Equilibrium Acidities and Homolytic Bond Dissociation Energies (BDEs) of the Acidic H−N Bonds in Hydrazines and Hydrazides

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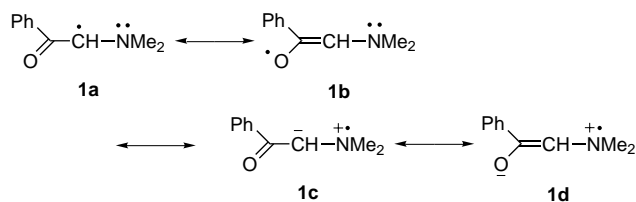
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Abstract: The equilibrium acidities in DMSO for phenylhydrazine, five of its *p*-substituted derivatives, 1,2-diphenylhydrazine, and 1,1,2-triphenylhydrazine were measured and the BDEs of their acidic N−H bonds were estimated by using the following equation: BDE = $1.37 pK_{HA} + 23.06 E_{ox}(A^-) + 73.3$ kcal/mol. The α-N−H bonds in the hydrazides $CH_3CONHNH_2$, $PhCONHNH_2$, NH_2NHCO_2Et, and $PhSO_2NHNH_2$ were found to be 2 to 4 pK_{HA} units more acidic than the α-N−H bonds in the corresponding amides, and the BDEs were estimated to be 23−27 kcal/mol weaker. Similarly, the BDE of a N−H bond in hydrazine was estimated to be 26 kcal/mol weaker than that of an N−H bond in NH_3. Introduction of a RCO group into hydrazine had little or no effect on the BDE, but introduction of RCO into the β-position of $PhCONHNH_2$ caused about an 8 kcal/mol increase in BDE. An increase in BDE was also observed for introduction of an RCO group into aniline. Here the carbonyl group is effectively destabilizing a nitrogen-centered radical by virtue of its strong electron-withdrawing effect. Incorporation of an open-chain carbohydrazide into a ring structure tends to strengthen the acidity of the N−H bond and weaken its BDEs.
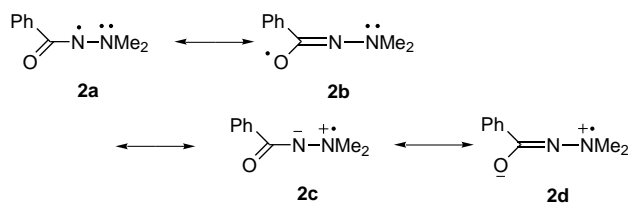
Introduction

Earlier studies have shown that substitution of a MeO group for an acidic hydrogen atom in $PhCOCH_3$ caused a 1.9 pK_{HA} unit (2.6 kcal/mol) increase in acidity and a 13 kcal/mol weakening of the acidic C−H bond in terms of its homolytic bond dissociation energy (BDE) (henceforth, kcal/mol will be abbreviated as kcal). Similarly, substitution of an α-Me_2N group into $PhCOCH_3$ caused a 1.2 pK_{HA} unit (1.6 kcal) increase in acidity and a 21 kcal weakening of the acidic C−H bond.[1] The small acidifying effects for these weak acceptor groups are expected, and their strong bond-weakening effects can be rationalized by calling attention to the powerful stabilization of the corresponding radicals by delocalization (e.g., **1a** ↔ **1b** ↔ **1c** ↔ **1d**).

1a   **1b**   **1c**   **1d**

The effects of substitution of α-RO or α-Me_2N groups for an acidic hydrogen atom in the nitrogen analogue, $PhCONH_2$, are similar but much larger, causing a 9.0 pK_{HA} unit (12.3 kcal) increase in acidity for α-$PhCH_2O$ substitution and a 5.0 pK_{HA} unit (6.8 kcal) increase in acidity for α-Me_2N substitution.[2]

The even larger bond-weakening effect of the α-Me_2N group on the N−H bond in $PhCONHNMe_2$ than on the acidic C−H bond in $PhCOCH_2NMe_2$ (24 vs 21 kcal) is intriguing and

suggests that the delocalizing effect is particularly strong in the $\dot{N}$−$\ddot{N}R_2$ moiety (**2**). Additional studies have now been made of the acidities and BDEs of compounds containing this moiety.

