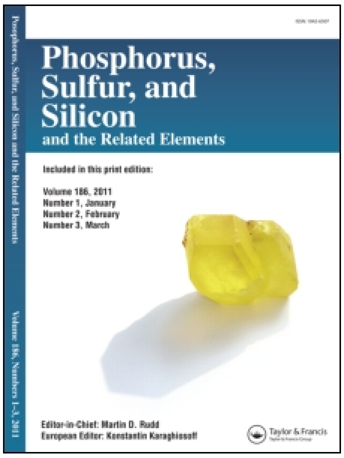

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Communication

ADDUCTS OF LACTAMS WITH THIOUREA OR UREA

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Lactams 1 form crystalline 1:1-adducts 3 with thiourea 2a or N-methyl-urea 2b. The adducts are stable in the solid state but decompose to their constituents if dissolved in organic solvents.

Key words: Adducts; lactams; thiourea; N-methylurea.

Recently the reaction of lactams 1 with thiourea 2a ($X = S$; $R^2 = H$) or N-methylurea 2b ($X = O$; $R^2 = CH_3$) was reported.[1] Crystalline products were obtained, which dissolve easily in water, but are sparingly soluble in organic solvents such as alcohols or hydrocarbons. They can be recrystallized from absolute ethanol. In the mass spectra both constituents 1 and 2 are found while higher peaks are missing. Further investigations have now revealed, that the original structural assignment as N-(w-aminobutyryl)-thiourea or -urea has to be revised.

Adduct 3b gives the same ^{13}C-NMR spectrum like an 1:1 mixture of constituents 1 ($n = 1$, $R^1 = Me$) and 2. Furthermore addition of either the lactam 1 or the corresponding thiourea 2a ($X = S$) or urea 2b ($X = O$) respectively to the ^{1}H-NMR-sample gives rise to an increase in already existing peaks rather than the formation of new ones. As a consequence the products obtained from the above-mentioned reaction must have decomposed on dissolving in the appropriate solvent. This result is consistent with the well-known property of thiourea and urea of forming inclusion compounds with a variety of liquid guests.[2,3] However the 1:1 stoichiometry and the melting points (which are different from those of the corresponding thiourea or urea) are not in agreement with this host-guest model. X-ray structure analysis of compound 3b revealed that the products obtained from lactams 1 and thiourea or urea are 1:1 adducts.

The two constituents are connected via hydrogen bonding between the O atom of lactam 1 and amino groups of two molecules of 2a. Furthermore, thiourea or urea units respectively are bound to each other by hydrogen bridging.

The above results are of potential analytical interest in order to purify lactams[4] or to separate lactams from their solutions in organic solvents. For instance, a solution of N-methyl-2-pyrrolidone 1 ($n = 1$, $R = CH_3$) in ethanol ($c_0 = 3.5$ mol%) was treated with thiourea. After filtration of the corresponding adduct 3b the remaining concentration of N-methyl-2-pyrrolidone in the mother liquor was only 0.3 mol%.

TABLE I

Adducts 3 from lactams 1 and thiourea or N-methylurea

3	yield [%]	m.p. [°C]	molecular formula (mol. mass)	m.s. m/z (%)
a1)	83	79-80	$C_5H_{11}N_3SO$	85(65); 76(99); 60(43); 43(89);
			(161.2)	42(34); 41(43); 32(23); 28(100)
b2)	88	107-109	$C_6H_{13}N_3SO$	99(81), 76(100); 60(33); 44(83);
			(175.2)	43(81); 42(85); 32(22); 28(53)
c	45	about 15	$C_7H_{15}N_3O_2$	99(92); 74(70); 58(34); 56(25);
			(173.2)	44(100); 42(78); 31(52); 28(37)
d3)	79	85-86	$C_7H_{15}N_3OS$	113(54); 76(96); 70(19), 60(33);
			(189.3)	44(100)

1) ^{1}H-NMR (D_2O) δ [ppm]: 2.5 (m, 4H), 3.7 (t, 2H, J = 7Hz)

2) ^{1}H-NMR (DMSO-d_6) δ [ppm]: 2.0 (m, 4H), 2.62 (s, 3H), 3.25 (t, 2H, J = 7Hz), 7.0 (br, 4H)

