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Alkylhydrazides and their protonated forms: physical methods and *ab initio* calculations

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The basicity of hydrazides of the highest aliphatic carboxylic acids $RC(O)NHNH_2$ ($R = C_nH_{2n+1}$, $n = 5-12$) has been studied by potentiometric titration, and IR and ^1H NMR spectroscopy. *Ab initio* Hartree—Fock calculations using the 6-31G* basis set with full optimization of geometry were carried out on the simplest acylhydrazines and their possible protonated forms. Based on these calculations, and the IR and ^1H NMR spectra, the tautomerism of alkylhydrazides and the structures of their protonated forms are discussed.

Key words: hydrazides of carbon acids, protonated forms, *ab initio* calculations, IR and PMR spectra.

The distinctive properties of the electronic effects in hydrazides, their chemical properties, their biologic activity and other features have received the attention of many workers (see, for example Refs. 1—8). But these compounds have not been adequately studied. The higher hydrazides of aliphatic carboxylic acids (HACA) have proved to be very effective extractants of nonferrous and rare metals, collectors of potassium chloride.[5,6] The basicity of some of the highest members of the HACA series and of the tautomeric and protonated forms of acet- and form-hydrazides were studied in this work by quantum-chemical methods and IR and ^1H NMR spectroscopy.

The basicity of HACA can be defined as pK_{01} of the conjugated acids of the hydrazides formed by the action of strong mineral acids. The potentiometric titration curves of HACA[9] have been used for pK_{01} measurement. The pK_{01} value of the molecule (Table 1) changes little as n varies in $H(CH_2)_nC(O)NHNH_2$ (n = 5 to 12), like many other properties of compounds in the homologous series $X(CH_2)_nY$ (see, for example, Ref. 10). The melting points of HACA presented in Table 1 also increase successively as n increases. Their values are close to those from Refs. 2 and 11.

Table 1. Basicity dissociation constants (pK_{01}) and melting points (T) of hydrazides $RC(O)NHNH_2$

R	pK_{01}	T/°C
C_5H_{11}	3.48±0.01	69.0—69.5
C_6H_{13}	3.78±0.01	79.0—79.5
C_7H_{15}	3.50±0.03	86.5—87.0
C_8H_{17}	3.74±0.02	90.0—90.5
C_9H_{19}	—	91.0—91.5
$C_{10}H_{21}$	3.57±0.11	100.0—100.5
$C_{12}H_{25}$	3.42±0.01	105.0—106.0

It appears that only in the protonated form are HACA effective extractants of rare and nonferrous metals as well as collectors of potassium chloride.[5,6] A consideration of the reactivity of some simple hydrazides shows that the β-N atom is the most nucleophilic. In some cases substitution can also take place at the α-N or O atom (see, for example, Ref. 7). It can be assumed that protonation is also most probable at the β-N atom. At the same time the carbonyl oxygen atom is the most electronegative in the HACA molecule, and seemingly should have the highest negative charge. This is the oxygen atom that is usually protonated in RC(O)NR'R" amides (see, for example Refs. 4, 7).

To establish the structure of the protonated form of HACA we recorded ^1H NMR and IR-spectra of some of these compounds and their HCl salts, and also carried out *ab initio* calculations of possible tautomeric and protonated forms of formyl- and acetylhydrazines. In all cases the origin of the coordinate system was placed at the nucleus of the O atom, the x axis was directed perpendicular to the plane of the molecule, and the z axis was directed along the O—C bond.

Experimental

The HACA studied were prepared using Curtius method by the interaction of the respective carboxylic acids with hydrazine hydrate[12] and purified by recrystallization from ethanol. The concentration of the main component (>97%) was determined by potentiometric titration in a non-aqueous solvent.[5,13] The protonation constants of the hydrazides were measured potentiometrically in methanol.[5,13] A solution of H_2SO_4 (0.5 M) in methanol seasoned for no less then a week was used as the

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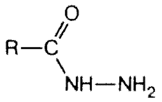
titrant. Potentiometric titration curves were based on the results of measurements with an EV-74 ionometer using an ESL-43-07 glass indicator electrode at ~20 °C.

The IR spectra of the compounds studied were recorded in vaseline oil with a Specord M80 spectrophotometer; ^{1}H NMR spectra were recorded with a Tesla BS 587A FT NMR spectrometer (working frequency 80 MHz).