2a   **2b**   **2c**   **2d**

Results and Discussion

Acidities and Homolytic Bond Dissociation Enthalpies (BDEs) of the Acidic N−H Bonds in Hydrazine and Phenylhydrazines. The BDE of the N−H bond in hydrazine has been difficult to obtain experimentally until recently because the N−N bond (BDE = 65.5 ± 0.4 kcal[3]) is weaker than the H−N bond. The N−H bond has been calculated to have a BDE of 87.5 kcal,[4a] and a recent experimental value of 80.8 ± 0.3 kcal has been reported.[4b]

A simple method of estimating homolytic bond dissociation enthalpies (BDEs) of the acidic H−A bonds in weak organic acids has been developed in our laboratory by combining pK_{HA} values and the oxidation potentials of their conjugate bases in DMSO according to eq 1.[5] This method has been found to give estimates of BDEs that agree with gas-phase values to ±3 kcal, or better for C−H and N−H bonds. The method cannot be used to estimate the BDE of the N−H bonds in alkylhydrazines because they are too weakly acidic for the pK_{HA} value to be measured in DMSO. It can be used to estimate BDEs of the

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Table 1. Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic H−N Bonds in Hydrazine and Phenylhydrazines

no.	weak acids	$pK_{HA}{}^a$	$E_{ox}(A^-)^f$	BDE^h	ΔBDE
1	NH_3	$(\sim41)^b$		107^i	(0.0)
2	NH_2NH_2			80.8^j	26
3	$PhNH_2$	30.6^c	-0.992^c	92^c	15
4	$C_6H_5NHNH_2$	28.8	-1.740	72.6	(0.0)
5	$p\text{-MeC}_6H_4NHNH_2$	29.2	-1.795	71.9	-0.7
6	$p\text{-ClC}_6H_4NHNH_2$	27.2	-1.630	73.0	0.4
7	$p\text{-EtOCOC}_6H_4NHNH_2$	25.6	-1.392	76.3	3.7
8	$p\text{-CF}_3C_6H_4NHNH_2$	25.7	-1.327	77.9	5.3
9	$p\text{-CNC}_6H_4NHNH_2$	25.1	-1.295	77.8	5.2
10	$PhNHNHPh$	26.2^d	-1.730^g	69.3	3.3
11	$PhNHNPh_2$	24.5	-1.117^g	81.1	-8.5
12	$2,4\text{-(NO}_2)_2C_6H_3NHNPh_2$	12.1	-0.292^g	83.1	-10.5
13	$2,4,6\text{-(NO}_2)_3C_6H_2NHNPh_2$	5.9^e	-0.093^g	80^k	-7.4

^{a} In pK_{HA} units; equilibrium acidities were measured in DMSO solution by the overlapping indicator method or the standard acid method (ref 8). See Table 4 unless otherwise noted. ^{b} Estimated by extrapolation (ref 16). ^{c} Reference 17. ^{d} Reference 18. ^{e} Estimated from the $E_{ox}(A^-)$ and BDE values by using eq 1. ^{f} In volts; irreversible oxidation potentials of the conjugate bases were measured by cyclic voltammetry (CV) in DMSO solution and referenced to the ferrocenium/ferrocene couple, unless otherwise noted. ^{g} Reversible oxidation potentials. ^{h} In kcal/mol, estimated by using eq 1. ^{i} Reference 19. ^{j} Reference 4. ^{k} Reference 20.

more acidic α-N−H bonds in phenylhydrazine and its derivatives, however, and the results of several such measurements are given in Table 1.

$$BDE_{HA} = 1.37\, pK_{HA} + 23.1 E_{ox}(A^-) + 73.3 \qquad (1)$$

The N−H bond in ammonia has a BDE value of 107 kcal. Comparison of the BDE values of the N−H bonds in hydrazine (entry 2 in Table 1) with that in ammonia (entry 1 in Table 1) shows that introduction of an amino group into ammonia to form hydrazine decreases the BDE of the N−H bond by about 26 kcal. This large bond-weakening effect is no doubt due primarily to the strong delocalization of the corresponding radical by the formation of the two-center three-electron bond, i.e.,
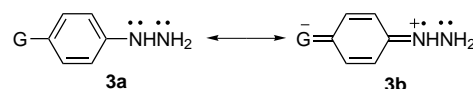

