of the C(3)-O(4)-C(5) and C(6)-O(7)-C(8) fragments.

Results and Conclusions

The presented low-temperature X-ray and neutron study on the complex of 18-crown-6 with two cyanamides shows that the bonding between the molecules consists, on the one hand, of hydrogen bridges and, on the other hand, of dipole-dipole interactions. As a result of these forces the "chemical symmetries", characteristic for the isolated molecules, are not preserved in the complex. Asymmetries are present in the molecular geometry as well as in the local features of the deformation density.

The N-H···O hydrogen bonds lead to extra charge concentration in the lone-pair region of the participating oxygen atoms in the direction of the proton. This excess density can formally be described as an enrichment in the distribution of the σ nonbonded orbital. As a result, only one maximum is found in the electron deformation density, calculated in the bisecting plane of the C-O-C angle. In contrast, the oxygen atom, which is not involved in a hydrogen bond, exhibits distinct lone-pair peaks. As there is no further charge accumulation between the donor and the acceptor, the hydrogen bond can be characterized as mainly an electrostatic interaction.

The significantly varying bond lengths indicate that some of the C-O bonds in the crown are more polarized than others. The stronger bonds exhibit a higher charge density midway between the atoms. The valence deformation of the oxygen atom in a nonsymmetric C-O-C fragment has a more depleted area in the longer than in the shorter bond. The analysis of the dipole-dipole interactions in terms of dipole moments, calculated from the multipole populations, revealed that these asymmetries in the crown are induced by the electric field of the cyanamide molecule.

In order to analyze the details of the host-guest interactions in crown ether complexes with ionic guests also, further experimental charge density studies are being undertaken.

Acknowledgment. We gratefully acknowledge the substantial support of this work by a grant from the Bundesminister für Forschung und Technologie under contract No. 03-Lu1FUB-0-D1-58 and financial assistance by the Fonds der Chemischen Industrie. We thank the ILL, Grenoble, for providing the neutron beam facilities. Experimental help was given by David Gregson.

Registry No. 18-Crown-6·2 cyanamide, 87157-16-2.

Effects of Structural Changes on Acidities and Homolytic Bond Dissociation Energies of the H-N Bonds in Amidines, Carboxamides, and Thiocarboxamides

Frederick G. Bordwell* and Guo-Zhen Ji

Contribution from the Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113. *Received April 3, 1991*

Abstract: The equilibrium acidities in DMSO have been measured for acetamidine, benzamidine, *N,N'*-diphenylbenzamidine, *N,N*-diethylbenzamidine, diphenylmethanimine, guanidine, *N,N'*-diphenylguanidine, *N,N'*-diphenylurea, and *N,N'*-diphenylthiourea. Combination of the resulting pK_{HA} values for these weak acids with the oxidation potentials of their conjugate bases gave estimates of their homolytic bond dissociation energies (BDEs). These acidities and BDEs are compared with those of the corresponding carboxamides and thiocarboxamides. The change in hybridization of nitrogen between NH_3 and $Ph_2C{=}NH$ causes the acidities and BDEs to increase by about 14 and 9 kcal/mol, respectively. These changes are similar to the increases in gas-phase acidities and BDEs observed for the change in hybridization between CH_3CH_3 and $CH_2{=}CH_2$ (12 and 12 kcal/mol, respectively). The BDE of the H-N bond in HN_3 is about 25 kcal/mol lower than that in $Ph_2C{=}NH$, despite the apparent similarities in hybridization. The acidities of the H-N bonds in acetamide, benzamide, and urea are 2.2, 4.6, and 2.2 kcal/mol higher than those of the H-N bonds in acetamidine, benzamidine, and guanidine, respectively, and their BDEs are 6, 5, and 7 kcal/mol higher. The acidities of the H-N bonds in thioacetamide, thiobenzamide, and thiourea are 9.6, 8.8, and 8.1 kcal/mol higher than those of the H-N bonds in acetamide, benzamide, and urea, respectively, and their BDEs are 17, 16, and 18 kcal/mol lower. The 6 kcal/mol lower BDEs for the H-N bonds in acetamidine and benzamidine than in ammonia point to the presence of resonance energy in $HN^{\bullet}C(R){=}NH$ radicals in contrast to its near absence in $HN^{\bullet}C(R){=}O$ radicals.