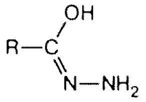
Ab initio calculations of the tautomeric forms of acetylhydrazine and of the protonated forms of formylhydrazine were carried out with full optimization of geometry at the Hartree-Fock level with split valence 6-31G* basis using the Gaussian 92 for Windows program (Gaussian Inc.).[14]

Results and Discussion

By analogy to RC(O)NHOH hydroxamic acids and taking into account the possibility of O→N rearrangement in HACA molecules (see, for example Ref. 7), one can suggest the existence of the HACA molecules as two tautomeric forms (**1** and **2**):



1

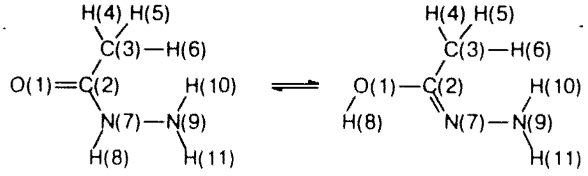


2

According to the X-ray data, the hydrazides of, *e.g.*, octan- and undecan-1 carboxylic acids[15,16] in the solid state exist in form **1**. This is also evidenced by published IR spectra (see, Refs. 2, 4), and by the IR spectrum of $CH_3C(O)NHNH_2$ obtained by us, which almost completely coincides with that previously recorded.

HACA have the same structure in solution, as can be seen from their ^{1}H NMR spectra.[17] The ^{1}H NMR spectrum of acetylhydrazine obtained by us in $CDCl_3$ (~23 °C) has only one narrow intense signal (δ 1.97 ppm), assigned to the CH_3 group, and two wide signals (δ 4.29 and 7.98 ppm), assigned to NH_2 and NH, respectively.

An analogous ^{1}H NMR spectrum of $CH_3C(O)NHNH_2$ was obtained in DMSO (δ(CH_3) 1.75 ppm, δ(NH_2) 3.66 ppm and δ(NH) 8.91 ppm). According to the *ab initio* calculations of the **1a** and **2a** tautomeric forms of acetylhydrazine, the **1a** form is energetically more favorable.



1a **2a**

Its total energy (−7155.687 eV) is ~14 kcal · mol^{-1} lower than that of the **2a** form (−7155.081 eV). The results of the optimization of geometry are presented in Table 2. As judged from the dihedral angles, the CC(O)NHN and CC(OH)NN fragments of **1a** and **2a**, respectively, are essentially planar, which agrees with the X-ray structures of the hydrazides of octan- and undecan-1-carboxylic acids.[7,15,16] The calculated bond lengths and valence angles (see Table 2) are also in reasonable agreement with the experimental data: in the hydrazide of octan-1-carboxylic acid[15] the C=O, C—N, and N—N bond lengths are equal to 1.249, 1.329, and 1.415 Å, respectively, and the CCO, CCN, NCO, and CNN angles are 122.5°, 116.6°, 120.9°, and 123.0°; in the hydrazide of undecan-1-carboxylic acid[16] these bond lengths and angles are equal to 1.211, 1.332, and 1.392 Å; 128.2°, 116.9°, 114.8°, and 130.0°, respectively.

Ab initio calculations of the $CH_3C(O)NHNH_2$ molecule show that the O and N atoms charges are very close (Table 3). In addition, the α-atom N has the highest negative charge, the charge on the β-N atom is somewhat less, and that on the O atom is still less. If one assumes that a proton would attach itself to the atom with the highest electron density, then the most favorable protonation sites of hydrazides should be the α- or β-N atoms.

The ^{1}H NMR spectra of $CH_3C(O)NHNH_2 \cdot HCl$, and $CH_3C(O)NHNH_2$, in DMSO each have one narrow signal (δ 1.95 ppm) corresponding to the methyl group and two wide signals (δ ~4.2 and ~11.0 ppm) corre-

Table 2. Bond lengths (*d*), bond angles (α), and dihedral angles (β) optimized at the RHF/6-31G* level

Bond	*d*/Å		Angle	α/deg		Angle	β/deg	
	1a	**2a**		**1a**	**2a**		**1a**	**2a**
O(1)—C(2)	1.199	1.337	O(1)C(2)C(3)	123.1	111.8	O(1)C(2)C(3)H(4)	−120.2	−58.4
C(2)—C(3)	1.510	1.497	C(2)C(3)H(4)	110.8	108.9	O(1)C(2)C(3)H(5)	0.3	58.4
C(3)—H(4)	1.083	1.084	C(2)C(3)H(5)	107.9	108.9	O(1)C(2)C(3)H(6)	120.9	180.0
C(3)—H(5)	1.080	1.084	C(2)C(3)H(6)	110.9	111.1	O(1)C(3)C(2)N(7)	180.2	180.0
C(3)—H(6)	1.083	1.077	C(3)C(2)N(7)	116.9	130.3	O(1)C(2)N(7)H(8)	0.9	—
C(2)—N(7)	1.361	1.256	C(2)N(7)H(8)	116.1	—	O(1)C(2)N(7)N(9)	178.9	180.0
N(7)—H(8)	0.998	—	C(3)N(7)N(9)	123.1	114.8	C(2)N(7)N(9)H(10)	−118.5	−124.6
N(7)—N(9)	1.383	1.424	N(7)N(9)H(10)	110.6	105.6	C(2)N(7)N(9)H(11)	120.4	124.7
N(9)—H(10)	1.001	1.003	N(7)N(9)H(11)	110.5	105.6	N(7)C(2)O(1)H(8)	—	0.0
N(9)—H(11)	1.000	1.003	C(2)O(1)H(8)	—	107.7			
O(1)—H(8)	—	0.952						

