Pyramidal amide nitrogen in N-acyloxy-N-alkoxyureas and N-acyloxy-N-alkoxy carbamates

Oleg V. Shishkin,a Roman I. Zubatyuk,a Vasily G. Shtamburg,b Alexander V. Tsygangov,b Evgeny A. Klots,b Alexander V. Mazepa1 and Remir G. Kostyanovskyyd

a STC ‘Institute for Single Crystals’, National Academy of Sciences of Ukraine, 61001 Kharkov, Ukraine.
E-mail: shishkin@xray.isc.kharkov.com
b Department of Chemistry, Dnepropetrovsk National University, 49050 Dnepropetrovsk, Ukraine
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A. V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, 65060 Odessa, Ukraine.
Fax: +38 0482 65 2012; e-mail: chemtor@paco.net
d N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation.
Fax: +7 495 137 8284; e-mail: kost@chph.ras.ru

The XRD studies of N-acyloxy-N-alkoxyamidies 1, 2 have revealed a highly pyramidal configuration of amide nitrogen in the O–N–O group.

Optically active compounds with asymmetric nitrogen in the open chain were obtained firstly for the series of N,N-dialkoxycarbamates [RN(OMe)OR], R–H, tert-alkyl (ΔG°mp = 19.0–24.6 kcal mol–1 at 64–175 °C2(60.8%)). The high pyramidality of the nitrogen in (MeO)2NH,2(60.8%) of 282 (6.3) [M + Na]+, 141 (64.1), 139 (100), 120 (6.7), 113 (4.1), 111 (17.3), 104 (6.7), 103 (6.7), 102 (6.7), 91 (11.1), 90 (11.1), 89 (11.1), 88 (11.1), 87 (11.1), 86 (11.1), 85 (11.1), 84 (11.1), 83 (11.1), 82 (11.1), 81 (11.1), 80 (11.1), 79 (11.1), 78 (11.1), 77 (11.1), 76 (11.1), 75 (11.1), 74 (11.1), 73 (11.1), 72 (11.1), 71 (11.1), 70 (11.1), 69 (11.1), 68 (11.1), 67 (11.1), 66 (11.1), 65 (11.1), 64 (11.1), 63 (11.1), 62 (11.1), 61 (11.1), 60 (11.1), 59 (11.1), 58 (11.1), 57 (11.1), 56 (11.1), 55 (11.1), 54 (11.1), 53 (11.1), 52 (11.1), 51 (11.1), 50 (11.1), 49 (11.1), 48 (11.1), 47 (11.1), 46 (11.1), 45 (11.1), 44 (11.1), 43 (11.1), 42 (11.1), 41 (11.1), 40 (11.1), 39 (11.1), 38 (11.1), 37 (11.1), 36 (11.1), 35 (11.1), 34 (11.1), 33 (11.1), 32 (11.1), 31 (11.1), 30 (11.1), 29 (11.1), 28 (11.1), 27 (11.1), 26 (11.1), 25 (11.1), 24 (11.1), 23 (11.1), 22 (11.1), 21 (11.1), 20 (11.1), 19 (11.1), 18 (11.1), 17 (11.1), 16 (11.1), 15 (11.1), 14 (11.1), 13 (11.1), 12 (11.1), 11 (11.1), 10 (11.1), 9 (11.1), 8 (11.1), 7 (11.1), 6 (11.1), 5 (11.1), 4 (11.1), 3 (11.1), 2 (11.1), 1 (11.1). The XRD studies of N-acyloxy-N-alkoxyamidies 1 and N-acyloxy-N-alkoxyurea 2 (Figures 1, 2) revealed that amide O–N–O nitrogen has a pyramidal configuration (the sum of bond angles centered at this nitrogen atom is 334.1° for carbamate 1 or 333.6° for urea 2). Analysis of Winkler–Dunitz parameters5 for amides demonstrates that some negligible twist around the C–N bond is observed (τ = 2.9° for 1 and τ = −6.8° for 2). The nitrogen pyramidality value (in carbamate 1, τN = −57.1°; in urea 2, τN = −57.1°) is some few as in N-acyloxy-N-alkoxy carbamates.

