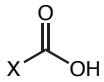
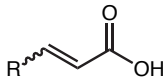
## INORGANIC ACIDS

| Substrate | pKa $H_2O$ | (DMSO) |
|---|---|---|
| $H_2O$ | 15.7 | (32) |
| $H_3O^+$ | -1.7 | |
| $H_2S$ | 7.00 | |
| HBr | -9.00 | (0.9) |
| HCl | -8.0 | (1.8) |
| HF | 3.17 | (15) |
| HOCl | 7.5 | |
| $HClO_4$ | -10 | |
| HCN | 9.4 | (12.9) |
| $HN_3$ | 4.72 | (7.9) |
| HSCN | 4.00 | |
| $H_2SO_3$ | 1.9, 7.21 | |
| $H_2SO_4$ | -3.0, 1.99 | |
| $H_3PO_4$ | 2.12, 7.21, 12.32 | |
| $HNO_3$ | -1.3 | |
| $HNO_2$ | 3.29 | |
| $H_2CrO_4$ | -0.98, 6.50 | |
| $CH_3SO_3H$ | -2.6 | (1.6) |
| $CF_3SO_3H$ | -14 | (0.3) |
| $NH_4Cl$ | 9.24 | |
| $B(OH)_3$ | 9.23 | |
| HOOH | 11.6 | |

## CARBOXYLIC ACIDS



| X= | pKa $H_2O$ | (DMSO) |
|---|---|---|
| $CH_3$ | 4.76 | (12.3) |
| $CH_2NO_2$ | 1.68 | |
| $CH_2F$ | 2.66 | |
| $CH_2Cl$ | 2.86 | |
| $CH_2Br$ | 2.86 | |
| $CH_2I$ | 3.12 | |
| $CHCl_2$ | 1.29 | |
| $CCl_3$ | 0.65 | |
| $CF_3$ | -0.25 | |
| H | 3.77 | |
| HO | 3.6, 10.3 | |
| $C_6H_5$ | 4.2 | (11.1) |
| *o*-$O_2NC_6H_4$ | 2.17 | |
| *m*-$O_2NC_6H_4$ | 2.45 | |
| *p*-$O_2NC_6H_4$ | 3.44 | |
| *o*-$ClC_6H_4$ | 2.94 | |
| *m*-$ClC_6H_4$ | 3.83 | |
| *p*-$ClC_6H_4$ | 3.99 | |
| *o*-$(CH_3)_3N^+C_6H_4$ | 1.37 | |
| *p*-$(CH_3)_3N^+C_6H_4$ | 3.43 | |
| *p*-$OMeC_6H_4$ | 4.47 | |

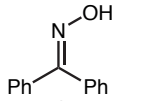


| R= | pKa $H_2O$ | (DMSO) |
|---|---|---|
| H | 4.25 | |
| *trans*-$CO_2H$ | 3.02, 4.38 | |
| *cis*-$CO_2H$ | 1.92, 6.23 | |

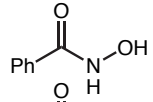
## ALCOHOLS

| | pKa $H_2O$ | (DMSO) |
|---|---|---|
| HOH | 15.7 | (31.2) |
| MeOH | 15.54 | (27.9) |
| *i*-PrOH | 16.5 | (29.3) |
| *t*-BuOH | 17 | (29.4) |
| *c*-$hex_3COH$ | 24 | |
| $CF_3CH_2OH$ | 12.5 | (23.5) |
| $(CF_3)_2CHOH$ | | (17.9) |
| $C_6H_5OH$ | 9.95 | (18.0) |
| *m*-$O_2NC_6H_4OH$ | 8.35 | |
| *p*-$O_2NC_6H_4OH$ | 7.14 | (10.8) |
| *p*-$OMeC_6H_4OH$ | 10.20 | (19.1) |
| 2-napthol | | (17.1) |

