5.1 ^a	202	193 ^b
[(CH ₃) ₂ N] ₂ CO	6.6 ^d	331	338 ^f
CH ₃ CON(CH ₃) ₂	6.8 ^a	345	345 ^b
(CH ₃) ₂ SO	6.9 ^e	350	359, ^b 366 ^e
Acid: HFIP			
CH ₃ CN	5.9 ^g	198	208 ± 10 ^g
CH ₃ COCH ₃	6.7 ^g	222	280 ± 10 ^g
CH ₃ CON(CH ₃) ₂	8.5 ^g	410	428 ± 10 ^g
(CH ₃) ₂ SO	8.7 ^g	402	449 ± 10 ^g

^a Reference 4d. ^b K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 2874 (1967). ^c Reference 17. ^d Reference 4c. ^e Reference 2f. ^f Private communication from H. F. Henneke reported in ref 2f. ^g Reference 4b.

trum was recorded several times (in general, six times¹⁶) and the frequency shifts measured with a pair of calipers and averaged. The measurements were found to be reproducible to ± 5 cm⁻¹. A linear regression of base concentration vs. frequency shift was computed by the method of least squares for each system. Extrapolation gave the frequency shifts at infinite base dilution.¹⁷

Several solutions of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were prepared and a 0.0637 M solution in CCl₄, used throughout the whole experiment, was found to be free of intermolecular hydrogen bonding. The infrared spectrum of HFIP shows two sharp peaks at 3610 and at 3575 cm⁻¹. The 3610-cm⁻¹ peak was used to compute the frequency shifts.¹⁸ The procedure used in the phenol studies was repeated with HFIP and the reproducibility was the same.

Table I shows the values of $-\Delta H$ and $\Delta\nu_{\text{OH}}$ used in determining the equations relating the two experimental variables in the systems under study. Least-squares regressions were calculated for the data presented in Table I. The resulting equations follow.

(a) for systems with phenol as the acid

$$-\Delta H = 0.0114\Delta\nu_{\text{OH}} + 2.88 \quad (1)$$

(with a correlation coefficient, $r = 0.998$)

(b) for systems with HFIP as the acid

$$-\Delta H = 0.0119\Delta\nu_{\text{OH}} + 3.8 \quad (2)$$

(with a correlation coefficient, $r = 0.984$)

Results and Discussion

Figure 1 is a least-squares plot of $(\Delta\nu_{\text{OH}})_{\text{PhOH}}$ vs. $(\Delta\nu_{\text{OH}})_{\text{HFIP}}$. The straight line indicates a relationship between the two sets of data given by the equation

$$(\Delta\nu_{\text{OH}})_{\text{HFIP}} = 1.131(\Delta\nu_{\text{OH}})_{\text{OH}} + 13.840 \quad (3)$$

The high correlation coefficient ($r = 0.979$) for the linear relationship between the two methods of estimating base strength from infrared frequency shifts indicates that the two methods are self-consistent and give equivalent results.

The results of the measurements are given in Table II (phenol) and Table III (HFIP) for both cyclic and acyclic compounds. The interactions of π bonding and inductive effects can readily be determined. In their simplest form they can be seen in the simple acyclic ketones, esters, and amides. Substitution of electron-withdrawing substituents lowers the basicity: acetone > alkyl acetates > dialkyl carbonates. In contrast, the substitution of an amido group *increases* the basicity: acetone < dimethylacetamide. The enhanced basicity of amides is ascribed to delocalization of the nitrogen lone pair into the carbonyl π system.⁶ We have found that insertion of a methylene group between the nitrogen atoms and the carbonyl group results in a decrease

Table II
OH Frequency Shift and Enthalpies of Phenol-Base Hydrogen Bonding Calculated from Spectrophotometric Data