In the gas phase, the acidity of the H-C bond in the series H_3CCH_3 (413) < $H_2C{=}CH_2$ (401) < $HC{\equiv}CH$ (370) is known to increase as the s-character of carbon increases along the series, as shown.[1] (The numbers in parentheses are gas-phase acidities, kcal/mol; henceforth, kcal/mol will be abbreviated as kcal.) At the same time, the homolytic bond dissociation energies (BDEs) of the H-C bonds increase from 98 to 110 to 132 kcal.[2,3] One would expect the heterolytic and homolytic bond dissociation energies of H-N bonds to show the same reverse trends with changes in hybridization of nitrogen, but there appears to be no literature addressing this point.[4] The two nitrogen atoms in acetamidine (**1**) are in different states of hybridization, and our

(1) Bartmess, J. E. Table of homolytic X-H bond strengths pertinent to the 1990 gas-phase acidity scale. A copy of this table may be obtained from Prof. J. E. Bartmess, Department of Chemistry, University of Tennessee, Knoxville, TN 37996.

(2) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Giles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750-5759.

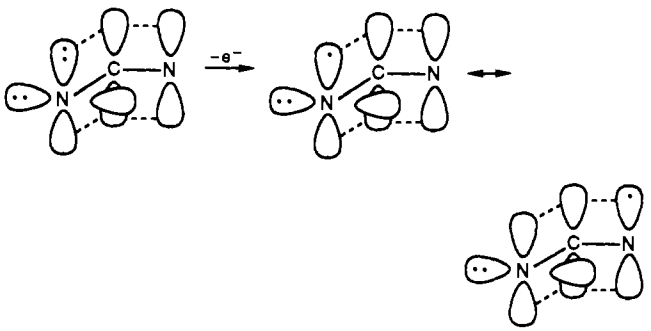
(3) Janousek, B. K.; Brauman, J. I.; Simons, J. *J. Chem. Phys.* **1979**, *71*, 2057-2061.

(4) There is a paucity of data available on the acidities and BDEs of H-N bonds. McMillen and Golden give BDE values for H-N bonds in only 7 compounds,[5] and Bartmess includes only 6 more in a list of 103 H-A bonds.[1] To the best of our knowledge, no measurements of the acidities or BDEs of the H-N bonds in amidines, guanidine, or imines have appeared in the literature.

(5) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493-532.

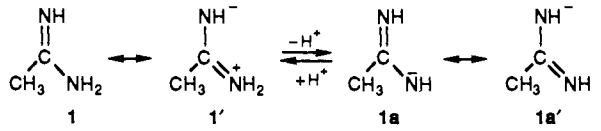
0002-7863/91/1513-8398$02.50/0

Scheme I

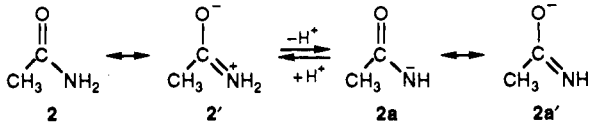


initial objective was to measure the acidities of each type of H–N bond and to estimate the H–N BDEs by means of eq 1.[6]

$$\mathrm{BDE} = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.06E_{\mathrm{ox}}(\mathrm{A}^-) + 56 \qquad (1)$$



There are several questions to be addressed concerning the acidity and bonding of the H–N bonds in amidines. First, we may ask which of the H–N bonds is more acidic, the sp^2 H—N= bond or the H—N bond in the amino group wherein the nitrogen is more nearly sp^3 hybridized. It is also of interest to compare the acidities and BDE of the H–N bond in the amino group of acetamidine with that in acetamide. Recent ab initio calculations have discounted the importance of resonance in amides, i.e., **2** ↔ **2′**.[7]



Indeed, the calculations suggest that the nitrogen in **2** has a slight negative charge rather than the positive charge imposed by resonance contributor **2′**. Nonetheless, resonance in the anion has not been ruled out, and could be an important acidifying factor in view of the absence of resonance in the neutral amide, particularly in the acetamidine anion where the equivalent resonance contributors (**1a** ↔ **1a′**) are formed. Is it possible that this acidifying factor for acetamidine can counter the much lower polarity of the C=N than the C=O bond and tend to equalize the acidities of acetamidine and acetamide?