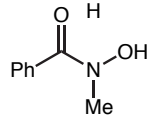
## OXIMES & HYDROXAMIC ACIDS



| pKa $H_2O$ | (DMSO) |
|---|---|
| 11.3 | (20.1) |



| pKa $H_2O$ | (DMSO) |
|---|---|
| 8.88 (NH) | (13.7) |

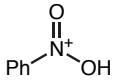


| pKa $H_2O$ | (DMSO) |
|---|---|
| | (18.5) |

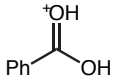
## PEROXIDES

| | pKa $H_2O$ |
|---|---|
| MeOOH | 11.5 |
| $CH_3CO_3H$ | 8.2 |

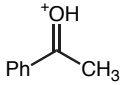
## PROTONATED SPECIES



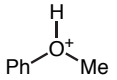
pKa $H_2O$: -12.4



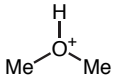
pKa $H_2O$: -7.8



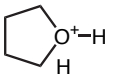
pKa $H_2O$: -6.2



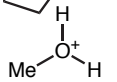
pKa $H_2O$: -6.5



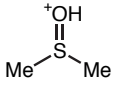
pKa $H_2O$: -3.8



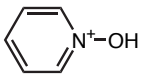
pKa $H_2O$: -2.05



pKa $H_2O$: -2.2

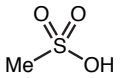


pKa $H_2O$: -1.8

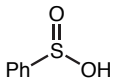


pKa $H_2O$: 0.79

## SULFINIC & SULFONIC ACIDS



pKa $H_2O$: -2.6



pKa $H_2O$: 2.1

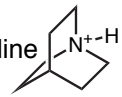
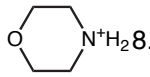
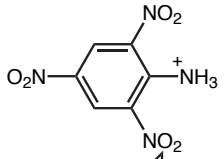
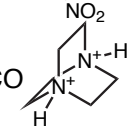
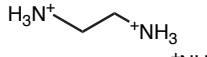
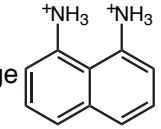
*Values <0 for $H_2O$ and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Bordwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

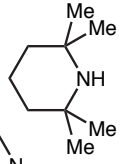
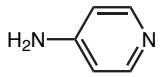
# pKa's of Nitrogen Acids



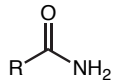
## PROTONATED NITROGEN

| Substrate | pKa $H_2O$ | (DMSO) |
|---|---|---|
| $N^+H_4$ | 9.2 | (10.5) |
| $EtN^+H_3$ | 10.6 | |
| *i*-$Pr_2N^+H_2$ | 11.05 | |
| $Et_3N^+H$ | 10.75 | (9.00) |
| $PhN^+H_3$ | 4.6 | (3.6) |
| $PhN^+(Me)_2H$ | 5.20 | (2.50) |
| $Ph_2N^+H_2$ | 0.78 | |
| 2-napthal-$N^+H_3$ | 4.16 | |
| $H_2NN^+H_3$ | 8.12 | |
| $HON^+H_3$ | 5.96 | |
| Quinuclidine  | 11.0 | (9.80) |
| Morpholine  | 8.36 | |
| N-Me morpholine | 7.38 | |
|  | -9.3 | |
| DABCO  | 2.97, 8.82 | (2.97, 8.93) |
|  | 6.90, 9.95 | |
| Proton Sponge  | -9.0, 12.0 | (--, 7.50) |
| $PhCN^+H$ | -10 | |

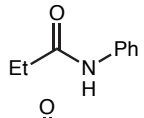
## AMINES

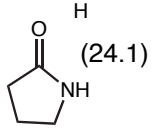
| Substrate | pKa $H_2O$ | (DMSO) |
|---|---|---|
| $HN_3$ | 4.7 | (7.9) |
| $NH_3$ | 38 | (41) |
| *i*-$Pr_2NH$ | (36 THF)) | |
| $TMS_2NH$ | 26(THF) | (30) |
| $PhNH_2$ | | (30.6) |
| $Ph_2NH$ | | (25.0) |
| $NCNH_2$ | | (16.9) |
|  | | (44) |
| TMP  | | (37) |
|  | | (26.5) |

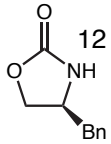
## AMIDES & CARBAMATES



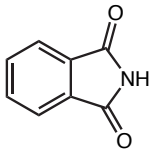
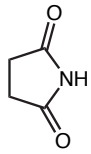
| R= | | | |
|---|---|---|---|
| | H | | (23.5) |
| | $CH_3$ | 15.1 | (25.5) |
| | Ph | | (23.3) |
| | $CF_3$ | | (17.2) |
| | $NH_2$ (urea) | | (26.9) |
| | OEt | | (24.8) |

 (21.6)

 (24.1)

 12 (20.5)

## IMIDES

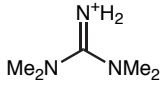
 8.30  (14.7)