Base	Registry no.	$\Delta\nu_{\text{OH}}, \text{cm}^{-1}$		$-\Delta H, \text{kcal/mol}$	
		This work	Lit. values	This work	Lit. values
Acetone	67-64-1	202	193 ^a	5.2	5.1 ^b
Acetonitrile	75-05-8	155	178, ^a 150 ^c	4.7	4.6 ^b
1-Acetylpiperidine	618-42-8	314		6.5	
Bis(pentamethylene)urea	57031-52-4	302		6.3	
γ -Butyrolactone	96-48-0	169		4.8	
Diethyl carbonate	105-58-8	156		4.7	
<i>N,N</i> -Dimethylacetamide	127-19-5	345	345 ^a	6.8	6.8 ^b
Dimethylaminoacetone	15364-56-4	215		5.3	
Dimethyl carbonate	616-38-6	151		4.6	
<i>N,N</i> -Dimethylethyleneurea	3715-67-1	311		6.4	
<i>N,N</i> -Dimethylpropionamide	758-96-3	282		6.1	
Dimethyl sulfoxide	67-68-5	350	359, ^a 366 ^d	6.9	6.9 ^d
<i>N,N</i> -Dimethyltrimethyleneurea	57031-53-5	352		6.9	
Ethylene carbonate	96-49-1	159		4.7	
ϵ -Hexanolactone	502-44-3	225		5.5	
Methyl acetate	79-20-9	160	171, ^d 164 ^e	4.7	4.8 ^f
<i>N</i> -Methylbutyrolactam	872-50-4	336		6.7	
<i>N</i> -Methylvalerolactam	931-20-4	360		7.0	
Neopentylene carbonate	3592-12-9	210		5.3	
β -Propiolactone	57-57-8	146		4.5	
Propylene carbonate	108-32-7	156		4.7	
Pyridine	110-86-1		465 \pm 10 ^g		8.0 ^f
Tetramethylurea	632-22-4	331	338 ^e	6.7	6.6 ^f
δ -Valerolactone	542-28-9	222		5.4	

^a K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 2874 (1967). ^b Reference 4d. ^c Reference 17. ^d Reference 2f. ^e Private communication from H. F. Henneke reported in ref 2f. ^f Reference 4c. ^g Private communication from H. F. Henneke reported in ref 4d.

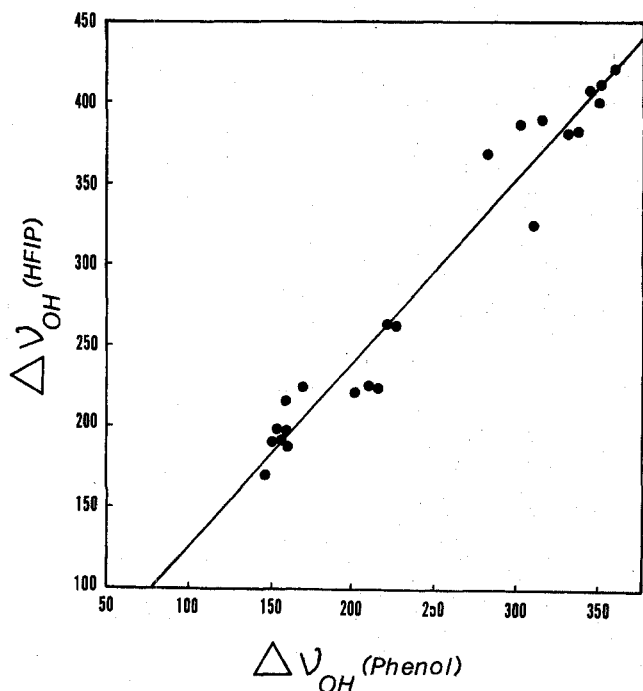
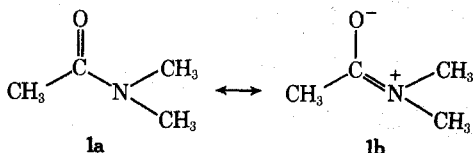


Figure 1. Correlation between $(\Delta\nu_{\text{OH}})_{\text{HFIP}}$ and $(\Delta\nu_{\text{OH}})_{\text{phenol}}$.

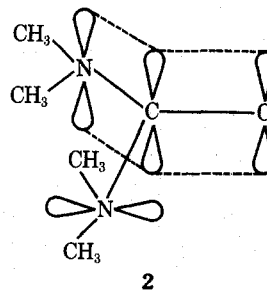
in enthalpy of adduct formation by about 1.5–2.2 kcal/mol which tends to confirm the importance of resonance as shown by 1a and 1b. Thus with phenol we obtain enthalpy



values of -6.8 (DMA) compared to -5.3 (*N,N*-dimethylaminoacetone) and with HFIP we obtain values of -8.7 and -6.5 , respectively.