Similar questions can be raised concerning the BDEs of the H–N bonds in the amino groups of acetamide and acetamidine. Although the H–N bond in acetamide is about 21 kcal more acidic than that in ammonia, the BDEs are nearly the same.[8a] In other words, the radical stabilization energies (RSEs) of the $H_2N^{\bullet}$ and $CH_3CONH^{\bullet}$ radicals appear to be the same, and little or no delocalization of the odd electron into the carbonyl group occurs. This is in sharp contrast to the 12–13-kcal stabilizing effect of the carbonyl group in carbon-centered radicals of the type $RCOCH_2^{\bullet}$.[8b] In order to explain this observation, we have suggested that in the oxidation of the conjugate base of a carboxamide the odd electron is removed from an orbital on nitrogen that is orthogonal to the π system of the N—C=O moiety.[8a] A more likely explanation is that a π radical may be formed,[9] but that, although delocalization occurs, the resonance energy provided thereby is small.[10] Will this be true also for loss of an electron from an amidinide ion to give a radical with nitrogen atoms at the termini of the allylic system? Or will the smaller electronegativity of nitrogen than oxygen and the equivalence of the radical contributors (Scheme I) provide a measurable resonance energy? We will try to answer these questions in the sections that follow.

Table I. Acidities and Homolytic Bond Dissociation Energies (BDEs) of Amidines, Guanidine, and Related Compounds

compound	pK_{HA}	$E_{ox}(A^-)^f$	BDE[g]	ΔBDE
NH_3	−41[a]		108	(0.0)
$PhC(=NH)NH_2$	26.7[b]	0.402 (77)	102	6
$PhC(=NH)NEt_2$	30.7[b]	0.902 (90)	119	−11
$Ph_2C=NH$	31.0[c]	0.818 (110)	117	−9
$HN=N^+=N^-$	7.9[d]	1.165 (89)	93	15
$PhC(=O)NH_2$	23.3$_5$[e]	0.824 (160)	107[e]	1
$PhC(=S)NH_2$	16.9[e]	0.499 (70)	91	17
$CH_3C(=NH)NH_2$	27.1[b]	0.387 (94)	102	6
$CH_3C(=O)NH_2$	25.5[e]	0.725 (110)	108[e]	0
$CH_3C(=S)NH_2$	18.5[e]	0.434 (110)	91[e]	17
$(H_2N)_2C=NH$	28.5[b]	0.407 (90)	104	4
$(H_2N)_2C=O$	26.9[e]	0.788 (170)	111[e]	−3
$(H_2N)_2C=S$	21.0[e]	0.361 (110)	93[e]	15

[a] Estimated (ref 11). [b] Measured against two or more indicators with standard deviations of ±0.05, or less. [c] One indicator. [d] Reference 12. [e] Reference 13. [f] Irreversible potentials measured under the conditions previously described and referenced to the standard hydrogen electrode[14] (wave widths, $E_p - E_{1/2}$ (mV), are given in parentheses). [g] Calculated by eq 1; BDEs estimated in this way have been found to agree within ±2 kcal/mol with the best gas-phase values for over 25 weak acids.[15] The CV wave widths are given as points of information. It is more difficult to assign precise potentials from broad CV waves than narrow CV waves, but at this time we have no reason to believe that assignments made from broad waves are less accurate than those made from narrow waves.

Results and Discussion

Hybridization Effects. The question as to which of the H–N bonds in amidines is more acidic was answered by measuring the acidities of *N,N*-diethylbenzamidine and diphenylmethanimine, $Ph_2C=NH$, and comparison with the acidity of benzamidine. The acidities and BDEs of these compounds are compared in Table I.