This but parameter for the amide carbon atom is higher than

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1 Asymmetric Nitrogen. Part 97. Geminal Systems. Part 55. Previous communications see ref. 1.
2 Methyl N-4-chloroacetoxy-N-methoxy carbamate 1. A solution of methyl N-4-chloro-N-methoxy carbamate(4.53 g, 3.80 mol) in MeCN (30 ml) and 4-CIC6H4CO2Na (1.36 g, 7.61 mmol) was stirred for 77 h at 20 °C. CH2Cl2 (10 ml) was added; the solid was filtered off and washed with CH2Cl2 (20 ml). The filtrate was concentrated in vacuo; the residue was extracted with CH2Cl2 (12 ml) at 5 °C. The extract was concentrated in vacuo; the residue was extracted with Et2O–hexane (1:5, the extract was concentrated in vacuo; yield, 0.76 g (77%) of I, white solid, mp 35–36 °C (x-hexane) (lit.,5,6 35–36 °C); [α]D20 = +20.0 (c = 0.1, CH2Cl2). 1H NMR (300 MHz, CDCl3) δ: 3.92 (s, 3H, NOMe), 3.97 (s, 3H, CO2Me), 7.47 (d, 2H, C(2)H, C(5)H, J = 8.4 Hz), 8.30 (d, 2H, C(2)H, C(6)H, J = 8.4 Hz). 13C NMR (75 MHz, CDCl3) δ: 55.3 (NOMe), 63.4 (CO2Me), 125.6 (C(4)), 129.2 (C(2)), 131.5 (C(2)), 135.1 (C(1)), 158.5 (CO2Me); 163.7 (CO2), IR (v/cm–1): 1785 (C=O). MS (FAB) m/z (%): 284 (1.6), 282 (6.3) [M + Na]+, 141 (64.1), 139 (100), 120 (67), 113 (4.1), 111 (17.1), 104 (60.5). Found (%): C, 76.7; H, 7.9; N, 3.5. Calc. for C9H13NO2C1: C, 76.2; H, 7.8; N, 3.5.

2 N-Acetoxy-N-ethoxyurea 2. A mixture of a solution of N-chloro-N-ethoxyurea (0.9 g, 11 mmol) was stirred at 20 °C for 40 h. CH2Cl2 (10 ml) was added; the precipitate was filtered off and washed with CH2Cl2. The filtrate was concentrated in vacuo, the residue was washed with Et2O (5 ml) and then extracted with CH2Cl2 (30 ml). The CH2Cl2 extract was concentrated in vacuo, the residue was kept at 20 °C and 2 Torr for 0.5 h; yield, 0.54 g (50.8%) of 2, colourless crystals, mp 104–105 °C [MeC(O)–EtO]2 at −5 °C (lit.,5,6 mp 93–95 °C). 1H NMR (300 MHz, CDCl3) δ: 1.32 (t, 3H, OCH2Me, J7 Hz), 2.19 (s, 3H, MeC(O)O(O)), 4.14 (q, 2H, OCH2Me, J7 Hz), 5.68 (brs, 5H, CH), 6.01 (brs, s, 1H, NH), IR (v/cm–1): 1798 (C=O), 1720 (C=O). Found (%): C, 51.7; H, 6.31; N, 17.15. Calc. for C4H8NO2Cl: C, 46.11; H, 6.32; N, 17.28.

DOI: 10.1070/MC2006v016n04ABEH002195

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Figure 1 Structure of molecule 1. Selected bond lengths (Å) and bond angles (°): (N(1)–C(2) 1.423(2), N(1)–O(1) 1.424(2), N(1)–O(4) 1.396(2), C(1)–O(1) 1.388(2), C(2)–O(5) 1.322(2), O(1)–N(1)–C(2) 111.4(1), C(2)– N(1)–O(4) 113.4(1), O(1)–N(1)–O(4) 109.3(1).

