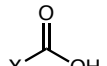
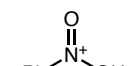
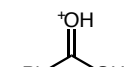
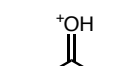
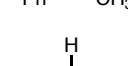
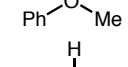
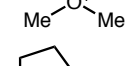
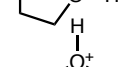
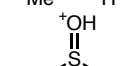
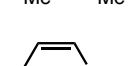
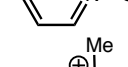
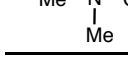
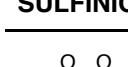
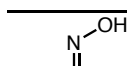
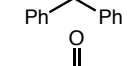
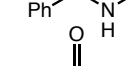
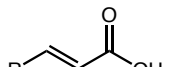
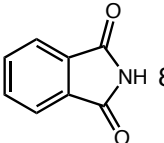
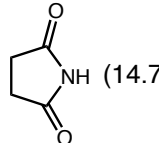
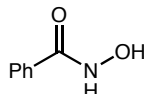
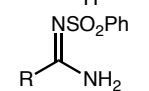
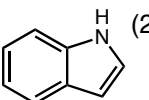
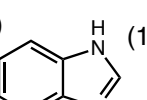
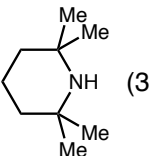
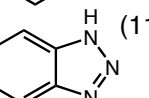
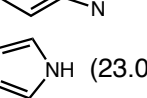
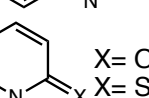
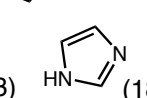
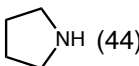
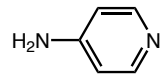
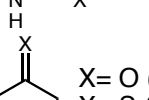
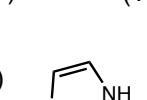
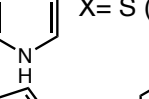
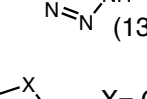
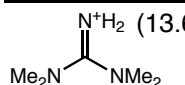
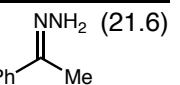
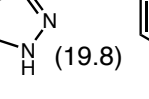
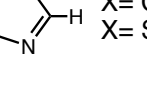
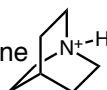
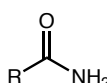
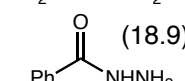
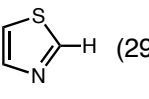
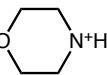
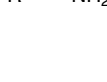
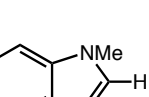
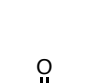
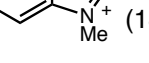
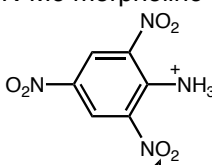
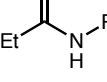
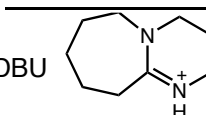
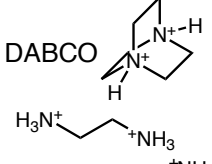
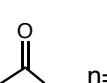
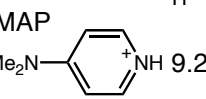
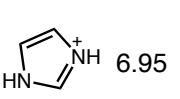
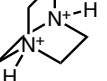
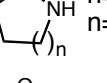
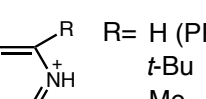
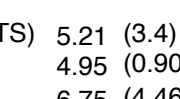
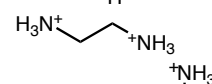
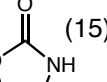
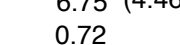
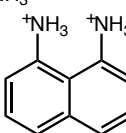
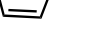


Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
INORGANIC ACIDS			CARBOXYLIC ACIDS			ALCOHOLS			PROTONATED SPECIES		
H ₂ O	15.7	(32)				HOH	15.7	(31.2)		-12.4	
H ₃ O ⁺	-1.7		X= CH ₃	4.76	(12.3)	MeOH	15.5	(27.9)		-7.8	
H ₂ S	7.00		CH ₂ NO ₂	1.68		<i>i</i> -PrOH	16.5	(29.3)		-6.2	
HBr	-9.00	(0.9)	CH ₂ F	2.66		<i>t</i> -BuOH	17.0	(29.4)		-6.5	
HCl	-8.0	(1.8)	CH ₂ Cl	2.86		<i>c</i> -hex ₃ COH	24.0			-3.8	
HF	3.17	(15)	CH ₂ Br	2.86		CF ₃ CH ₂ OH	12.5	(23.5)		-2.05	
HOCl	7.5		CH ₂ I	3.12		(CF ₃) ₂ CHOH	9.3	(18.2)		-2.2	
HCIO ₄	-10		CHCl ₂	1.29		C ₆ H ₅ OH	9.95	(18.0)		-1.8	
HCN	9.4	(12.9)	CCl ₃	0.65		<i>m</i> -O ₂ NC ₆ H ₄ OH	8.4			0.79	(+1.63)
HN ₃	4.72	(7.9)	CF ₃	-0.25		<i>p</i> -O ₂ NC ₆ H ₄ OH	7.1	(10.8)		(+5.55)	
HSCN	4.00		H	3.77		<i>p</i> -OMeC ₆ H ₄ OH	10.2	(19.1)	SULFINIC & SULFONIC ACIDS		
H ₂ SO ₃	1.9, 7.21		C ₆ H ₅	3.6, 10.3		2-naphthol		(17.1)		-2.6	
H ₂ SO ₄	-3.0, 1.99		<i>o</i> -O ₂ NC ₆ H ₄	2.17		OXIMES & HYDROXAMIC ACIDS				2.1	
H ₃ PO ₄	2.12, 7.21, 12.32		<i>m</i> -O ₂ NC ₆ H ₄	2.45			11.3	(20.1)			
HNO ₃	-1.3		<i>p</i> -O ₂ NC ₆ H ₄	3.44			8.88	(13.7) (NH)			
HNO ₂	3.29		<i>o</i> -ClC ₆ H ₄	2.94				(18.5)			
H ₂ CrO ₄	-0.98, 6.50		<i>m</i> -ClC ₆ H ₄	3.83		PEROXIDES					
CH ₃ SO ₃ H	-2.6	(1.6)	<i>p</i> -ClC ₆ H ₄	3.99		MeOOH	11.5				
CF ₃ SO ₃ H	-14	(0.3)	<i>o</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄	1.37		CH ₃ CO ₃ H	8.2				
NH ₄ Cl	9.24		<i>p</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄	3.43							
B(OH) ₃	9.23		<i>p</i> -OMeC ₆ H ₄	4.47							
HOOH	11.6										
			R= H	4.25							
			<i>trans</i> -CO ₂ H	3.02, 4.38							
			<i>cis</i> -CO ₂ H	1.92, 6.23							

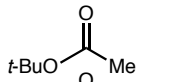
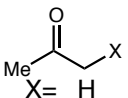
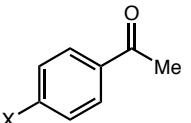
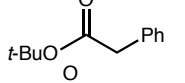
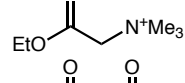
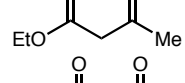
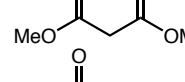
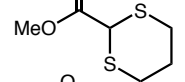
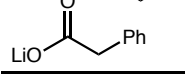
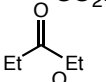
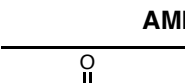
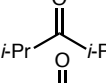
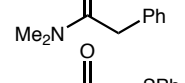
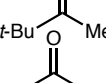
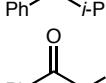
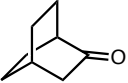
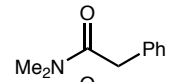
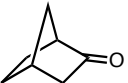
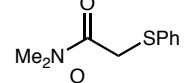
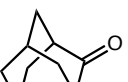
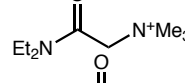
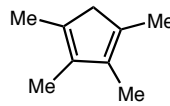
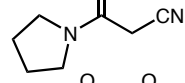
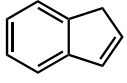
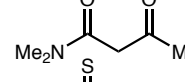
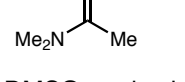
*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

