Supporting Information

Unusual protonation of N-(1,1-dimethyl-3-oxobutyl)amides in strong acid media

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General remarks

NMR measurements.

NMR spectra in solutions were recorded on a Bruker Avance III 400 MHz instrument (100 MHz frequency for ^{13}C). NMR ^{13}C chemical shifts for solutions in DMSO-d_6 are referenced to the solvent's central signal (δ_C 39.52 ppm for DMSO-d6). H_2SO_4 (70 wt. % in D_2O) solutions were prepared by diluting of concentrated sulfuric acid with D_2O. Acetonitrile (10% solution of CH_3CN in a mixture of H_2SO_4-D_2O) was used as a standard for ^{13}C NMR spectra in ~70% H_2SO_4 solutions. Chemical shifts were recorded relative to the δ_C signal of 119.68 ppm for the CN group. Solid state ^{13}C NMR spectra were recorded using a Bruker Avance III WB 400 MHz spectrometer. The samples were rotated at a magic angle with a frequency of 10 kHz using $^{13}C\{1H\}$ cross-polarization (CP/MAS).

XRD study.

Single crystal X-ray analysis was performed at single crystal diffractometer Xcalibur EOS. A suitable crystal was selected and studied on the diffractometer. The crystal was kept at 100(2) K during data collection. The structure was solved using Olex2,[1] with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL refinement package using least squares minimization. CCDC number 1026534 (compound **4a**) contains the supplementary crystallographic data, which can be obtained free of charge from The

[1] O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341
[2] G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122

CambridgeCrystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Some crystallographic parameters and structure refinement details of **4a** are given in the Tables 1-4.

Determination of amides basicity.

Stock solutions of the amides (~5-6·10^{-2} mol/L) were prepared in ~50% aqueous isopropanol. Using a 50 μL Hamilton 705 N microsyringe, the required volume of the resulting solution (30-40 μL) was injected into a volumetric flask containing exactly 25 mL of aqueous sulfuric acid of known concentration, thermostatted at 25°C, thoroughly mixed, and placed in a quartz cuvette of the spectrophotometer. UV spectra of the resulting solutions were recorded in the range of 196-280 nm relative to sulfuric acid of the same concentration. The calculation of ionization ratios (*I*) was carried out according to equation:

$I = [BH^+] / [B] = (D - D_B) / (D_{BH^+} - D)$,

using optical densities (*D*) at analytical wavelengths λ_{analyt}. The concentrations of amides and the λ_{analyt} values are given in Table 5.