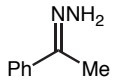
$Ac_2NH$ (17.9)

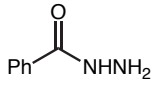
## SULFONAMIDE

| | | |
|---|---|---|
| $MeSO_2NH_2$ | | (17.5) |
| $PhSO_2NH_2$ | | (16.1) |
| $CF_3SO_2NH_2$ | 6.3 | (9.7) |
| $MeSO_2NHPh$ | | (12.9) |

## GUANIDINIUM, HYRDAZONES,- IDES, & -INES

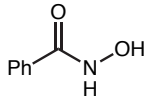
 (13.6)

 (21.6)

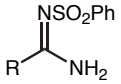
 (18.9)

| | |
|---|---|
| $PhSO_2NHNH_2$ | (17.2) |
| PhNHNHPh | (26.1) |

## HYDROXAMIC ACID

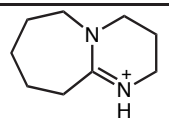
 8.88 (NH) (13.7)

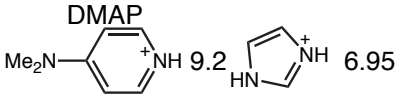
## AMIDINES

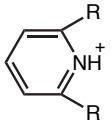


| R= | | |
|---|---|---|
| | Me | (17.3) |
| | Ph | (15.0) |

## PROTONATED HETEROCYCLES

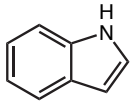
DBU  (12) (estimate)

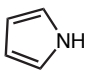
DMAP 



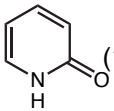
| R= | | | |
|---|---|---|---|
| | H (PPTS) | 5.21 | (3.4) |
| | *t*-Bu | 4.95 | (0.90) |
| | Me | 6.75 | (4.46) |
| | Cl, H | 0.72 | |

## HETEROCYCLES

 (20.95)

 (23.0)  (18.6)

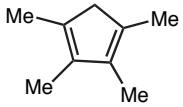
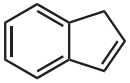
1,2,3 triazole

 (17.0)  (13.9)

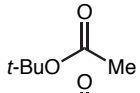
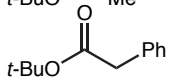
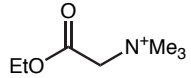
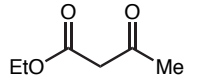
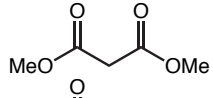
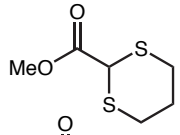
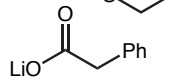
*Values <0 for $H_2O$ and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Bordwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

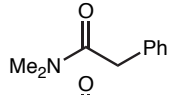
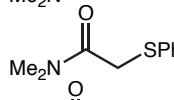
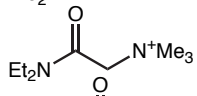
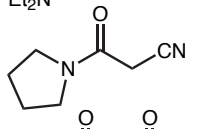
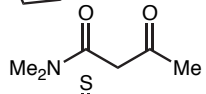
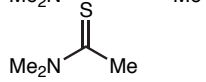
## HYDROCARBONS

| Substrate | pKa $H_2O$ | (DMSO) |
|---|---|---|
| $(Me)_3CH$ | 53 | |
| $(Me)_2CH_2$ | 51 | |
| $CH_2{=}CH_2$ | 50 | |
| $CH_4$ | 48 | (56) |
| △ | 46 | |
| $CH_2{=}CHCH_3$ | 43 | (44) |
| PhH | 43 | |
| $PhCH_3$ | 41 | (43) |
| $Ph_2CH_2$ | 33.5 | (32.2) |
| $Ph_3CH$ | 31.5 | (30.6) |
| HCCH | 24 | |
| PhCCH | 23 | (28.8) |
| $XC_6H_4CH_3$ | | |
| X= *p*-CN | | (30.8) |
| *p*-$NO_2$ | | (20.4) |
| *p*-COPh | | (26.9) |
|  | | (26.1) |
|  | 20 | (20.1) |
|  | 15 | (18.0) |
| $H_2$ | ~36 | |

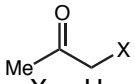
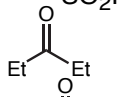
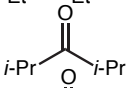
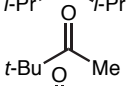
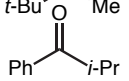
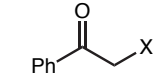
## ESTERS