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

Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)			
PROTONATED NITROGEN			AMINES			IMIDES			HYDROXAMIC ACID & AMIDINES					
N ⁺ H ₄	9.2	(10.5)	HN ₃	4.7	(7.9)		8.30			8.88	(13.7) (NH)			
EtN ⁺ H ₃	10.6		NH ₃	38	(41)	Ac ₂ NH				R= Me	(17.3)			
<i>i</i> -Pr ₂ N ⁺ H ₂	11.05		<i>i</i> -Pr ₂ NH	(36 THF))						Ph	(15.0)			
Et ₃ N ⁺ H	10.75	(9.00)	TMS ₂ NH	26(THF)	(30)	SULFONAMIDE			HETEROCYCLES					
PhN ⁺ H ₃	4.6	(3.6)	PhNH ₂	(30.6)		RSO ₂ NH ₂	R = Me	(17.5)		(20.95)		(16.4)		
PhN ⁺ (Me) ₂ H	5.20	(2.50)	Ph ₂ NH	(25.0)			Ph	(16.1)		(11.9)		(23.0)		
Ph ₂ N ⁺ H ₂	0.78		NCNH ₂	(16.9)		MeSO ₂ NHPh	CF ₃	6.3 (9.7)		X= O (24)		(18.6)		
2-napthal-N ⁺ H ₃	4.16			(44)						X= S (13.3)		(13.9)		
H ₂ NN ⁺ H ₃	8.12					GUANIDINIUM, HYDRAZONES, -IDES, & -INES				X= O (14.8)		(24.4)		
HON ⁺ H ₃	5.96		AMIDES & CARBAMATES				(13.6)		(21.6)		X= S (11.8)		(27.0)	
Quinuclidine 	11.0	(9.80)		R= H	(23.5)		(18.9)		(17.2)		X= S (27.0)			
Morpholine 	8.36			CH ₃	15.1 (25.5)	PhSO ₂ NHNH ₂			(26.1)					
N-Me morpholine	7.38			Ph	(23.3)	PhNHNHPh								
	-9.3			CF ₃	(17.2)	PROTONATED HETEROCYCLES				(12) (estimate)				
	2.97, 8.82 (2.97, 8.93)			(urea) NH ₂	(26.9)	DMAP 	Me ₂ N	9.2		6.95				
DABCO 	6.90, 9.95			OEt	(24.8)		R= H (PPTS)	5.21 (3.4)						
	-9.0, 12.0 (-, 7.50)			Bn	(20.5)		<i>t</i> -Bu	4.95 (0.90)						
Proton Sponge 	-10			n= 1 (24.1)			Me	6.75 (4.46)						
PhCN ⁺ H				n= 2 (26.4)			Cl, H	0.72						
				(15)										
				(12.1)										

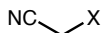
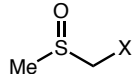
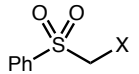
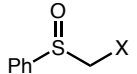
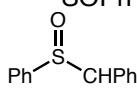
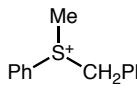
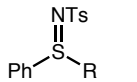
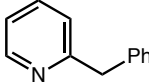
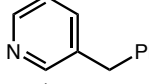
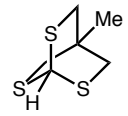
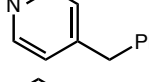
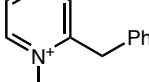
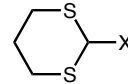
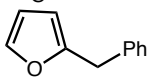
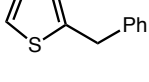
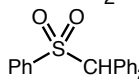
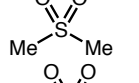
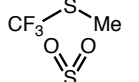
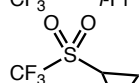
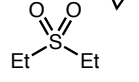
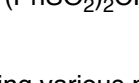
*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

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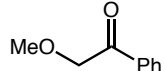
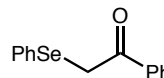
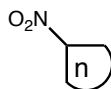
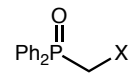
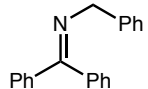
Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
HYDROCARBONS			ESTERS			KETONES					
(Me) ₃ CH	53			24.5	(30.3)						
(Me) ₂ CH ₂	51				(23.6)	X= H		(26.5)	X= H		(24.7)
CH ₂ =CH ₂	50				(20.0)	Ph		(19.8)	OMe		(25.7)
CH ₄	48	(56)			(14.2)	SPh		(18.7)	NMe ₂		(27.5)
	46			11	(14.2)	COCH ₃	9	(13.3)	Br		(23.8)
CH ₂ =CHCH ₃	43	(44)			(15.7)	SO ₂ Ph		(12.5)	CN		(22.0)
PhH	43			13	(15.7)		19-20	(27.1)		n	
PhCH ₃	41	(43)			(20.9)			(28.3)	n= 4		(25.1)
Ph ₂ CH ₂	33.5	(32.2)			[30.2 (THF)]			(27.7)	5		(25.8)
Ph ₃ CH	31.5	(30.6)						(26.3)	6		(26.4)
HCCH	24					X= H		(24.7)	7		(27.7)
PhCCH	23	(28.8)				CH ₃		(24.4)	8		(27.4)
XC ₆ H ₄ CH ₃			AMIDES			Ph		(17.7)			(28.1)
X= p-CN		(30.8)			(26.6)	COCH ₃		(14.2)			(29.0)
p-NO ₂		(20.4)			(25.9)	COPh		(13.3)			(25.5)
p-COPh		(26.9)			(24.9)	CN		(10.2)			(32.4)
		(26.1)			(17.2)	F		(21.6)			
	20	(20.1)			(18.2)	OMe		(22.85)			
	15	(18.0)			(25.7)	OPh		(21.1)			
H ₂	~36					SPh		(16.9)			