Now the concept of resonance or its equivalent molecular orbital delocalization requires that the six (or five) atoms composing the amide (or ester)¹⁹ group be planar or nearly so.

Molecular orbital calculations²¹ show that the charge on the oxygen of acetone is 0.12 unit less negative than that on the oxygen of the amide. Since urea is known to be planar,²² it is reasonable to assume that similar compounds like *N,N*-dimethylamide and tetramethylurea are also planar unless steric effects prohibit it. Based on this assumption, Middaugh, Drago, and Niedzielski²³ calculated that the electron density on the oxygen atom of tetramethylurea (2) should be 0.08 charge unit more negative than that of the oxygen atom in *N,N*-dimethylacetamide (1). Therefore, TMU should be more basic than DMA, but the opposite is observed experimentally. This surprising result has been explained²³ on the basis of the steric requirements of resonance described above. If the methyl groups of TMU interact sufficiently to prevent planarity, the increased delocalization expected in TMU will not obtain, and the basicity will be of the same extent as in DMA.



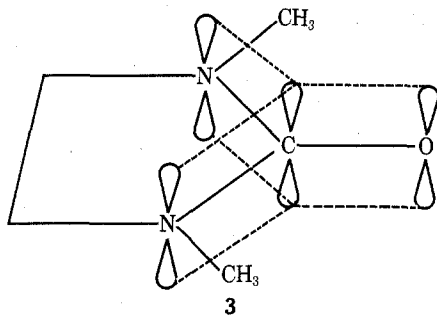
We have therefore tested a series of cyclic compounds in which the geometry of the amide linkage is known or can be approximated fairly well. Although the formation of a planar or quasi-planar ring system should reduce such steric inhibition of resonance, our results show that in every case the basicity of the cyclic compound is either the same as or

Table III
OH Frequency Shift and Enthalpies of HFIP-Base Hydrogen Bonding Calculated from Spectrophotometric Data

Base	$\Delta\nu_{\text{OH}}, \text{cm}^{-1}$		$-\Delta H, \text{kcal/mol}$	
	This work	Lit. values	This work	Lit. values
Acetone	222	280 ± 10^a	6.4	6.7^a
Acetonitrile	198	208 ± 10^a	6.2	5.9^a
1-Acetylpiperidine	391		8.4	
Bis(pentamethylene)urea	387		8.4	
γ -Butyrolactone	224		6.5	
Diethyl carbonate	197		6.1	
<i>N,N</i> -Dimethylacetamide	410	428 ± 10^a	8.7	8.5^a
<i>N,N</i> -Dimethylaminoacetone	223		6.5	
Dimethyl carbonate	190		6.1	
<i>N,N</i> -Dimethylethyleneurea	326		7.7	
<i>N,N</i> -Dimethylpropionamide	370		8.2	
Dimethyl sulfoxide	402	449 ± 10^a	8.6	8.7^a
<i>N,N</i> -Dimethyltrimethyleneurea	414		8.7	
Ethylene carbonate	189		6.1	
ϵ -Hexanolactone	263		6.9	
Methyl acetate	216		6.4	
<i>N</i> -Methylbutyrolactam	384		8.4	
<i>N</i> -Methylvalerolactam	423		8.8	
Neopentylene carbonate	225		6.5	
β -Propiolactone	170		5.8	
Propylene carbonate	191		6.1	
Tetramethylurea	383		8.4	
δ -Valerolactone	264		6.9	

^a Reference 4b.

less than that of the open-chain compound. Particularly important in this regard is *N,N'*-dimethyleneurea (3), in



which the nitrogen p orbitals are optimally aligned for delocalization, in contrast to the sterically favored staggered arrangement of 2. However, our results show that toward phenol the cyclic compound yields a reaction enthalpy 0.3 kcal/mol less than dimethylacetamide and towards HFIP the enthalpy is 0.7 kcal/mol less. In the corresponding carbonates there is no significant difference in the cyclic and acyclic compounds. In contrast, in the *nonplanar*²⁴ six-membered rings, the basicity is increased for all compounds studied. We therefore conclude that whether a *second* nitrogen (or oxygen) atom has its p orbital parallel or nonparallel to the first has little or no effect on the basicity of the carbonyl group.