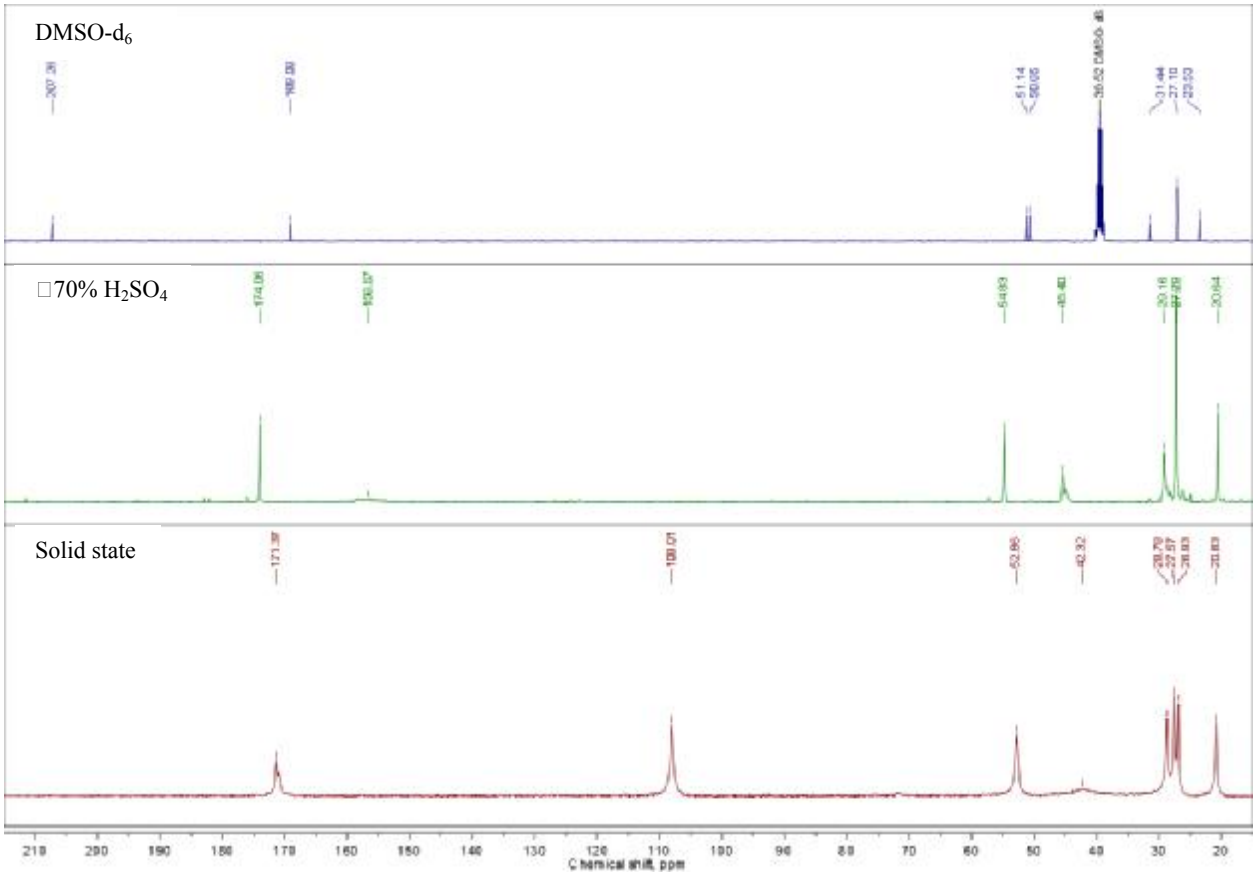


Figure 1. ^{13}C NMR spectra of N-(1,1-dimethyl-3-oxobutyl)acetamide **2** in DMSO-d6, □70% H_2SO_4 (□70 wt. % in D_2O) and solid state ^{13}C NMR spectrum of 2,4,4,6-tetramethyl-6-hydroxy-5,6-dihydro-4*H*-1,3-oxazin-3-ium hydrosulfate **2a**

Table 1. Crystallographic data and parameters of the XRD experiment for the structure **4a**

Chemical formula	$C_{13}H_{19}NO_6S$
Formula weight *(M)*	317.35
Temperature / K	100.01(10)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.4742(3)
b/Å	15.0664(5)
c/Å	10.4608(4)
α/°	90
β/°	91.398(3)
γ/°	90
Volume /Å^3	1492.75(9)
Z	4
d_{calc} /g·cm^{-3}	1.412
μ/mm^{-1}	0.243
Θ_{max}/°	27.500
T_{min}/T_{max}	0.995/1.000
Number of reflections	7857
measured	3431
independent	2968
I/σ*I*(I)	29.6
(R_{int})	2.32%
Number of parameters refined	195
GOOF	1.052
R_1 ($I > 2\sigma(I)$)	0.0340
wR_2	8.59%
$(\Delta\rho_{min}/\Delta\rho_{max})/e\cdot$Å^{-3}	0.3/−0.5

Table 2. Main bonds lengths in compound **4a**

Atom	Atom	Bond length, Å
C4	C5	1.5374(19)
C4	C8	1.5270(19)
C4	C9	1.531(2)
C2	C11	1.4722(19)
O1	C6	1.5067(16)
O1	C2	1.3115(16)
O10	C6	1.3777(17)
N3	C2	1.3009(17)
N3	C4	1.4854(18)
C6	C5	1.5192(19)
C6	C7	1.5147(19)

Table 3. Main valence angles in compound **4a**

Atom	Atom	Atom	Angle, °
N3	C2	C11	121.40(12)
C12	C11	C2	120.99(12)
C16	C11	C2	118.47(12)
C2	O1	C6	118.02(10)
C2	N3	C4	126.37(12)
O1	C6	C5	106.81(11)
O1	C6	C7	103.49(10)
O10	C6	O1	107.42(11)
O10	C6	C5	110.33(11)
O10	C6	C7	113.99(12)
C7	C6	C5	114.11(12)
O1	C2	C11	115.40(11)
N3	C2	O1	123.19(13)
N3	C4	C5	107.68(11)
N3	C4	C8	107.86(11)
N3	C4	C9	106.90(11)
C8	C4	C5	114.00(12)
C8	C4	C9	109.85(12)
C9	C4	C5	110.25(12)
C6	C5	C4	113.73(12)

Table 4. Main torsion angles in compound **4a**

Atom	Atom	Atom	Atom	Angle, °
O1	C6	C5	C4	56.24(15)
O1	C2	C11	C12	−157.11(13)
O1	C2	C11	C16	24.97(18)
O10	C6	C5	C4	−60.20(15)
N3	C2	C11	C12	24.2(2)
N3	C2	C11	C16	−153.73(13)
N3	C4	C5	C6	−38.62(15)
C6	O1	C2	N3	15.26(19)
C6	O1	C2	C11	−163.42(11)
C2	O1	C6	O10	73.90(14)
C2	O1	C6	C5	−44.47(15)
C2	O1	C6	C7	−165.22(12)
C2	N3	C4	C5	7.14(18)
C2	N3	C4	C8	−116.31(15)
C2	N3	C4	C9	125.60(14)
C4	N3	C2	O1	5.2(2)
C4	N3	C2	C11	−176.19(12)

C8	C4	C5	C6	81.00(15)
C7	C6	C5	C4	169.95(12)
C9	C4	C5	C6	−154.91(12)

Table 5. The concentrations of amides and the λ_{analyt} values

Amide	**1**	**4**	**7**	**8**	**9**	**10**	**11**
$c \cdot 10^5$, mol/L	6.88	6.06	7.30	4.65	9.58	4.24	5.15
$\lambda_{ан.}$, nm	220	265	218	218	220	226	262