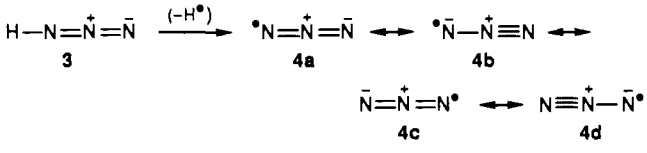
Examination of Table I shows that the =N—H bonds of *N,N*-diethylbenzamidine and diphenylmethanimine are more acidic than the H—N bond of ammonia by about 10 pK_{HA} units (13.7 kcal), but are about 4 kcal less acidic than the H—N bond of the amino group in benzamidine. The BDEs of these H—N= bonds are about 10 kcal higher than that of ammonia, a difference similar to that found for the sp^2 H—C= bond in ethene compared to the sp^3 H—C bond in ethane (12 kcal).[2] The difference in acidities between these H—N= bonds and that in ammonia is also similar to that between the gas-phase acidities of ethene and ethane (12 kcal).[1]

The BDE of the H—N bond of the amino group in benzamidine is about 16 kcal lower than that of an H—N= bond, and 6 kcal lower than the H—N bond in ammonia. The latter result suggests that the electron is being removed as shown in Scheme I, and that the equivalence of resonance contributors and the replacement of the oxygen atom in a carboxamide by a nitrogen atom has led

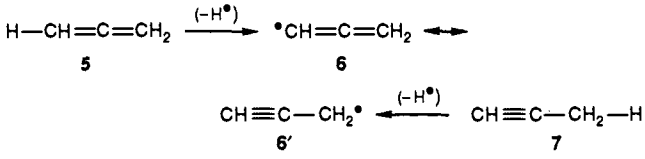
(6) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229–1231.
(7) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935–5943.
(8) (a) Bordwell, F. G.; Harrelson, J. A., Jr.; Lynch, T.-Y. *J. Org. Chem.* **1990**, *55*, 3337–3341. (b) Bordwell, F. G.; Lynch, T.-Y. *J. Am. Chem. Soc.* **1989**, *11*, 7558–7562.
(9) Danen, W. C.; Gellert, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 6853–6854. Nelsen, S. F. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 21.
(10) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 3347–3348. Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513–2519.
(11) Bordwell, F. G.; Algrim, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 2965–2967.
(12) Ritchie, C. D.; Uschold, R. E. *J. Am. Chem. Soc.* **1967**, *89*, 1721–1725.
(13) Bordwell, F. G.; Algrim, D. J.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 5903–5904.
(14) Bordwell, F. G.; Harrelson, J. A., Jr.; Satish, A. V. *J. Org. Chem.* **1989**, *54*, 3101–3105.
(15) Reference 6 and unpublished results.

to an increase in resonance energy.[16]

The only other BDE for an H—N= type bond that appears to have been measured is that in hydrazoic acid, H—N=N⁺=N⁻. The BDE of the H-N bond in hydrazoic acid was difficult to establish because of its instability, but in 1981 the measurement of the proton affinity of the azide ion in the gas phase by ion cyclotron resonance enabled Brauman to obtain the first reliable BDE, i.e., 92 ± 5 kcal.[17] Measurement of the oxidation potential of the azide ion by cyclic voltammetry in DMSO and combination with the pK_{HA} according to eq 1 gave an estimated BDE of 93 kcal. At first sight, this value appears to be much too low for an sp^2 =N—H bond, but perhaps the low value can be rationalized by delocalization of the odd electron in the radical (**4a–4d**).



A similar relatively low BDE (87.6 ± 2 kcal) has been reported for the =C—H bond in allene (**5**).[1] Here the radical (**6** ↔ **6′**) is the same as that derived by scission of the sp^3 H-C bond in methylacetylene (**7**), which has a BDE of 89.4 ± 2 kcal.[18]