The BDE of the acidic N−H bond in PhNHNH$_2$ (entry 4 in Table 1) is estimated by eq 1 to be 72.6 kcal. Inspection of the BDE values of N−H bonds in entries 3 and 4 in Table 1 shows that introduction of an amino group into the amino group of aniline to form phenylhydrazine causes a decrease in BDE of 19 kcal. This is to be compared with the 26 kcal decrease in BDE between NH$_3$ and NH$_2$NH$_2$. The smaller substituent effect on the BDE of the N−H bond in aniline than that in ammonia by substitution of an amino group is expected because of a leveling effect (compare the 92 kcal value for the BDE of the parent N−H bond in aniline with the 107 kcal for the parent BDE of the N−H bond in ammonia). For the same reason, introduction of a phenyl group into hydrazine causes an 8 kcal decrease in the BDE of the N−H bond, whereas introduction of a phenyl group into ammonia causes a 15 kcal decrease in BDE of the N−H bond.

Comparison of acidity and BDE data for six para-substituted phenylhydrazines in Table 1 with those of the corresponding aniline's shows that introduction of a second amino group into an aniline causes a slight increase in acidity (0.22 to 2.7 kcal) and a large decrease in BDE averaging, about 18 kcal. The latter confirms the inherent large delocalizing effect in a N̈−N̈R$_2$ moiety.

A fairly good Hammett plot of pK_{HA} versus σ_p values for the six phenylhydrazines was obtained ($pK_{HA} = 28.46 - 5.34\sigma_p$; $r = 0.987$). It is worthy of note that ordinary σ_p values rather than $\sigma_p{}^-$ values were appropriate in this plot[6] for the p-CO$_2$Et and p-CN substituents, although the ρ value of 5.3 is not much smaller than $\rho_p{}^-$ for a Hammett plot of anilines ($\rho_p{}^- = 5.6$; $r = 0.99$).[17]
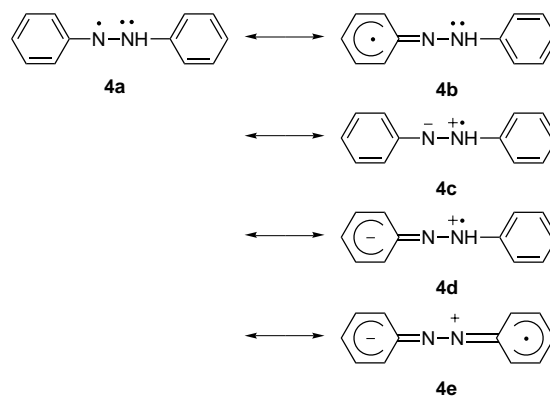
A Hammett plot of BDE for para-substituted phenylhydrazines versus σ_p values was roughly linear (BDE $= 72.63 + 8.03\sigma_p$; $r = 0.952$), but with a 1.5-fold steeper slope than a corresponding Hammett plot of BDE for para-substituted anilines. The greater increase in BDEs for para-substituted phenylhydrazines than for para-substituted anilines with increases in electron withdrawal of the para substituent can be rationalized in terms of greater delocalization of the electron pair adjacent to the benzene ring because of four electron

repulsions (**3a** ↔ **3b**). The greater delocalization causes a greater decrease in ground state energy and a greater increase in BDE.

Examination of the BDE values of para-substituted phenylhydrazines in Table 1 also reveals that introduction of para-substituted electron-withdrawing groups into the benzene ring of phenylhydrazine increases the BDE of the acidic N−H bond in PhNHNH$_2$ by 0.4−5.3 kcal, as is true also for the BDEs of para-substituted phenols[7] and anilines.[17]

The phenyl group in phenylhydrazine (BDE = 72.6 kcal) lowers the BDE of the N−H bond by about 8 kcal, relative to that in hydrazine itself (81 kcal), by virtue of its delocalizing effect. Introduction of a phenyl group into hydrazine to give symmetric PhNHNHPh increases the acidity by 2.3 pK_{HA} units (statistically corrected) and decreases the BDE of the N−H by an additional 4 kcal (BDE = 69 kcal). The 4 kcal decrease in BDE caused by the introduction of the second phenyl group

is attributed to the additional delocalization of the corresponding radical when involved in the larger conjugated system (**4a** ↔ **4b** ↔ **4c** ↔ **4d** ↔ **4e**).

