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N,*O*-diacylhydroxylamines—structures in crystals and solutions†

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The structures of four *N*,*O*-diacylhydroxylamines (RCOHNOCOR′, R, R′ = Me, Ph) were determined in the solid state by X-ray diffraction and studied by NMR and IR spectroscopies in solution. The interpretation of the results was supported by *ab-initio* calculations of various tautomers and conformers, rotational barriers and chemical shifts. The results indicate the absence of OH tautomers (R–C(OH)=N–O–C(O)–R′, *N*-acyloxyimidic acid); the NH tautomers (R–C(O)–NH–O–C(O)–R′, *O*-acylhydroxamic acid) are present in DMSO solutions as equilibrium mixtures of a few conformers, their exchange being the likely source of ^{15}N and ^{13}C NMR line broadening.

Introduction

Our systematic investigation of hydroxamic acid derivatives was directed mainly to silyl derivatives and took advantage of the NMR spectroscopy of ^{29}Si, ^{15}N and ^{13}C nuclei as the main experimental method. The structures, tautomerism, configurations and conformations of many derivatives have been determined in this way.[1–4] On the other hand, these silyl derivatives can be hardly exploited for determining the structures of the parent compounds—as is often done in the case of other classes of compounds.[5] Silylation of the –C(O)–NH–O– fragment is usually associated with isomerization and the reaction often yields two products in a variable ratio: their structure brings new problems. Such a case was observed recently during silylation of *N*,*O*-diacylhydroxylamines **1–4** (Scheme 1): the ratio of the two products formed was considerably different in aliphatic and aromatic derivatives.[6] This led us to extend our studies to the parent compounds using additional experimental methods.

R-C(O)-NH-O-C(O)-R' **1A - 4A**

R-C(OH)=N-O-C(O)-R' **1B - 4B**

	R	R'
1	CH_3	CH_3
2	CH_3	Ph
3	Ph	CH_3
4	Ph	Ph

Scheme 1 Tautomer formulae of the studied *N*,*O*-diacylhydroxylamines.

N,*O*-Diacylhydroxylamines represent the key intermediates in the successive acylation of hydroxylamine. They are usually obtained as the main or unique product, are well characterized and can serve for preparing trisubstituted derivatives.[7] Their structure has never been doubted. It has been confirmed by IR spectra[8–10] and in a few cases by X-ray diffraction;[11] the conformation in solution was deduced from dipole moments.[12] Nevertheless, these proofs have a weakness that they all have been obtained on aromatic derivatives, mostly on **4**. In contrast, it is just the difference between aromatic and aliphatic derivatives which is important for our purpose.

Therefore, we prepared *N*,*O*-diacetylhydroxylamine **1**, *N*-acetyl-*O*-benzoyl-hydroxylamine **2**, *N*-benzoyl-*O*-acetylhydroxylamine **3**, and *N*,*O*-dibenzoylhydroxylamine **4**, and investigated them by X-ray analysis, NMR spectroscopy, IR spectroscopy and by calculations within the framework of the density functional theory. Particular attention was given to the possible presence of two tautomers (NH tautomers **1A–4A**, *O*-acylhydroximic acid, and OH tautomers **1B–4B**, *N*-acyloxyimidic acid) and to the conformers arising from the rotation around the C–N and/or N–O bonds. To the best of our knowledge the tautomers have never been sought out, although there are good proofs of the tautomerism of *O*-alkylhydroxamic acids,[13] particularly of *O*-benzylbenzohydroxamic acid[13,14] which is structurally rather similar to **4**.

Results and discussion

Structures in the solid state. The most important results of X-ray structure analysis of low temperature data are summarized in Table 1 together with the results of previous X-ray analyses of closely related *O*-acylbenzhydroxamic acids **5–8**.[11,15] (For more details including ORTEP drawings and types of supramolecular structures for each compound studied see electronic supplementary information (ESI).†) In the solid state all the compounds have the structure of NH tautomers (*e.g.*, **1A–4A**). Our results for **4** agree well with the previous work performed at ambient temperature.[11]

The bond distances and angles are very similar in all described molecules **1–8**. The most interesting for conformational analysis is the dihedral angle τ = C–N–O–C, which is within the range 84.5 ± 3.2° except for **1** and **8**. The angle τ was estimated[12] to be 70° in a solution of **4**; evidently it is not substantially affected by packing forces. The nonplanar and rather rigid conformation of the C–N–O–C fragment resembles the conformation of the C–O–O–C fragment in peroxides.[16] Conformations of the C–N and O–C single bonds are the same in all the derivatives, no significant differences between molecular structures of aliphatic and aromatic derivatives were found. Differences were, however, found in crystal supramolecular structures (see electronic supplementary information (ESI)†).