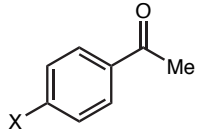
| | pKa $H_2O$ | (DMSO) |
|---|---|---|
|  | 24.5 | (30.3) |
|  | | (23.6) |
|  | | (20.0) |
|  | 11 | (14.2) |
|  | 13 | (15.7) |
|  | | (20.9) |
|  | | [30.2 (THF)] |

## AMIDES

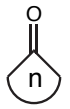
| | | |
|---|---|---|
|  | | (26.6) |
|  | | (25.9) |
|  | | (24.9) |
|  | | (17.2) |
|  | | (18.2) |
|  | | (25.7) |

## KETONES

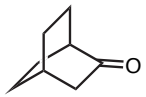
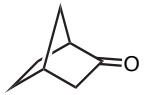
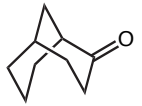
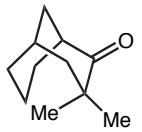
| | pKa $H_2O$ | (DMSO) |
|---|---|---|
|  | | |
| X= H | | (26.5) |
| Ph | | (19.8) |
| SPh | | (18.7) |
| $COCH_3$ | 9 | (13.3) |
| $SO_2Ph$ | | (15.1) |
|  | 19-20 | (27.1) |
|  | | (28.3) |
|  | | (27.7) |
|  | | (26.3) |
|  | | |
| X= H | | (24.7) |
| $CH_3$ | | (24.4) |
| Ph | | (17.7) |
| $COCH_3$ | | (12.7) |
| COPh | | (13.3) |
| $CO_2Et$ | | (22.7) |
| CN | | (10.2) |
| F | | (21.6) |
| OMe | | (22.85) |
| OPh | | (21.1) |
| SPh | | (16.9) |
| SePh | | (18.6) |
| $NPh_2$ | | (20.3) |
| $N^+Me_3$ | | (14.6) |
| $NO_2$ | | (7.7) |
| $SO_2Ph$ | | (11.4) |



| | | |
|---|---|---|
| X= H | | (24.7) |
| OMe | | (25.7) |
| $NMe_2$ | | (27.5) |
| Br | | (23.8) |
| CN | | (22.0) |



| | | |
|---|---|---|
| n= 4 | | (25.1) |
| 5 | | (25.8) |
| 6 | | (26.4) |
| 7 | | (27.7) |
| 8 | | (27.4) |

| | |
|---|---|
|  | (28.1) |
|  | (29.0) |
|  | (25.5) |
|  | (32.4) |

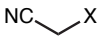
*Values <0 for $H_2O$ and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Bordwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

# pKa's of CH bonds at Nitrile, Heteroaromatic, and Sulfur Substituted Carbon

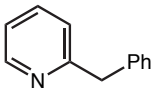
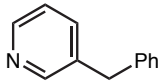
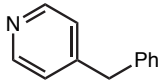
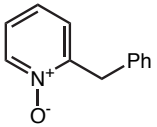
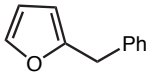
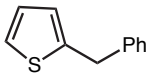


## NITRILES



| X= | | pKa $H_2O$ | pKa (DMSO) |
|---|---|---|---|
| | H | | (31.3) |
| | $CH_3$ | | (32.5) |
| | Ph | | (21.9) |
| | COPh | | (10.2) |
| | $CONR_2$ | | (17.1) |
| | $CO_2Et$ | | (13.1) |
| | CN | 11 | (11.1) |
| | OPh | | (28.1) |
| | $N^+Me_3$ | | (20.6) |
| | SPh | | (20.8) |
| | $SO_2Ph$ | | (12.0) |

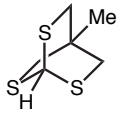
## HETERO-AROMATICS

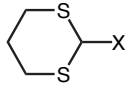
| | | |
|---|---|---|
|  | | (28.2) |
|  | | (30.1) |
|  | | (26.7) |
|  | | (25.2) |
|  | | (30.2) |
|  | | (30.0) |

## SULFIDES

$PhSCH_2X$

| X= | | pKa (DMSO) |
|---|---|---|
| | Ph | (30.8) |
| | CN | (20.8) |
| | $COCH_3$ | (18.7) |
| | COPh | (16.9) |
| | $NO_2$ | (11.8) |
| | SPh | (30.8) |
| | $SO_2Ph$ | (20.3) |
| | $SO_2CF_3$ | (11.0) |
| | $POPh_2$ | (24.9) |

| | |
|---|---|
| $MeSCH_2SO_2Ph$ | (23.4) |
| $PhSCHPh_2$ | (26.7) |
| $(PhS)_3CH$ | (22.8) |
| $(PrS)_3CH$ | (31.3) |
|  | (30.5) |
| $(PhS)_2CHPh$ | (23.0) |