Introduction of a third phenyl group into hydrazine to give PhNHNPh$_2$ causes a further 2 pK_{HA} unit increase in acidity, but the BDE is *increased* by 12 kcal relative to that in PhNHNHPh because of steric crowding, which reduces the extent of efficient delocalization of the odd electron in the corresponding radical. Introduction of 2,4-dinitro groups or

(6) Hammett constants $\sigma_p{}^-$ and σ_p are taken from: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

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2,4,6-trinitro groups into the benzene ring at position 2 of 1,1,2-triphenylhydrazine increases the acidity by 12 and 18 pK_{HA} units, respectively, but the effect on the BDE is negligible. Nitro groups have been shown to exert dual effects on the stabilities of radicals: (a) stabilizing by virtue of their delocalizing effect on the odd electron and (b) destabilizing by virtue of their electron-withdrawing effect.[8] The steric repulsion effect between the 2-nitro or 2,6-dinitro and the benzyl N−H bond may also play an important role, at least in the latter case. (In our previous studies,[9] the increases in ground state energies of the neutral precursors caused by the steric strains of groups adjacent to the acidic H−A bonds, as in the 2,6-di-*tert*-butyl-4-G-substituted phenols, have been shown to greatly weaken the H−A bonds.)

It was also of interest to examine the electrochemical behavior of the conjugate bases of the hydrazines. For example, the oxidation potential of the anion derived from phenylhydrazine is not reversible, but introduction of a second phenyl group in the β-position causes the oxidation potential of the anion derived from 1,2-diphenylhydrazine to become reversible. This means that the corresponding radical must have a sufficient lifetime on the CV scan scale (sweep rate: 100 mV/s) for the reverse wave to be observed. For a radical to display such kinetic stability, it must possess some or all of the following properties: (a) substantial delocalization of the unpaired electron, (b) steric congestion in the vicinity of the atom bearing the unpaired electron, and/or (c) substitution appropriate to prohibit disproportionation of the radical.[10,11] In the case of 1,2-diphenylhydrazine, large substituents are absent and delocalization of the corresponding radical must play the primary role to account for the kinetic stability of the radical. The oxidation potentials of the anions derived from 1,1,2-triphenylhydrazine, 1,1-diphenyl-2-(2,4-dinitrophenyl)hydrazine, and 1,1-diphenyl-2-(2,4,6-trinitrophenyl)hydrazine are also reversible. In these examples, both the delocalization of the unpaired electron and the steric congestion around the function holding the unpaired electron are believed to account for the special stabilities of the corresponding radicals.
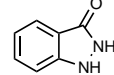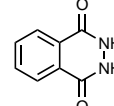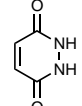
Effects of Structural Changes on the Acidities and Homolytic Bond Dissociation Enthalpies (BDEs) of the Acidic N−H Bonds in Hydrazides. The acidities and BDEs of acetamide, benzamide, ethyl carbamate, and benzenesulfonamide, as well as the corresponding hydrazides, are given in Table 2. The acidities of the hydrazides derived from the two carboxamides and ethyl carbamate are slightly higher than those of their parent amides, but that of benzenesulfonohydrazide is one pK_{HA} unit less acidic. The amides have BDEs of 106 ± 1 kcal, which means that in the corresponding radicals the delocalizing effects of the adjacent carbonyl, ethoxylcarbonyl, or benzenesulfonyl groups, which have been found to stabilize carbon-centered radicals, are either absent or masked by the electron-withdrawing properties of the carbonyl group. The BDEs of four hydrazides are 81 ± 1 kcal. Evidently the substitution of an NH_2 group for one of the N−H hydrogen atoms in the amide has caused a 25 ± 2 kcal weakening of the acidic N−H bond. This is comparable to the 26 kcal weakening of the N−H bond in NH_3 on introducing an NH_2 group. Clearly the weakening of the N−H bonds in these hydrazides is essentially independent of the nature of the β substituent (H,