Table 3. *Ab initio* calculated total energies (*E*) and charges on atoms (*q*) of molecules **1a—5a**

Molecule	*E*/eV	O(1)	C(2)	C(3)	H(4)	H(5)	H(6)	N(7)	H(8)	N(9)	H(10)	H(11)
1a	−7155.698	−0.60	0.74	−0.56	0.19	0.20	0.19	−0.63	0.38	−0.62	0.36	0.36
2a	−7155.081	−0.71	0.66	−0.56	0.19	0.19	0.23	−0.50	0.46	−0.67	0.35	0.35
		O(1)	C(2)	H(3)	N(4)	H(5)	N(6)	H(7)	H(8)	H(9)		
3a	−6101.795	−0.41	0.50	0.21	−0.57	0.46	−0.65	0.48	0.49	0.50		
4a	−6101.539	−0.32	0.47	0.30	−0.65	0.47	−0.61	0.44	0.42	0.48		
5a	−6102.189	−0.58	0.57	0.33	−0.52	0.46	−0.61	0.42	0.42	0.52		

sponding to hydrogens bonded to β- and α-N atoms, respectively. The ratio of the integral intensities of the lines in the highest and the lowest fields is 3 : 1. The integral intensity of the central signal is several times higher than that of the CH_3 signal. When the concentration of the substance in solution increases, this central signal shifts downfield (to ~8.4 ppm). In addition, the signal of the methyl group does not shift much, while the signal of the NH group at first stays in the same place, but with a significant increase in concentration it shifts upfield region and becomes masked by an adjacent intense broad signal.

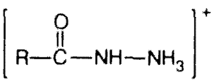
One can suggest that the central line is the result of the superposition of the signals of the H atom bonded to the β-N atom and that of the water, occurring in the solution. This spectrum does not allow one to determine the number of H atoms at the β-N atom. We expected the ^1H NMR spectrum of $CH_3C(O)NHNH_2 \cdot HCl$ in $CDCl_3$ to be more informative. But the substance does not significantly dissolve in this solvent at room temperature. When $CH_3C(O)NHNH_2 \cdot HCl$ in $CDCl_3$ is heated up to 333 K its solubility increases only insignificantly, and its spectrum is also proved to uninformative.

In the spectrum of $CH_3(CH_2)_7C(O)NHNH_2 \cdot HCl$ in DMSO there are two distinct triplets: ($\delta(CH_3)$ 0.8 ppm and $\delta(CH_2)$ 2.2 ppm), an unresolved multiplet ($\delta(CH_2)$ 1.5 ppm), and overlapping it an intense signal ($\delta(CH_2)_5$ 1.2 ppm). This whole collection of signals corresponds to the $CH_3(CH_2)_7$ group. In the ^1H NMR spectrum of this substance there are also two broad signals, one intense, the other weak. When the concentration of the substance in solution increases, both signals shift at first downfield region (the intense one — from ~3.4 to ~9.2 ppm, the weak one — from ~10.8 to ~12.1 ppm), and then in the reverse direction. As this takes place the widths of the signals change.

This pattern of changes in the ^1H NMR upon concentration variation is probably determined by peculiarities of the formation of hydrogen bonds. The integral intensities of the signals in this spectrum show that one H atom is connected to the α-N atom. The number of H atoms at the β-N atom remains still unknown.

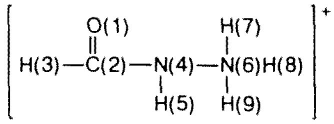
The IR spectrum of $CH_3C(O)NHNH_2 \cdot HCl$ recorded by us has the characteristic bands[18,19] of $(RNH_3)^+A^-$ at 3150 and 3100 cm^{-1} (νNH_3), complex bands at 2670 and 1954 cm^{-1}, as well as a band at 1582 cm^{-1} (δNH_3). In this spectrum the band at 3268 cm^{-1} can be assigned to ν(NH) vibration, and the bands at 1682 and 1672 cm^{-1} can be assigned to C=O vibrations (free and bound). The band at 1528 cm^{-1} was assigned to the vibration modes of form **2** (νCN + δNH), the bands at 1454 and 1378 cm^{-1} were assigned to $\delta(CH_3)$, and the band at 1270 cm^{-1} corresponds to a vibration mode of form **3**.