^{13}C-NMR (D_2O) δ [ppm]: 17.5, 29.8, 31.2, 50.6, 178.4, 182.5

3) ^{1}H-NMR (D_2O) δ [ppm]: 1.78 (m, 4H), 2.22 (t, 2H, J = 7Hz), 2.9 (s, 3H), 3.35 (t, 2H, J = 7Hz)

^{13}C-NMR (D_2O) δ [ppm]: 20.8, 22.7, 31.8, 35.8, 50.6, 173.6, 182.5

EXPERIMENTAL

Melting points are corrected and were determined at a BOETIUS heating block. The spectra were recorded by the following instruments: I.R.: Specord IR 71, VEB Carl Zeiss Jena; ^{1}H-NMR: BS 487C (80 MHz), Tesla Brno; ^{13}C-NMR: Bruker AC 300; M.S.: HP 5995 A (70 eV) Hewlett Packard; Gas chromatography: GC Chromatron 18.3, phase: 10% OV-101 on Chromaton N, AW, DMCS; N_2, 150°. All compounds but 3c gave satisfactory results (C, H, N, ± 0.3%) in elemental analysis.

Crystal structure analysis of the adduct 3b. The adduct crystallizes in the monoclinic space group $P2_1/n$ with cell constants (at −95°C) a 7.640(2), b 8.636(2), c 14.399(3)A, β 104.82(2)°. The structure was refined anisotropically (without H atoms) to R 0.098. The impossibly high temperature factors of the ring carbon atom C(4) indicate some form of static disorder. Since the broad features of the crystal packing were clear, no further refinement was attempted. Details of structure determination are available from PGJ.

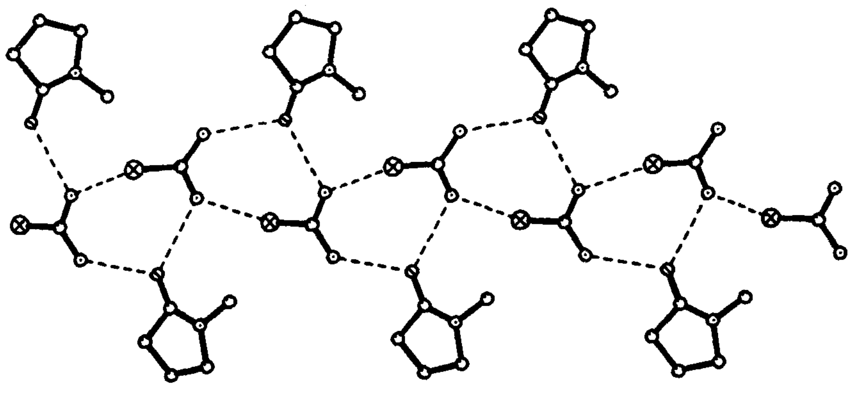

FIGURE 1 Structure plot of adduct 3b

Adducts 3 of Lactams 1 and Thiourea 2a (X = S; R^2 = H) or N-Methyl-urea 2b (X = O; R^2 = CH_3)—General Procedure (See Table I). 0.1 mol lactam 1 and 7.6 g (0.1 mol) of thiourea 2a are briefly heated in 20 ml absolute ethanol until all the thiourea is dissolved. After keeping the resulting solution in a refrigerator overnight the adduct 3 is filtered off by suction and recrystallized from absolute ethanol. In case of the N-methyl-urea adduct 3c an oil was obtained, which was decanted and washed with a small amount of cold ethanol.

1 2 3

2a (X = S, R^2 = H)

2b (X = O, R^2 = Me)

3	n	R^1	R^2	X
a	1	H	H	S
b	1	CH_3	H	S
c	1	CH_3	CH_3	O
d	2	CH_3	H	S

Determination of remaining concentration of N-methyl-2-pyrrolidone in ethanol after addition of thiourea. 3 g (0.04 mol) thiourea 2a are added to a solution of 3 g (0.03 mol) N-methyl-2-pyrrolidone in 50 ml dry ethanol. After brief heating to the boiling point the resulting solution is placed in the refrigerator (−5°) overnight. After filtration of the adduct 3b the mother liquor is analyzed by gas chromatography. The remaining concentration of N-methyl-2-pyrrolidone was 0.3 mol per cent.

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