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Glover reported\(^{10(b)}\) (in carbamate 1, \(\chi_2 = 7.9\); in urea 2, \(\chi_2 = 7.6\)). That reveals at some distortion of the planar configuration of the carbon atom. This also accompanies some deviation of the sum of bond angles, centered on amide carbon atom, from 360° (359.4° in urea 1 and 359.5° in urea 2).

In compounds 1 and 2 bond lengths with amide nitrogen participation are really equivalent. The nitrogen lone pair conjugates with the \(\pi\) system of the carbonyl group. In both molecules, the alkoxyl group is in conformation close to anticyclan with respect to the C–N bond [the C–N–O–C torsion angle is 139.6(2)° in carbamate 1 or –131.3(3)° in urea 2]. The ester substituent has synclinal orientation relatively the same bond [the C–N–O–C torsion angle is 59.0(2)° in carbamate 1 or –56.7(3)° in urea 2]. At the same time, contrary to compounds studied by Glover, the carbonyl group of the ester substituent is in sc-conformation with respect to the amide nitrogen atom [the N–O–C=O torsion angle is –2.6(2)° in carbamate 1 or 3.3(3)° in urea 2]. Quantum-chemical calculations\(^6\) using the MP2/6-311+G(2\(d,2p\))//B3LYP/6-311+G(2\(d,2p\)) method demonstrated that such a configuration of the amide nitrogen atom is 3.43 or 4.24 kcal mol\(^{-1}\) more stable contrary to inverted configuration for molecules of 1 and 2, respectively.

The smaller pyramidality of the amide nitrogen atom arouses some shortening of the C–N amide bond as compared to N-acryloxy-N-alkoxybenzamides.\(^{6,\text{b}}\) The considerable differences of the N–O bond lengths attract attention. The N–O\(\text{acyl}\) bond is significantly longer as compared to the N–O\(\text{org}\) bond. This bond difference results\(^{2,6,7}\) in significant degree from the anomeric interaction within the O–N–O fragment, particularly by donation of lone pair of the oxygen atom into the non-bonding orbital of the N–O\(\text{acyl}\) bond (\(\eta_2 \rightarrow \sigma^*_{\text{O-C(acyl)}}\)). In addition, it is observed significant non-equivalence of the O–C(=O) bonds in the molecule of carbamate 1. The C–O bond elongation in the ester substituent may also be explained by anomeric interactions within the N–O–C fragment. The analysis of intramolecular interactions using the NBO theory\(^{8,9}\) for the wavefunction calculated by the B3LYP/6-311+G(2\(d,2p\)) method demonstrated that, in the molecule under consideration, the donation of a lone pair of the amide nitrogen atom on non-bonding orbital of the C–O bond is observed (\(\eta_2 \rightarrow \sigma^*_{\text{O-C(O)}}\)).

In conclusion, it should be noted that nitrogen pyramidality observed in crystalline structure, as well as in solution, as in gaseous phase, is mutual property of the compounds with configurationally stable nitrogen, such as aziridines,\(^{10(a),10(b)}\) diaziridines,\(^{10(c)}\) and oxaziridines.\(^{10(d)}\) The high pyramidality of the P atom was also found in acylphosphines.\(^{10(e)}\)

This work was supported by the Russian Academy of Sciences.

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Figure 2 Structure of molecule 2. Selected bond lengths (Å) and bond angles (°) N(1)–C(2): 1.426(5), N(1)–O(1): 1.246(2), N(1)–O(4): 1.398(2), C(1)–O(1): 1.377(3), O(1)–N(1)–C(2): 111.6(2), C(2)–N(1)–O(4): 113.5(2), O(1)–N(1)–O(4): 108.5(2).

Received: 27th February 2006; Com. 06/2690