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Table 2. Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic H−N Bonds in Amides and Hydrazides[a]

weak acids	pK_{HA}[b]	$E_{ox}(A^-)$[e]	BDE[f]	ΔBDE
CH_3CONH_2	25.5	−0.025	107	(0.0)
$CH_3CONHNH_2$	21.8	−0.890	82	25
$PhCONH_2$	23.35	0.074	107	(0.0)
$PhCONHNH_2$	18.9	−0.818	80	27
NH_2COOEt	24.6[c]	−0.075[d]	105[d]	(0.0)
$NH_2NHCOOEt$	22.2[d]	−0.954[d]	82[d]	23
$PhSO_2NH_2$	16.1	0.425	105	(0.0)
$PhSO_2NHNH_2$	17.1	−0.702	81	24

[a] Data taken from ref 2 unless otherwise noted. [b] In pK_{HA} units; equilibrium acidities were measured in DMSO solution by the overlapping indicator method or the standard acid method (ref 8). See Table 4 unless otherwise noted. [c] Reference 21. [d] This work. [e] In volts; irreversible oxidation potentials of the conjugate bases were measured by cyclic voltammetry (CV) in DMSO solution, and referenced to the ferrocenium/ferrocene couple. [f] In kcal/mol, estimated by using eq 1.

Table 3. Effects of Structural Change on Acidities and BDEs of Amides and Hydrazides

no.	weak acids	pK_{HA}[a]	$E_{ox}(A^-)$[h]	BDE[j]	ΔBDE
1	NH_3	(~41)[b]		107[k]	(0.0)
2	CH_3CONH_2	25.5[c]	−0.025[c]	107[c]	0
3	$PhCONH_2$	23.35[c]	0.074[c]	107[c]	0
4	$PhNH_2$	30.6[d]	−0.992[d]	92[d]	15
5	$PhNHCOCH_3$	21.5[e]	−0.159[e]	99[e]	8
6	$PhNHCOPh$	18.8[e]	−0.085[e]	97[e]	10
7	NH_2NH_2			80.8[l]	(0.0)
8	$CH_3CONHNH_2$	21.8[c]	−0.890[c]	82[c]	−1
9	$CH_3CONHNHCOCH_3$	16.7[f]	−0.190[f]	87.6[f]	−6.8
10	$PhCONHNH_2$	18.9[c]	−0.818[c]	80[c]	1
11	$PhCONHNHCOPh$	13.7	−0.121	89	−8
12	$CH_3CONHNHPh$	18.4	−0.864	78.6	(0.0)
13		15.3	−0.885[i]	73.9	4.7
14	$PhCONHNH_2$	18.9[c]	−0.818[c]	80.3[c]	(0.0)
15		14.9	−0.693	77.7	2.6
16	$PhCONHNHCOPh$	13.7	−0.121	89.3	(0.0)
17		12.7[g]	−0.166[g]	86.8[g]	2.5
18		13.2	−0.158	87.7	1.6

[a] In pK_{HA} units; equilibrium acidities were measured in DMSO solution by the overlapping indicator method or the standard acid method (ref 8). See Table 4 unless otherwise noted. [b] Extrapolated (ref 16). [c] Reference 2. [d] Reference 17. [e] Reference 22. [f] Reference 10. [g] Measured by X.-M. Zhang. [h] In volts; irreversible oxidation potentials of the conjugate bases were measured by cyclic voltammetry (CV) in DMSO solution unless otherwise noted, and referenced to the ferrocenium/ferrocene couple. [i] Reversible oxidation potentials were obtained. [j] In kcal/mol, estimated by using eq 1. [k] Reference 19. [l] Reference 4.

RCO, CO_2Et, or $PhSO_2$) and the stabilizing effect on the radical is brought about entirely by the three-electron $\dot{N}-\ddot{N}H_2$ moiety. It was of interest, therefore to explore further the effect of β substituents and also the effect of incorporation of the NHNH moiety into a ring structure (Table 3).

Comparison of entries 1−3 in Table 3 shows that substitution of CH_3CO or $PhCO$ groups into NH_3 increases the acidity by about 17 pK_{HA} units but has a negligible effect on the BDE.