Comparisons of the Acidities of the H–N Bonds of Acetamide, Acetamidine, and Thioacetamide. The factors controlling the acidities of $CH_3C(=X)NH_2$ amides where X is O, NH, or S should be similar to those controlling the acidity of acetic acid, $CH_3C(=O)OH$. In a recent analysis of the factors making acetic acid more acidic than ethanol, a three-parameter equation containing terms for (a) a field/inductive (*F*) effect, (b) a polarizability (*P*) effect, and (c) a resonance (*R*) effect was used.[19] The *F* effect was found to be dominant here, its influence being about half again as large as the *P* and *R* effects, which were nearly equal.[19] For acetamide, acetamidine, and thioacetamide, we can make a qualitative evaluation of the effects of these three factors on acidity. The *F* factor should decrease in the order of the dipole moments, which are C=S (2.95 D) > C=O (2.5 D) > C=N (1.8 D).[20] The *P* and *R* factors should also be large for thioacetamide because of the relative weakness of the C=S bond and the greater ability of sulfur than oxygen to accommodate a negative charge. (Note the greater acidity of thiols than alcohols, and of thiophenols than phenols.) These three factors combine to make thioacetamide more acidic than acetamide and acetamidine by 9.6 and 11.8 kcal, respectively. The *R* factor should be larger for acetamidine than acetamide because of the equivalence of its resonance contributors (**1a** ↔ **1a′**), but the *F* factor apparently wins out, making acetamide more acidic than acetamidine by 2.2 kcal.

Replacement of the methyl group in thioacetamide by an amino group causes a 3.4-kcal decrease in acidity. Similar, but smaller (1.9 kcal) decreases occur for replacement of the methyl groups in acetamide and acetamidine by amino groups. These effects can be attributed to lowering the ground-state energies of these molecules (**8** ↔ **8′**), the effect being larger for the more polarizable thiourea molecule. The lower ground-state energies make it more difficult to remove the proton from these amides.

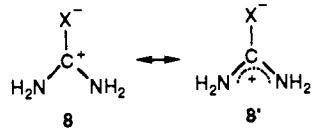


Table II. Phenyl Effects on the Acidities and BDEs of Carboxamides, Amidines, and Related Compounds

amide	pK_{HA}	$E_{ox}(A^-)^c$	BDE[d]	ΔBDE[e]
CH_3CONH_2	25.5[a]	0.725 (110)	107.5[a]	(0.0)
$CH_3CONHPh$	21.45[a]	0.605 (70)	99.5[a]	8
$PhCONH_2$	23.35[a]	0.824 (160)	107[a]	(0.0)
PhCONHPh	18.77[b]	0.681 (48)	97	10
$PhC(=NH)NH_2$	26.7[b]	0.402 (77)	102	(0.0)
PhC(=NPh)NHPh	20.8[b]	0.309 (42)	92	10
$PhC(=NPh)NHNMe_2$	22.9[b]	−0.867 (60)	85	17
$(H_2N)_2C=NH$	28.5[b]	0.407 (90)	104	(0.0)
$(PhNH)_2C=NH$	22.45[b]	0.235 (49)	92	12
$(H_2N)C=O$	26.9[a]	0.788 (170)	111[a]	(0.0)
$(PhNH)_2C=O$	19.5[a]	0.425 (70)	93[a]	18
$(H_2N)_2C=S$	21.0[a]	0.361 (110)	93[a]	(0.0)
$(PhNH)_2C=S$	13.5[a]	0.561 (50)	87[a]	6

[a] Reference 13. [b] Present work. [c] Irreversible potentials measured under the conditions previously described and referenced to the standard hydrogen electrode[14] (wave widths, $E_p - E_{1/2}$ (mV), are given in parentheses). [d] Calculated by eq 1; BDEs estimated in this way have been found to agree within ±2 kcal/mol with the best gas-phase values for over 25 weak acids.[15] The CV wave widths are given as points of information. It is more difficult to assign precise potentials from broad CV waves than narrow CV waves, but at this time we have no reason to believe that assignments made from broad waves are less accurate than those made from narrow waves. [e] The parent amides, amidines, ureas, etc. are used as zero reference points in order to estimate the size of the effects of phenyl substitution on BDEs.