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† Electronic supplementary information (ESI) available: Pictures giving details of intermolecular interaction and molecular packing, IR spectra, details of NMR measurements, reasoning and assignment, details of molecular modelling including conformer geometries, and potential energy curves. See http://www.rsc.org/suppdata/ob/b4/b403728f/

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Table 1 Selected structural parameters for **1–4** and related compounds **5–8**[a]

			dihedral angles/°			distances/Å			angle/°
Compd.	R	R′	O–C–N–O	C–N–O–C	N–O–C–O	N–H	H···O	N···O	N–H···O
1	Me	Me	6.4(4)	−93.9(3)	5.0(4)	0.93(2)	1.85(2)	2.747(2)	159(2)
2	Me	Ph	3.7(2)	−82.9(1)	−0.5(2)	0.87(2)	1.96(2)	2.812(1)	167(2)
3	Ph	Me	8.5(2)	−83.2(1)	0.1(2)	0.86(2)	1.93(2)	2.780(2)	175(2)
4	Ph	Ph	5.2(2)	−81.4(2)	−2.8(2)	0.92(3)	1.93(3)	2.836(2)	169(2)
5[b]	Ph	2-Me–C_6H_4	6.2	−81.8	1.3	1.00	1.96	2.88	152
6[c]	Ph	4-Me–C_6H_4	0.5	−83.7	−6.8	1.04	1.78	2.75	154
7[d]	2-Cl–C_6H_4	2-Cl–C_6H_4	−3.9	−87.7	5.2	0.96	1.94	2.85	158
8[e]	Ph	X[f]	3.4	−75.0	−8.3	0.91	1.99	2.88	—

[a] Compound **4** crystallizes in a noncentrosymmetric space group. The other structures contain also molecules with the opposite signs of the measured dihedral angles; structures **5–8** were found in the Cambridge Structure Database (CSD, version 5.25, November 2003) searching for the C–C(O)–NH–O–C(O)–C structural fragment. [b] *N*-Benzoyl-*O*-*o*-toluoylhydroxylamine (*BOTLHD*).[11] [c] *N*-Benzoyl-*O*-*p*-toluoylhydroxylamine (*BTHYDX*).[11] [d] *N*,*O*-Bis(2-chlorbenzoyl)hydroxylamine (*CBZHYX*).[11] [e] *N*-[(2-Methyl-4,5-diphenyl-1*H*-pyrrole-3-carbonyl)oxy]benzamide (*IDUKOH*).[15] [f] X = 2-Methyl-4,5-diphenyl-1*H*-pyrrole-3-yl.

Structures in solution and calculated structures

We have not noticed the presence of any isomeric species in any of the measured NMR spectra, always only one set of lines attributable to one structure was present. The observed ^{15}N chemical shifts (Table 2) are not substantially affected by the substituents R and R′, the δ values are in the range characteristic for hydroxamic acids ($\delta \sim -210$),[4,17–19] sufficiently far away from the values encountered in derivatives of hydroximic acids ($\delta \sim -80$).[1–3] This confirms that the compounds have in solution predominantly tautomeric structures **1A–4A**; forms **1B–4B**, if present at all, have concentrations below 10% (considering both the detection limits of ^{13}C NMR spectroscopy in the case of slow exchange and the observed shift together with the shifts in hydroxamic and hydroximic models in the case of fast exchange). The failure of NMR to detect the tautomers **1B–4B** is in agreement with the early studies by standard infrared spectroscopy restricted to the ν(C=O) bands,[10] or concerned only with the compound **4**.[20–22] Our masurements of IR spectra (Table S1, electronic supplementary information (ESI)†) provided no evidence for the presence of the alternative tautomer in even smaller amounts in two solvents (tetrachloromethane and acetonitrile).