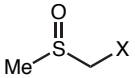
| X= | | pKa (DMSO) |
|---|---|---|
| | Ph | (30.7) |
| | $CO_2Me$ | (20.8) |
| | CN | (19.1) |

$RSCH_2CN$

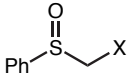
| R= | | pKa (DMSO) |
|---|---|---|
| | Me | (24.3) |
| | Et | (24.0) |
| | *i*-Pr | (23.6) |
| | *t*-Bu | (22.9) |

| | | |
|---|---|---|
| $PhSCH=CHCH_2SPh$ | | (26.3) |
| BuSH | 10-11 | (17.0) |
| PhSH | ≈7 | (10.3) |

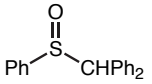
## SULFOXIDES



| X= | | pKa (DMSO) |
|---|---|---|
| | H | (35.1) |
| | Ph | (29.0) |
| | SPh | (29.0) |



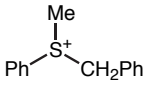
| X= | | pKa (DMSO) |
|---|---|---|
| | H | (33) |
| | Ph | (27.2) |
| | SOPh | (18.2) |



(24.5)

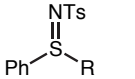
## SULFONIUM

| | |
|---|---|
| $Me_3S^+=O$ | (18.2) |

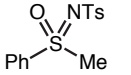


(16.3)

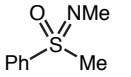
## SULFIMIDES & SULFOXIMINES



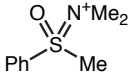
| R= | | pKa (DMSO) |
|---|---|---|
| | Me | (27.6) |
| | *i*-Pr | (30.7) |



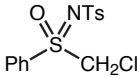
(24.5)



(33)

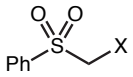


(14.4)

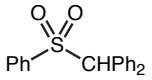


(20.7)

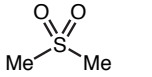
## SULFONES



| X= | | pKa (DMSO) |
|---|---|---|
| | H | (29.0) |
| | $CH_3$ | (31.0) |
| | *t*-Bu | (31.2) |
| | Ph | (23.4) |
| | $CH=CH_2$ | (22.5) |
| | CH=CHPh | (20.2) |
| | CCH | (22.1) |
| | CCPh | (17.8) |
| | COPh | (11.4) |
| | COMe | (12.5) |
| | OPh | (27.9) |
| | $N^+Me_3$ | (19.4) |
| | CN | (12.0) |
| | $NO_2$ | (7.1) |
| | SMe | (23.5) |
| | SPh | (20.5) |
| | $SO_2Ph$ | (12.2) |
| | $PPh_2$ | (20.2) |



(22.3)



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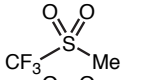
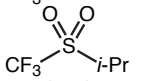


(18.8)



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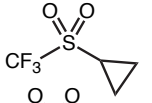
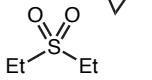


(26.6)



(32.8)

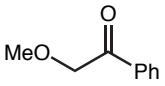
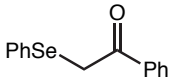
$(PhSO_2)_2CH_2Me$ (14.3)

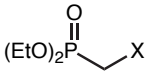
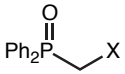
*Values <0 for $H_2O$ and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

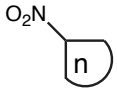
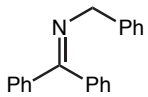
For a comprehensive compilation of Bordwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