On the other hand, introduction of a Ph group into NH_3 (entry 4) increases the acidity by about 10 pK_{HA} units (14 kcal) and decreases the N−H BDE by 15 kcal. Evidently the delocalization of the odd electron occurs to the phenyl group in the corresponding radical, but apparently not to a carbonyl group. Examination of entries 7, 8, and 10 in Table 3 shows that substitution of CH_3CO or PhCO groups into NH_2NH_2 also has a negligible effect on the BDE. For example, the N−H bond in hydrazine has a BDE of about 81 kcal, which is about the same as that of the acidic N−H bond in $PhCONHNH_2$.[1] This suggests that the PhCO group has little or no ability to effect additional stabilization of the $PhCON\dot{H}NH_2$ radical beyond that caused by the $\dot{N}-NH_2$ moiety. It is possible that delocalization does occur, but has negligible stabilizing effect, as is true of $O=C-O^\bullet$ radicals.[12] Alternatively, the destabilizing electron-withdrawing effect of the carbonyl group may mask its delocalizing effects.
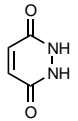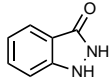
In contrast to the negligible substituent effects of CH_3CO or PhCO groups on BDEs of the acidic N−H bonds in NH_3 and NH_2NH_2, introduction of a CH_3CO or a PhCO group into the amino group in aniline (entries 5 and 6) *increases* the BDE of the N−H bond by 7 and 5 kcal, respectively. Here the carbonyl group is effectively destabilizing the nitrogen-centered radical by virtue of its strong electron-withdrawing effect.

Comparison of the BDE values of entries 2 and 3 with those of entries 9 and 11 shows that substitution of an acidic hydrogen atom in CH_3CONH_2 or $PhCONH_2$ by a $NHCOCH_3$ or a NHCOPh group, respectively, to convert an amide function to a RCONHNHCOR hydrazide function decreases the BDE of the N−H bonds by 19 and 18 kcal, respectively. Further inspection of the BDEs of entries 8 and 9 reveals that β-CH_3CO substitution in $CH_3CONHNH_2$ has a large substituent effect, causing a 5.1 pK_{HA} unit increase in acidity and a 6 kcal *increase* in BDE of the α-N−H bond. Note that the presence of the β-CH_3CO substitution destroys the powerful bond weakening effect of the NH−NH moiety. The β-PhCO substitution in $PhCONHNH_2$ has a similar effect. On the other hand, examination of the BDE values of entries 8 and 12 shows that a β-Ph substituent increases the acidity by 3.4 pK_{HA} unit and *decreases* the BDE by 3.4 kcal.

Ring Closure Effect on Acidities and Homolytic Bond Dissociation Enthalpies (BDEs) of the Acidic N−H Bonds in Hydrazides. Previous studies in our group[13] and other groups[10,14] have shown that ring closure has varied substituent effects on pK_{HA} and BDE values depending on the specific structures of the weak acids. For example, ring closures for ketones, carboxamides, or thiocarboxamides usually cause little change in their equilibrium acidities in DMSO,[13a] although Meldrum's acid was found to be 8.6 pK_{HA} units more acidic in DMSO than its acyclic analogue, dimethyl malonate.[14] Our recent studies have shown that the equilibrium C−H or N−H bond acidities of cyclic carboxylic esters or carbamates are usually *ca.* 4 pK_{HA} units more acidic than those of their acyclic analogues. On the other hand, these structural changes were found to cause little or no changes in the BDEs of the acidic C−H or N−H bonds in these esters or carbamates.[13b]

Comparison of the BDE of entries 12 and 13 shows that incorporation of the hydrazide moiety of entry 12 into a five-

Table 4. Equilibrium Acidities of Hydrazines and Hydrazides

weak acids	HIn[a]	pK_{HIn}	$pK_{HA} \pm$ std dev	no. of runs
p-MeC$_6$H$_4$NHNH$_2$	DDH[b]	29.4	29.21 ± 0.02	2
C$_6$H$_5$NHNH$_2$	DDH[b]	29.4	28.80 ± 0.01	2
p-ClC$_6$H$_4$NHNH$_2$	PXH[c]	27.9	27.20 ± 0.03	2
p-EtOCOC$_6$H$_4$NHNH$_2$	HB1[d]	26.1	25.62 ± 0.09	2
p-CF$_3$C$_6$H$_4$NHNH$_2$	HB1[d]	26.1	25.73 ± 0.03	2
p-CNC$_6$H$_4$NHNH$_2$	TP2H[e]	25.6	25.12 ± 0.06	2
PhNHNPh$_2$	TBUFH[f]	24.4	24.50 ± 0.01	2
PhCONHNPh$_2$	PFH[g]	17.9	17.09 ± 0.01	2
2,4-(NO$_2$)$_2$C$_6$H$_3$NHNPh$_2$	NBY300[h]	12.25	12.09 ± 0.01	2
NH$_2$NHCOOEt	FH[i]	22.6	22.19 ± 0.03	2
(pyridazinedione structure)	HZFO2[j]	12.95	13.16 ± 0.06	2
PhNHNHCOCH$_3$	MClPFH[k]	16.8	18.47 ± 0.01	1
	CNAH[l]	18.9	18.38 ± 0.01	2
(isoindole-dione structure)	HZF[m]	14.95	14.90 ± 0.02	2
PhCONHNHCOPh	HZFP2[n]	14.15	13.68 ± 0.07	2
(pyrazolidinone structure)	HZF[m]	14.95	15.24 ± 0.00	2