Results of *ab-initio* calculations for several conformers of the two tautomers (Table 3; for more information see electronic supplementary information (ESI)†) fully support the experimental findings for **1** and **3**. The most favorable conformers of **1B** and **3B** are some 12 kJ mol^{-1} higher in energy than their **1A** and **3A** counterparts. The calculated ^{15}N chemical shifts for low-energy conformers of **1A** and **3A** are all around $\delta = -210$, which is in good agreement with the shifts observed here (−204.3 and −204.7, respectively). In line with the chemical expectations, the shifts predicted for the OH tautomers **1B** and **3B** (around $\delta = -78$) are significantly paramagnetically shifted and do not correspond to any observed signal. The relevance of the ^{15}N chemical shift is apparent from a comparison with the shifts −64/−82 and −69/−76 observed in *E*/*Z* pairs of *tert*-butyldimethylsilylated derivatives of **1B** and **3B**, respectively.[6]

The line-widths of the ^{1}H, ^{15}N and ^{13}C NMR signals from the C(O)–NH–O–C(O) moiety depend on the concentration of the solute and on the molecular structure (Table 4). The variations in line-widths together with our failure to resolve the large one-bond coupling (approx. 90 Hz) between ^{15}N and ^{1}H in **2** and **3** indicate that some exchange processes are taking place in the studied solutions.

Considerations involving possible sources of line broadening and quantum chemical calculations (see electronic supplementary information (ESI)†) indicate that an interplay of several stable conformers with different ^{15}N and ^{13}C chemical shifts combined with suitably different exchange rates is the most likely source of the line-width variations.

Conclusions

Irrespective of the nature of substituents R and R′, all the *N*,*O*-diacylhydroxylamines R–CO–NH–O–CO–R′ assume both in the solid state and in solution structures of NH tautomers. The only experimentally observed difference between "aliphatic" (**1–2**) and "aromatic" (**3–4**) *N*,*O*-diacylhydroxylamines (*i.e.*, an effect controlled by the substituent R) is the difference in the linewidths of ^{13}C and ^{15}N NMR lines of the C(O)–N moiety. Calculations indicate some differences in conformations and populations of conformers, their interchange can explain the observed broadening.

Experimental

Synthesis and purification

Methods of preparations and m.p. of *N*,*O*-diacylamines **1–3** were the same as those described in the literature: *N*,*O*-diacetylhydroxylamine, **1**, m.p. 96–8 °C,[23] *N*-acetyl-*O*-benzoylhydroxylamine, **2**, m.p. 99–100 °C,[10] *N*-benzoyl-*O*-acetylhydroxylamine, **3**, m.p. 125–6 °C.[24] *N*,*O*-dibenzoylhydroxylamine, **4**, was prepared by heating the heterogenous mixture of anhydrous sodium carbonate (15 mmol), hydroxylamine hydrochloride (10 mmol) and benzoyl chloride (20 mmol) in dioxane (10 ml) under reflux for 20 min. The mixture was poured into an excess of water and the separated raw product (90%) was crystallized from propan-2-ol. Found m.p. 167–8, literature 165–6 °C.[25] In view of the large line-width in the ^{15}N NMR spectra, the compounds were several times recrystallized from various solvents but with little or no effect on the line-width.

Crystal preparation

Compounds **1–3**: a chloroform solution of the compound was treated with pentane until a white precipitate appeared in the solution. Single crystals of **1–3** were obtained from this chloroform–pentane mixture in 14 days. Single crystals of **4** were prepared similarly but from a methanol–water mixture.[11]

X-Ray diffraction

Data were collected at 150(2) K on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation in the 1–28° θ range. The structures were solved by direct methods.[26] The whole structures were refined anisotropically by full matrix least squares on F values.[27] Hydrogen atoms were located from the expected geometry and from a Fourier difference electron density map and were refined only isotropically.

It was not possible to determine the actual conformer from Mo data of **4**. The value of the Flack parameter was 0.5 ± 0.14. It was necessary to recollect the data using Cu radiation. New data were collected using a Enraf-Nonius CAD4 diffractometer with graphite monochromated Cu-Kα radiation ($T = 293$ K). the final structure,

Table 2 Chemical shifts (δ in ppm) and coupling constants (J in Hz) of R–C(O)–NH–O–C(O)–R′ measured in 1 M DMSO solutions[a]