Comparison of the BDEs of the H–N Bonds in Carboxamides, Amidines, and Thiocarboxamides. Examination of Table I shows that benzamidine and acetamidine both have BDEs of 102 kcal, compared to 108 kcal for NH_3. These radical stabilizing effects are similar to those observed for carbonyl functions adjacent to a carbon radical center, but are smaller in magnitude. On the other hand, the H–N bonds in thioacetamide and thiobenzamide each have BDEs 17 kcal lower than that of ammonia, suggesting that the $CH_3C(=S)NH^•$ and $PhC(=S)NH^•$ radicals are stabilized strongly by delocalization. This is understandable in view of the much weaker C=S π bond, the better ability of sulfur than oxygen or nitrogen at accommodating an odd electron, and the much lower electronegativity of sulfur than oxygen.

The lower ground-state energies for the analogues urea, thiourea, and guanidine, where an amino group has replaced Me or Ph (**8** ↔ **8′**) exhibit similar effects. The H–N bond in guanidine has a 4-kcal lower BDE than ammonia. That in urea has a BDE 3 kcal *higher* than ammonia, and that in thiourea has a BDE 18 kcal lower than urea.

Phenyl Effects on Acidities and BDEs. The effects on acidities and BDEs of substituting one or two phenyl groups at acidic sites of some of the compounds in Table I are summarized in Table II.

Examination of Table II shows that introduction of a phenyl group for one of the hydrogen atoms attached to nitrogen in acetamide increases the acidity by 4 pK_{HA} units (5.5 kcal) and lowers the BDE of the H–N bond by 8 kcal. For benzamide, the *N*-phenyl increases the acidity by 6.3 kcal and lowers the BDE by 10 kcal. (These effects are similar to, but somewhat smaller than, those observed for H–C bonds. For example, substitution of one of the hydrogen atoms of acetone by phenyl causes a 9.2-kcal increase in acidity and an 11-kcal lowering of BDE.[21]) Introducing a phenyl group at each of the nitrogen atoms of

(16) Fodor, G.; Philips, B. A. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; Wiley-Interscience: New York, 1975; Chapter 2, p 91 list the activation energies in C—N bond rotations of $RC(=S)NMe_2$, $RC(=O)NMe_2$, and $RC(=NH)NMe_2$ to be 25.9, 20.3, and 18.2 kcal/mol, respectively.

(17) Pellerite, M. J.; Jackson, R. L.; Brauman, J. I. *J. Phys. Chem.* **1981**, *85*, 1625–1626.

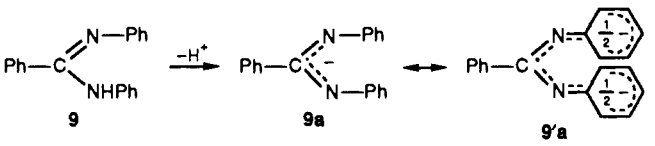
(18) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 687–711.

(19) Taft, R. W.; Koppel, I. A.; Topsom, R. D.; Auvia, F. *J. Am. Chem. Soc.* **1990**, *112*, 2047–2052.

(20) Exner, O. *Dipole Moments in Organic Chemistry*; George Thieme Publishers: Stuttgart, Germany, 1975; p 33.

(21) Bordwell, F. G.; Harrelson, J. A., Jr. *Can. J. Chem.* **1990**, *68*, 1714–1718.

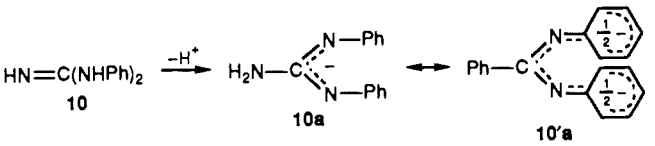
benzamidine has a similar effect, i.e., a 5.9-kcal increase in acidity and a 10-kcal decrease in BDE. At first sight, this is surprising because the negative charge in the anion or odd electron in the radical can be delocalized equally over *two* nitrogen atoms and the phenyl groups attached thereto (**9** → **9a** ↔ **9a′**).