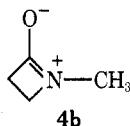
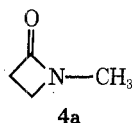
Our data thus show the importance of the delocalization of the nitrogen lone pair (in the decreased basicity of those compounds in which the delocalization is interrupted by insertion of a methylene group) in amides and its relative unimportance in the case of urea compounds (where steric inhibition of resonance seems to be unimportant). We believe that this apparent paradox can be rationalized by considering the importance of *charge capacity*.²⁵ Small atoms such as oxygen and fluorine have a relatively low ability to accept charge and can be readily "saturated" by a good electron-donating group.²⁶⁻³⁰ In such cases, the addition of a second donating group is not expected to increase the charge density on the oxygen or fluorine to any great extent.

An important trend that may be observed in the data is that in all of the series studied, the basicity increases: four-membered ring < five-membered ring < six-membered ring < seven-membered ring. This order of basicity for the lactones has been reported previously by Tsuda et al.,³¹ though the factors involved have not been thoroughly elucidated. We interpret these data in terms of three factors particularly important in cyclic compounds: the inductive effect (charge capacity), hybridization, and steric inhibition of resonance. With respect to the inductive effect, larger rings will exhibit a greater charge capacity of the methylene groups to donate electron density through the σ system to the carbonyl group.

The second factor is the change in hybridization, and hence in electronegativity, of the carbonyl carbon as the ring size is varied. The smaller the ring, the more p character must be utilized in the intraring bonding and the more s character is directed toward the exocyclic oxygen atom. Since electronegativity increases with increasing s character,^{26,32} the smaller the ring, the more electronegative the carbonyl carbon will appear to the exocyclic oxygen. Thus more electron density is withdrawn from the latter making it less basic. Similar effects have been observed in the acid-base properties of biphenylene,³³ quinoxalines,³⁴ and phosphinic acids.³⁵ Further evidence that the effect is inherent in the ring size and is not due to solvation effects comes from the gas-phase proton affinities of cyclic ketones,³⁶ which follow the order reported here.

It is noteworthy that the changes in carbonyl basicity in cyclic compounds parallel similar changes in the infrared stretching frequencies, and the latter can be quantitatively related to rehybridization and electronegativity effects.³⁷ We thus feel that these two independent approaches to the electronic structure of the carbonyl group serve to substantiate each other. The idea that carbonyl basicity and stretching frequencies should be related is not new,³⁸ but it has been suggested³⁹ that this effect does not extend to cyclic compounds.

Finally, delocalization in small rings will suffer from steric inhibition of resonance since added strain energy of canonical form 4b will reduce its contribution to the reso-



nance hybrid. This effect, like the hybridization of the carbonyl carbon atom, will always be affected by the bond angle and strain and therefore the two effects will always work in concert. Thus, although this latter effect may be involved in the basicity of cyclic compounds, it is of little heuristic value and we therefore discount its importance in this regard.

Our order of basicity confirms the one reported by Tsuda et al., who investigated the donor abilities toward deuterioethanol in benzene. They also reported the pK_b 's of those bases as

β -propiolactone	$pK_b = 10.05$
γ -butyrolactone	$pK_b = 6.12$
δ -valerolactone	$pK_b = 5.10$
ϵ -hexanolactone	$pK_b = 5.31$

This is the order one would expect based on inductive effects if solvation effects appear for the bulky last compound in the series and then only in aqueous solution. The corresponding lactones (and carbonates) are less basic than their nitrogen counterparts for the obvious reason that the oxygen in the ring is such a poor π donor. Whereas the π -bonding ability of nitrogen is very marked, that of oxygen is virtually nil.

We conclude, therefore, that although our data are consonant with the delocalization of π electrons, the constraints of cyclic compounds reveal important σ effects such as charge capacity and hybridization which may be more important than some π effects such as minor changes in geometry or addition of a second heteroatom donor. Such effects are presumably also present, though to a lesser degree and less clearly delineated, in the more relaxed acyclic systems. Furthermore, although none of the explanations presented here is novel, we believe that our data allow the evaluation of the predominant influence of hybridization and concomitant electronegativity effects on the acid-base properties of cyclic systems. Further supportive data and discussion will be presented in a forthcoming publication.⁴⁰

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Supplementary Material Available. A listing of the phenol, HFIP, and base concentrations, cell path length, number of scans, and experimental values of $\Delta\nu$ described in this paper (8 pages) will appear following these pages in the microfilm edition of this volume of the journal.

References and Notes

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