*Values <0 for H₂O 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>

Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
NITRILES			SULFIDES			SULFOXIDES			SULFONES		
			PhSCH ₂ X								
X= H		(31.3)	X= Ph		(30.8)	X= 		(35.1) (29.0) (29.0)	X= H		(29.0)
CH ₃		(32.5)	CN		(20.8)				CH ₃		(31.0)
Ph		(21.9)	COCH ₃		(18.7)				<i>t</i> -Bu		(31.2)
COPh		(10.2)	COPh		(16.9)	X= 		(33) (27.2) (18.2)	Ph		(23.4)
CONR ₂		(17.1)	NO ₂		(11.8)				CH=CH ₂		(22.5)
CO ₂ Et		(13.1)	SPh		(30.8)			(24.5)	CH=CHPh		(20.2)
CN	11	(11.1)	SO ₂ Ph		(20.5)				CCH		(22.1)
OPh		(28.1)	SO ₂ CF ₃		(11.0)	SULFONIUM			CCPh		(17.8)
N ⁺ Me ₃		(20.6)	POPh ₂		(24.9)	Me ₃ S ⁺ =O		(18.2)	COPh		(11.4)
SPh		(20.8)	MeSCH ₂ SO ₂ Ph		(23.4)			(16.3)	COMe		(12.5)
SO ₂ Ph		(12.0)	PhSCHPh ₂		(26.7)	SULFIMIDES & SULFOXIMINES			OPh		(27.9)
HETERO-AROMATICS			(PhS) ₃ CH		(22.8)			(27.6) (30.7)	N ⁺ Me ₃		(19.4)
		(28.2)	(PrS) ₃ CH		(31.3)	R= Me		(24.3)	CN		(12.0)
		(30.1)			(30.5)	Et		(24.0)	NO ₂		(7.1)
		(26.7)	(PhS) ₂ CHPh		(23.0)	<i>i</i> -Pr		(23.6)	SMe		(23.5)
		(25.2)				<i>t</i> -Bu		(22.9)	SPh		(20.5)
		(30.2)	X= Ph		(30.7)	PhSCH=CHCH ₂ SPh		(26.3)	SO ₂ Ph		(12.2)
		(30.0)	CO ₂ Me		(20.8)	BuSH	10-11	(17.0)	PPh ₂		(20.2)
			CN		(19.1)	PhSH	≈7	(10.3)			(22.3)
			RSCH ₂ CN								(31.1)
			R= Me		(24.3)						(18.8)
			Et		(24.0)						(21.8)
			<i>i</i> -Pr		(23.6)						(26.6)
			<i>t</i> -Bu		(22.9)						(32.8)
			PhSCH=CHCH ₂ SPh		(26.3)				(PhSO ₂) ₂ CH ₂ Me		(14.3)
			BuSH	10-11	(17.0)						
			PhSH	≈7	(10.3)						