			C(O)–NH–O–C(O)							unit R					unit R′				
Compd.	R	R′	$\delta(^{15}N)$	$^1J(^{15}N–^1H)$	$\delta(^1H)$	$\delta(^{13}CON)$	$J(^{13}C–^1H)$[b]	$\delta(^{13}COO)$	$J(^{13}C–^1H)$[c]	$^1J(\underline{C}{=}O, \underline{C}\alpha)$	$\delta(^{13}C\alpha)$	$\delta(^{13}C\text{-}2,6)$	$\delta(^{13}C\text{-}3,5)$	$\delta(^{13}C\text{-}4)$	$^1J(\underline{C}{=}O, \underline{C}\alpha)$	$\delta(^{13}C\alpha)$	$\delta(^{13}C\text{-}2,6)$	$\delta(^{13}C\text{-}3,5)$	$\delta(^{13}C\text{-}4)$
1	Me	Me	−204.3	99.7	11.522	167.47[d]	5.7	169.03[e]	6.8	50.7	19.52	—	—	—	58.9	18.31	—	—	—
2	Me	Ph	−204.4	—[f]	11.981	167.79	6.3	164.69	3.7	50.7	19.65	—	—	—	77.2	127.32	129.37	129.82	134.56
3	Ph	Me	−204.7	—[f]	12.467	165.18	—[f]	169.12	7.0	64.9	131.52	129.00	127.86	132.63	58.8	18.44	—	—	—
4	Ph	Ph	−204.9	86.8	12.682	165.14	—[f]	164.63	3.9	65	131.48	129.92[g]	129.39[g]	134.61[g]	75.1	127.35	127.93[g]	129.00[g]	132.68[g]

[a] Chemical shifts in δ scale relative to external CH_3NO_2 (^{15}N) or tetramethylsilane (^{13}C and ^1H). Cα denotes either methyl carbon (R, R′ = Me) or C-1 carbon of the phenyl ring (R, R′ = Ph). Coupled nuclei underscored in the column heading. [b] Depending on the nature of R, the coupling is over 2 (Me) or 3 (Ph) bonds and to 3 or 2 equivalent protons, respectively. [c] Depending on the nature of R′, the coupling is over 2 (Me) or 3 (Ph) bonds and to 3 or 2 equivalent protons, respectively. [d] $^2J(^{13}C–N–^1H) = 6.2$ Hz. [e] $^3J(^{13}C–O–N–^1H) < 0.5$ Hz. [f] Not resolved. [g] Tentative assignment only.

with the Flack enantiomorph parameter[28] equal to 0.27 ± 0.34, was in agreement with the published structure[11] (0.73 ± 0.34 for the wrong one). Data from Cu radiation are of lower quality, *e.g.* it was not possible to find the NH hydrogen in the difference Fourier map. The correct conformer was recalculated from the Mo data.

X-Ray data for 1. $C_4H_7O_3N_1$, $M = 117.1$ g mol^{-1}, monoclinic system, space group Cc, $a = 7.9830(3)$, $b = 11.5960(5)$, $c = 6.9720(2)$ Å, $\beta = 114.019(2)°$, $Z = 4$, $V = 589{,}52(4)$ Å^3, $D_c = 1.32$ g cm^{-3}, μ(Mo Kα) = 0.114 cm^{-1}, crystal dimensions of 0.1 × 0.2 × 0.25 mm, final $R = 0.0271$ and $R_w = 0.0293$ using 650 independent reflections. CCDC reference number 232620.

X-Ray data for 2. $C_9H_9O_3N_1$, $M = 179.2$ g mol^{-1}, monoclinic system, space group $C2/c$, $a = 13.8160(3)$, $b = 9.4200(3)$, $c = 13.4890(4)$ Å, $\beta = 94.839(2)°$, $Z = 8$, $V = 1749.29(9)$ Å^3, $D_c = 1.36$ g cm^{-3}, μ(Mo Kα) = 0.103 cm^{-1}, crystal dimensions of 0.25 × 0.3 × 0.3 mm, final $R = 0.0383$ and $R_w = 0.0434$ using 1570 independent reflections. CCDC reference number 232618.

X-Ray data for 3. $C_9H_9O_3N_1$, $M = 179.2$ g mol^{-1}, orthorhombic system, space group $Pbca$, $a = 12.0470(3)$, $b = 8.3520(1)$, $c = 17.5390(5)$ Å, $Z = 8$, $V = 1764.71(8)$ Å^3, $D_c = 1.35$ g cm^{-3}, μ(Mo Kα) = 0.103 cm^{-1}, crystal dimensions of 0.1 × 0.2 × 0.4 mm, final $R = 0.0558$ and $R_w = 0.0485$ using 1561 independent reflections. CCDC reference number 232619.