^{a} HIn (indicator). ^{b} DDH: biphenyldiphenylmethane. ^{c} PXH: 9-phenylxanthene. ^{d} HB1: iminostilbene. ^{e} TP2H: 1,1,3-triphenylpropene. ^{f} TBUFH: 9-*tert*-butylfluorene. ^{g} PFH: 9-phenyl fluorene. ^{h} NBY300: bis(phenylsulfonyl)methane. pK_a measured by standard acid method and dimsyl was quenched by dibenzyl sulfone. ^{i} FH: fluorene. ^{j} HZFO2: 9-fluorenone 2-chlorophenylhydrazone. ^{k} MClPFH: 9-(m-chlorophenyl)fluorene. ^{l} CNAH: 4-chloro-2-nitroaniline. ^{m} HZF: 9-fluorenone phenylhydrazone. ^{n} HZFP2: 9-fluorenone 4-chlorophenylhydrazone.

membered ring (entry 13) causes a 3.1 pK_{HA} unit increase in acidity and a 4.7 kcal decrease in BDE. The decrease in BDE is presumably due to the enforced coplanarity of the orbitals in the hydrazide moiety. A similar effect of cyclization and/or phenyl substitution is observed for entry 15 vs 14, and for entries 17 and 18 vs entry 16, and the six-membered ring seems to have smaller ring closure effect on both pK_{HA} and BDE values than the five-membered ring does.

Summary and Conclusions. The substitution of a NH_2 group for a hydrogen atom in anilines or carboxamides to give hydrazines and hydrazides has been found to cause small effects on the acidities, but strong bond-weakening effects. The introduction of a phenyl group into ammonia causes both a large acid-strengthening effect and a strong bond-weakening effect by virtue of its strong delocalizing ability. In contrast to NH_2 and Ph effects, RCO (R = Ph, Me) exerts a large acid-strengthening effect by virtue of its strong electron-withdrawing ability, but a negligible effect on the BDEs. Incorporation of the hydrazide moiety into a ring structure increases the acidities and decreases the BDEs, usually causing a larger effect in a five-membered ring than in a six-membered ring.

Experimental Section

Triphenylhydrazine, 1,1-diphenyl-2-(2,4-dinitrophenyl)hydrazine, and 1,1-diphenyl-2-(2,4,6-trinitrophenyl)hydrazine were prepared according to the method of Vogel.[15] Other compounds were commercially available from Aldrich. They were purified by distillation for liquids

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and recrystallization for solids and checked for purity by ^{1}H NMR spectroscopy and their physical properties.

The equilibrium acidities were measured in DMSO by either the overlapping indicator method or the standard acid method as previously reported.[8] The results, together with the indicators or standard acids used, are summarized in Table 4.

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The oxidation potentials of the conjugate bases were measured by cyclic voltammetry (CV) in DMSO. The working electrode (BAS) consists of a 1.5-mm-diameter platinum disk embedded in a cobalt glass seal. It was polished with a 0.05-mm Fischer polishing aluminum or cleaned with an ultrasonic instrument, rinsed with ethanol, and dried before each run. The counter electrode was a platinum wire (BAS). The reference electrode was Ag/AgI, and the reported potentials were referenced to the ferrocenium/ferrocene (Fc$^+$/Fc) couple. Tetraethyl-ammonium tetrafluoroborate was used as the supporting electrolyte. All electrochemical experiments were carried out under argon atmosphere.

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