# pKa's of CH bonds at Heteroatom Substituted Carbon & References



| Substrate | pKa $H_2O$ | (DMSO) |
|---|---|---|
| **ETHERS** | | |
| $CH_3OPh$ | | (49) |
| $MeOCH_2SO_2Ph$ | | (30.7) |
| $PhOCH_2SO_2Ph$ | | (27.9) |
| $PhOCH_2CN$ | | (28.1) |
|  | | (21.1) |
| **SELENIDES** | | |
|  | | (18.6) |
| $PhSeCHPh_2$ | | (27.5) |
| $(PhSe)_2CH_2$ | | (31.3) |
| $PhSeCH_2Ph$ | | (31.0) |
| $PhSeCH{=}CHCH_2SePh$ | | (27.2) |
| **AMMONIUM** | | |
| $Me_3N^+CH_2X$ | | |
| X= CN | | (20.6) |
| $SO_2Ph$ | | (19.4) |
| COPh | | (14.6) |
| $CO_2Et$ | | (20.6) |
| $CONEt_2$ | | (24.9) |

| Substrate | pKa $H_2O$ | (DMSO) |
|---|---|---|
| **PHOSPHONIUM** | | |
| $P^+H_4$ | | -14 |
| $MeP^+H_3$ | | 2.7 |
| $Et_3P^+H$ | | 9.1 |
| $Ph_3P^+CH_3$ | | (22.4) |
| $Ph_3P^+i\text{-}Pr$ | | (21.2) |
| $Ph_3P^+CH_2COPh$ | | (6.2) |
| $Ph_3P^+CH_2CN$ | | (7.0) |
| **PHOSPONATES & PHOSPHINE OXIDES** | | |
|  | | |
| X= Ph | | (27.6) |
| CN | | (16.4) |
| $CO_2Et$ | | (18.6) |
| Cl | | (26.2) |
| $SiMe_3$ | | (28.8) |
|  | | |
| X= SPh | | (24.9) |
| CN | | (16.9) |
| **PHOSPHINES** | | |
| $Ph_2PCH_2PPh_2$ | | (29.9) |
| $Ph_2PCH_2SO_2Ph$ | | (20.3) |

| Substrate | pKa $H_2O$ | (DMSO) |
|---|---|---|
| **NITRO** | | |
| $RNO_2$ | | |
| R= $CH_3$ | ≈10 | (17.2) |
| $CH_2Me$ | | (16.7) |
| $CHMe_2$ | | (16.9) |
| $CH_2Ph$ | | (12.2) |
| $CH_2Bn$ | | (16.2) |
| $CH_2SPh$ | | (11.8) |
| $CH_2SO_2Ph$ | | (7.1) |
| $CH_2COPh$ | | (7.7) |
|  | | |
| n= 3 | | (26.9) |
| 4 | | (17.8) |
| 5 | | (16.0) |
| 6 | | (17.9) |
| 7 | | (15.8) |
| **IMINES** | | |
|  | | (24.3) |

Oxime ethers are ~ 10 pka units less acidic than their ketone counterparts
Streitwieser, JOC 1991, 56, 1989

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JOC 41, 2508 (1976)
JOC 42, 1817 (1977)
JOC 42, 321 (1977)
JOC 42, 326 (1977)
JOC 43, 3113 (1978)
JOC 43, 3095 (1978)
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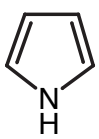
See cited website below for additional data

*Values <0 for $H_2O$ and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Brodwell pKa data see: **http://www.chem.wisc.edu/areas/reich/pkatable/index.htm**

# DMSO Acidities of Common Heterocycles

Bordwell, ACR, **1988**, *21*, 456



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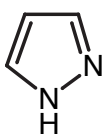

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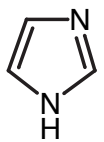

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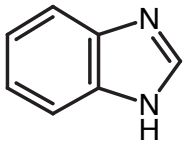

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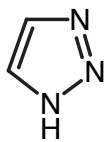

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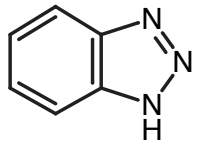

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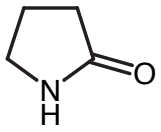

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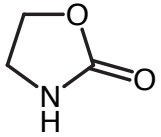

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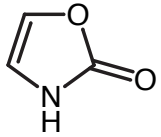

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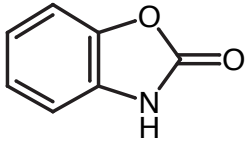

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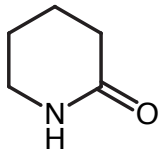

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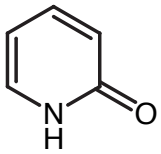

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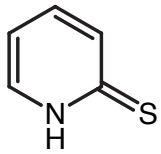

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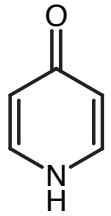

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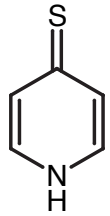

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