X-Ray data for 4. $C_{14}H_{11}O_3N_1$, $M = 241.3$ g mol^{-1}, orthorhombic system, space group $P2_12_12_1$, $a = 8.9570(2)$, $b = 9.2420(2)$, $c = 14.0600(4)$ Å, $Z = 4$, $V = 1163.90(5)$ Å^3, $D_c = 1.38$ g cm^{-3}, μ(Mo Kα) = 0.098 cm^{-1}, crystal dimensions of 0.2 × 0.2 × 0.5 mm, final $R = 0.0329$ and $R_w = 0.0379$ using 1365 independent reflections. CCDC reference number 232617. See http://www.rsc.org/suppdata/ob/b4/b403728f/ for crystallographic data in .cif or other electronic format.

NMR spectra measurements

The spectra were measured in dry dimethylsulfoxide-d$_6$ (DMSO) solutions in two concentrations approx. 1 M and 10 mM. ^1H, ^{13}C, and ^{15}N NMR spectral measurements were performed on a Varian Inova-500 spectrometer (operating at 499.868 MHz for ^1H, at 125.703 MHz for ^{13}C, and at 50.667 MHz for ^{15}N NMR measurements) and Mercury-Vx-300 (operating at 299.983 MHz for ^1H and at 75.438 MHz for ^{13}C) using 5 mm switchable broad-band probes. All the spectra were recorded at 25 °C.

Computations

The theoretical studies employed the density functional method B3LYP[29,30] in conjunction with the Gaussian set 6-311+G(d,p) as implemented in the Gaussian 98 suite of programs.[31] For all optimized structures, frequency analysis at the same level of theory was carried out in order to assign them as genuine minima and determine zero-point vibrational energies (ZPEs). The potential energy curves were calculated at the same level of theory but with the basis set 6-31G(d,p). The given torsion angle was frozen, the rest of geometrical parameters were optimized. The magnetic shielding tensors were calculated by the GIAO (gauge independent atomic orbital) method[32–35] at the B3LYP/6-311+G(d,p) level of theory. The NMR chemical shifts of carbon atoms were calculated relative to TMS and chemical shifts of nitrogen atoms relative to nitromethane.

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Table 3 Selected geometrical parameters, relative electronic energies, relative energies at 0 K and ^{15}N and ^{13}C NMR chemical shifts calculated for the most stable conformers of the compounds **1A, 1B, 3A**, and **3B**[a]

	Dihedral angles/°					Chemical shifts δ [ppm]		
	O–C–N–O	C–N–O–C	N–O–C–O	E_{rel}/kJ mol^{-1}	E_{rel}(0 K)/kJ mol^{-1}	δ(N)[b]	δ(N–CO)[c]	δ(O–CO)[c]
1Aa	−11.9	−79.7	−8.3	0/−437.172086[d]	0/−437.057445[e]	−217.0	175.1	179.7
1Ba	0.0	180.0	180.0	11.06	12.10	−80.8	166.7	176.1
3Aa	−6.8	−82.3	−8.5	0/−628.953421[d]	0/−628.785322[e]	−217.8	175.1	179.8
3Ba	0.0	180.0	180.0	11.85	11.88	−78.1	164.2	176.4

[a] Energies are related to the most stable isomers of the given molecules (**1a** and **3a**, respectively). Total electronic energies as well as energies at 0 K in Hartrees are given only for most stable isomers **1a** and **3a**, respectively. [b] Chemical shifts of nitrogen atoms are related to the calculated value for nitromethane (−152.4). [c] Chemical shifts of carbon atoms are related to the calculated value for TMS (184.0). [d] B3LYP/6-311+G(d,p) total electronic energy in Hartrees. [e] B3LYP/6-311+G(d,p) energy at 0 K (includes zero point vibrational energy) in Hartrees.

Table 4 Widths of selected ^{1}H, ^{13}C and ^{15}N NMR lines of R–C(O)–NH–O–C(O)–R′ in DMSO solutions[a]

			C(O)–HN–O–C(O)			
Compd.	R	*R′*	^{1}H	^{15}N	^{13}C–N	^{13}C–O
1	Me	Me	4.9	5.4	2.8	2.1
2	Me	Ph	7.5	14	2.9	2.2
3	Ph	Me	2.9	16	4.9	0.7
4	Ph	Ph	2.8	20	5.0	1.2

[a] The linewidths in Hz, the ^{13}C and ^{15}N data are from concentrated solutions while ^{1}H data are from diluted solutions.

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