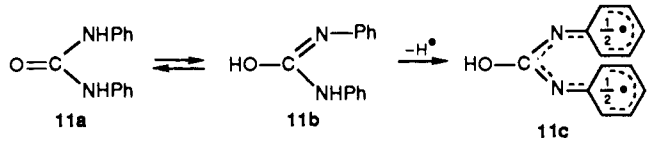
Examination of scalar molecular models shows, however, that there is a strong steric interaction between the two phenyl groups attached to the nitrogen atoms, and only one phenyl group can overlap effectively with the negative charge or odd electron.

Substitution of NMe_2 for the Ph attached to NH causes a 2.1 pK_{HA} unit decrease in acidity and a 7-kcal lowering of BDE. The 17-kcal lowering of the H–N BDE in $PhN{=}C(Ph)NHNMe_2$, relative to that of $H{-}NH_2$, is comparable to that in $O{=}C(Ph){-}NHNMe_2$ ($\Delta BDE = 24$).[8c]

In the basic DMSO solution, under the conditions that the pK_{HA} and CV measurements are made, tautomerism of $HN{=}C{-}(NHPh)_2$ may occur to give an ion of comparable structure to that generated from **9** (**10** → **10a** ↔ **10a′**). It is not surprising



then that the effect of introducing a phenyl group into each of the amino groups of guanidine is about the same (8-kcal increase in acidity and 12-kcal lowering of BDE) as that of introducing a phenyl group into each of the nitrogen atoms of benzamidine. Somewhat similar effects are observed on introducing a phenyl group into each of the nitrogen atoms of urea, i.e., a 10-kcal increase in acidity and an 18-kcal lowering of BDE. Here too tautomerism can occur, and steric effects will prevent coplanarity of the two phenyl groups in the radical. Note that the BDEs of **9**, **10**, and **11** are essentially identical. The difference in ΔBDEs



stems from the difference in BDEs of the parents 102, 104, and 111 kcal, respectively. The effect of comparable phenyl substitution into thiourea leads to a 10-kcal increase in acidity and a 6-kcal lowering of BDE. Here the BDE of the parent is only 93 kcal, which suggests that decrease in this BDE, relative to those of diphenylguanidine and diphenyl urea, is a saturation effect.

Experimental Section

General Procedure. Proton NMR spectra were obtained by using a Varian EM-390 spectrometer. Melting points are uncorrected and were determined by using a Thomas-Hoover Unimelt capillary melting point apparatus.

The purification of Me_2SO and the preparation and standardization of $CH_3SOCH_2^-K^+$ (potassium dimsyl solution), as well as the methods for the pK_a determinations and the measurements of the oxidation potentials of the corresponding anions by cyclic voltammetry with a Bioanalytical Systems instrument (West Lafayette, IN), have been described previously.[14]

Materials. Acetamidine hydrochloride, benzamidine hydrochloride hydrate, guanidine hydrochloride, 1,3-diphenylguanidine, and benzophenone imine were obtained from Aldrich Chemical Co.

Acetamidine was prepared by the method of Crossland and Grevil.[22] A solution of acetamidine hydrochloride (9.4 g) in methanol (30 mL) was added to a sodium methoxide solution, prepared from sodium (2.3 g) and methanol (25 mL). The reaction mixture was stirred and cooled in an ice–water bath for 10 min, filtered through Celite, concentrated in vacuo, and distilled, and the fraction (bp 45 °C (2mm)) was collected. It solidified in the refrigerator; mp 56–58 °C. Recrystallization from methylene chloride gave colorless crystals, mp 65–67 °C (lit.[22] mp 66–67 °C). ^1H NMR (90 MHz, $CDCl_3$): δ 2.00, 5.03, 7.33 ($CHCl_3$, was formed due to exchange of deuterium with hydrogen. The sum of the integral at δ 5.03 and 7.33 was equal to the integral at δ 2.00).

Benzamidine was prepared by the following procedure: Benzamidine hydrochloride hydrate (5 g) was added to 4 N sodium hydroxide solution (20 mL). The reaction mixture was stirred at room temperature for 0.5 h and then extracted with chloroform. After evaporation of the solvent, the solid was crystallized from benzene/hexane; mp 65–69 °C. Repeated recrystallization raised the mp to 78–79 °C (lit.[23] mp 80 °C). ^1H NMR (90 MHz, $CDCl_3$): δ 5.47–5.57 (m), 7.27–7.70 (m).