Thus the ^1H NMR spectra show that in the protonated form of alkyl hydrazides one H atom is connected to the α-N atom, which is compatible with structures **3** and **5**. The IR spectrum of $CH_3C(O)NHNH_2 \cdot HCl$ most closely corresponds to structure **3**. Based on these experimental data one can assume that protonated form **3** is the most probable for alkylhydrazides.



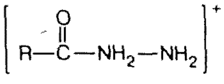
$[\mathrm{R{-}C({=}O){-}NH{-}NH_3}]^+$

3



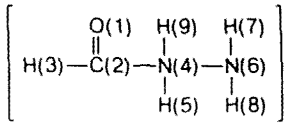
$[\mathrm{H(3){-}C(2)({=}O(1)){-}N(4)H(5){-}N(6)H(7)H(8)H(9)}]^+$

3a



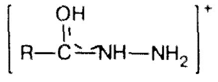
$[\mathrm{R{-}C({=}O){-}NH_2{-}NH_2}]^+$

4



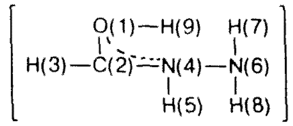
$[\mathrm{H(3){-}C(2)({=}O(1)){-}N(4)H(5)H(9){-}N(6)H(7)H(8)}]^+$

4a



$[\mathrm{R{-}C(OH){\cdots}NH{-}NH_2}]^+$

5



$[\mathrm{H(3){-}C(2)(O(1){-}H(9)){\cdots}N(4)H(5){-}N(6)H(7)H(8)}]^+$

5a

The *ab initio* calculations of possible protonated forms of formylhydrazine show form **5a** to be energetically most favorable; it is more stable than form **3a** by ~9.1 kcal · mol^{-1}, and more stable than form **4a** by 15.0 kcal · mol^{-1} (see Table 3). In addition, the highest negative charge in forms **3a** and **5a** is localized on the β-N atom, and in form **4a** on the α-N atom. In forms **3a** and **4a** the O atom has the least negative charge, and in form **5a** the α-N atom has the smallest negative charge.

The positive charge in all three forms is distributed on the C and H atoms. The discrepancy between the experimental and calculated results is probably due to the presence of intermolecular hydrogen bonds in HACA that are not taken into account in the calculations.

It is assumed that in molecules having a —C(O)N group (amides, imides, hydrazides, *etc.*) the lone pair of the N atom participates in p,π-conjugation with the π-electron system of the carbonyl group. This conjugation explains the geometry of above mentioned molecules, the existence of structural isomers, and many of their chemical and physical properties (see, for example, Ref. 7). The results of studies of conjugation in different compounds (carboxylic acid chlorides, substituted ethylenes, *etc.*) by ^{35}Cl NQR and quantum chemical methods show that its role is grossly exaggerated. Explaining some of the properties of the compounds by conjugation makes no sense (see, for example, Refs. 20—23). The same is true for molecules having a —C(O)N group.

The CC(O)NHN fragment in the $CH_3C(O)NHNH_2$ molecule is essentially planar (see above). *Ab initio* calculations of this molecule show that the O atom of the carbonyl group has an excess of $p_\pi(p_x)$-electron density ($Np_x(O)$ = 1.497e), while the C atom has a deficit ($Np_x(C)$ = 0.636e). This is caused by polarization of the C=O bond by the nearest O atom, as well as by the negatively charged N atom directly through field (see, for example, Refs. 23—25). The population of the p_x-AO of the C and O atoms is slightly higher than 2e (2.133e). This excess on the carbonyl group is created at the expense of other atoms of the molecule, and also involves the shift of the lone pair electrons of the α-N atom (the population of its AO $Np_x(N)$ = 1.807e). The deficit of electrons on this AO (0.193e) exceeds the excess on the carbonyl group atoms. It seems likely that the lone pair orbital of the α-N atom is delocalized across the other atoms of the molecule.

The results of the calculations of the AO populations in the $CH_3C(O)NHNH_2$ molecule do not allow one to say what contribution each atom of the molecule brings to the excess p_x-electron density, and consequently, what part of this excess is caused by p,π-conjugation of the lone pair of α-N atom electrons with the π-system of the carbonyl group. An analysis of the MOs of the $CH_3C(O)NHNH_2$ molecule shows that none of them is formed mainly at the expense of the p_x-AO of the O and C atoms of the carbonyl group, or of the α-N atom. All MOs having a contribution from the p_x-AO of these atoms also have similar contributions from the p_x-AO of the other atoms of the molecule, forming a multicentered bond.

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