*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

Substrate	pKa	H ₂ O	(DMSO)	Substrate	pKa	H ₂ O	(DMSO)	Substrate	pKa	H ₂ O	(DMSO)	REFERENCES
ETHERS				PHOSPHONIUM				NITRO				
CH ₃ OPh		(49)		P ⁺ H ₄		-14		RNO ₂				DMSO:
MeOCH ₂ SO ₂ Ph		(30.7)		MeP ⁺ H ₃		2.7		R= CH ₃		≈10	(17.2)	JACS <u>97</u> , 7007 (1975)
PhOCH ₂ SO ₂ Ph		(27.9)		Et ₃ P ⁺ H		9.1		CH ₂ Me			(16.7)	JACS <u>97</u> , 7160 (1975)
PhOCH ₂ CN		(28.1)		Ph ₃ P ⁺ CH ₃		(22.4)		CHMe ₂			(16.9)	JACS <u>97</u> , 442 (1975)
		(22.85)		Ph ₃ P ⁺ <i>i</i> -Pr		(21.2)		CH ₂ Ph			(12.2)	JACS <u>105</u> , 6188 (1983)
				Ph ₃ P ⁺ CH ₂ COPh		(6.2)		CH ₂ Bn			(16.2)	JOC <u>41</u> , 1883 (1976)
				Ph ₃ P ⁺ CH ₂ CN		(7.0)		CH ₂ SPh			(11.8)	JOC <u>41</u> , 1885 (1976)
				PHOSPONATES & PHOSPHINE OXIDES				CH ₂ SO ₂ Ph			(7.1)	JOC <u>41</u> , 2786 (1976)
SELENIDES				(EtO) ₂ P(=O)CH ₂ X				CH ₂ COPh			(7.7)	JOC <u>41</u> , 2508 (1976)
		(18.6)		X= Ph		(27.6)						JOC <u>42</u> , 1817 (1977)
PhSeCHPh ₂		(27.5)		CN		(16.4)		n= 3			(26.9)	JOC <u>42</u> , 321 (1977)
(PhSe) ₂ CH ₂		(31.3)		CO ₂ Et		(18.6)		4			(17.8)	JOC <u>42</u> , 326 (1977)
PhSeCH ₂ Ph		(31.0)		Cl		(26.2)		5			(16.0)	JOC <u>43</u> , 3113 (1978)
PhSeCH=CHCH ₂ SePh		(27.2)		SiMe ₃		(28.8)		6			(17.9)	JOC <u>43</u> , 3095 (1978)
								7			(15.8)	JOC <u>43</u> , 1764 (1978)
AMMONIUM				X= SPh		(24.9)		IMINES				JOC <u>45</u> , 3325 (1980)
Me ₃ N ⁺ CH ₂ X				CN		(16.9)					(24.3)	JOC <u>45</u> , 3305 (1980)
X= CN		(20.6)		PHOSPHINES								JOC <u>45</u> , 3884 (1980)
SO ₂ Ph		(19.4)		Ph ₂ PCH ₂ PPh ₂		(29.9)		Oxime ethers are ~ 10 pka units less acidic than their ketone counterparts				JOC <u>46</u> , 4327 (1981)
COPh		(14.6)		Ph ₂ PCH ₂ SO ₂ Ph		(20.2)		Streitwieser, JOC 1991, 56, 1989				JOC <u>46</u> , 632 (1981)
CO ₂ Et		(20.0)										JOC <u>47</u> , 3224 (1982)
CONEt ₂		(24.9)										JOC <u>47</u> , 2504 (1982)
												Acc. Chem. Res. <u>21</u> , 456 (1988)
												Unpublished results of F. Bordwell
												Water:
												Advanced Org. Chem., 3rd Ed.
												J. March (1985)
												Unpublished results of W. P. Jencks
												THF:
												JACS <u>110</u> , 5705 (1988)
												See cited website below for additional data

*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

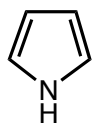
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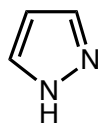
DMSO Acidities of Common Heterocycles

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

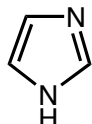
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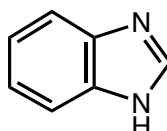
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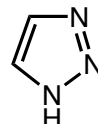
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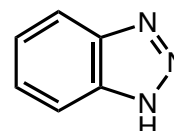
18.6



16.4



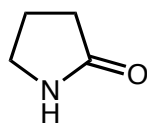
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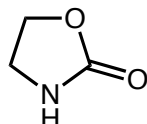
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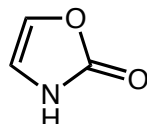
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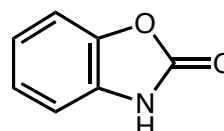
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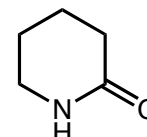
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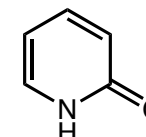
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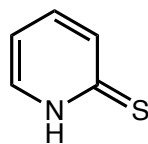
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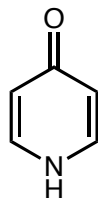
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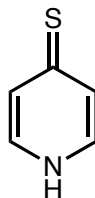
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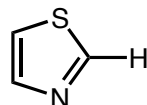
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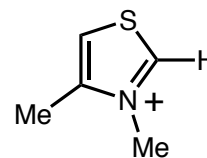
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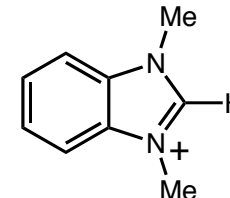
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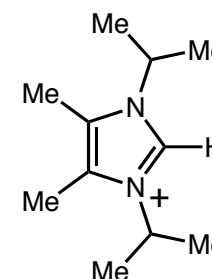
29.4



16.5



18.4



24