Guanidine was prepared by the following procedure: A solution of guanidine hydrochloride (9.5 g) in methanol (35 mL) was added to a sodium methoxide solution, prepared from sodium (2.3 g) and methanol (25 mL). The reaction mixture was stirred at 0 °C for 15 min and filtered through Celite under nitrogen, and then the solvent was evaporated in vacuo. The white solid was washed with 3 × 15 mL of methanol, dried at room temperature in vacuo for 24 h, and kept under a dry argon atmosphere. It was weighed by adding to a cell which was capped immediately with a three-way stopcock. The cell was evacuated and purged with argon. A solution of guanidine in DMSO (0.6 M) prepared in this way was used for CV measurements.

***N,N*-Diethylbenzamidine** was prepared by a procedure similar to that of Hullin, Miller, and Short.[24] A solution of diethylamine (7.3 g, 0.1 mol) in anhydrous ether (30 mL) was added with stirring to 35 mL of methylmagnesium bromide solution (2.85 M in ether solution, Aldrich Chemical Co.) and heated to reflux for 0.5 h, and then 7.0 g of benzonitrile in 40 mL of dry ether was added in 20 min. The reaction mixture was heated for another 1.5 h. After cooling, 100 mL of ether–HCl solution (20 mL of 35% HCl in 100 mL of ether) and 100 mL of cold water were added sequentially, and then 10 g of NaOH in 50 mL of water was added. The magnesium hydroxide was washed with chloroform, and the filtrate was extracted with 3 × 50 mL of chloroform. After the solvent was evaporated, the residue was distilled under vacuum. A fraction of bp 88–90 °C (0.5 mm) was collected (lit.[24] bp 95 °C (2 mm)). ^1H NMR (90 MHz, $CDCl_3$): δ 7.37 (m, 5 H, ph), 6.05 (br, 1 H, NH), 3.30 (q, 4 H, CH_2), 1.17 (t, 6 H, CH_3).

1,1-Dimethyl-2-(*N*-phenylbenzimidoyl)hydrazine was prepared according to the method of Smith.[25]

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Registry No. 1, 143-37-3; **1a**, 136342-65-9; **2a**, 63285-19-8; **3**, 7782-79-8; **9**, 2556-46-9; **9a**, 136342-66-0; **10**, 102-06-7; **10a**, 136342-68-2; $PhC(NH)NH_2$, 618-39-3; $(H_2N)_2C{=}NH$, 113-00-8; $PhC(=NH)NEt_2$, 50458-37-2; $PhC(=NPh)NHNMe_2$, 27808-65-7; $Ph_2C{=}NH$, 1013-88-3; $PhC(=S)NH_2$, 2227-79-4; $PhC(=O)NHPh$, 93-98-1; $PhC(=NH)NM^-$, 136342-62-6; $PhC(=N^-)NEt_2$, 136342-63-7; $Ph_2C{=}N^-$, 136342-64-8; $N^-{=}N^+{=}N^-$, 14343-69-2; PhC(|dbdO)NH⁻, 72409-60-0; $PhC(=S)NH^-$, 126501-65-3; $CH_3C(=S)NH^-$, 126501-66-4; $(H_2N)_2C{=}N^-$, 63575-00-8; $H_2NC(=O)NH^-$, 30535-92-3; $H_2NC(=S)NH^-$, 121782-79-4; $CH_3C(=O)N^-Ph$, 61057-08-7; $PhC(=O)N^-Ph$, 61057-09-8; $PhC(=NPh)N^-NMe_2$, 136342-67-1; $PhNHC(=O)N^-Ph$, 136342-69-3; $PhNHC(=S)N^-Ph$, 136342-70-6; $HN^{\cdot}CH{=}NH$, 50614-04-5; $MN^{\cdot}CH{=}O$, 14753-22-1; diethylamine, 109-89-7; benzonitrile, 100-47-0; benzamidine hydrochloride, 1670-14-0; guanidine hydrochloride, 50-01-1.

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