

SIMPLE AMIDINIUM CARBOXYLATES — AN MO TREATMENT OF MOLECULAR GEOMETRY AND ELECTRONIC STRUCTURE

Jiří KRECHL, Stanislav BÖHM, Svatava SMRČKOVÁ and Josef KUTHAN

Department of Organic Chemistry,

Prague Institute of Chemical Technology, 166 28 Prague 6

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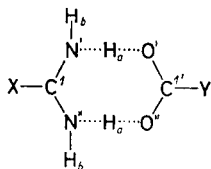
Carboxylates of amidines (*I, II*), substituted guanidine (*III*) and iso(thio)ureas (*IV, V*) were prepared. Nonempirical quantum chemical treatment of the electronic structure of simple compounds *I–V*, based on total molecular geometry optimization, their preparation and physico-chemical data are reported. Interaction between the two amidinium nitrogens and carboxylate oxygens is mediated by hydrogen bonds and alternation of charge distribution.

Interaction of carboxylic acids with guanidine moiety of aminoacid arginine is an important mode of carboxylic substrate fixation in enzymatic conversions and other biointeractions^{1,2}. MO methods have been applied to clear up several aspects of the interaction. Alternative mutual orientations of guanidinium and carboxylate components were considered by approximative stepwise optimization procedures on the basis of CNDO/2 (ref.³) and *ab initio* STO-3G (ref.⁴) methods. Effect of amidinium fixation on the reactivity of guanidinium pyruvate was subject of another STO-3G calculation⁵. Possible energy contribution of methylguanidinium–pyruvate (lactate) interaction to the stabilization of the lactate dehydrogenase active centre fragment involving also NAD and histidine models was calculated for lactate oxidation⁶ and pyruvate reduction⁷ within the CNDO/2 method. An attempt was also made to calculate stabilization energies of (methyl)guanidinium formate⁸ and guanidinium carbonate⁹ by *ab initio* STO-4G, 6-31G and 6-31G* methods using, however, only stepwise optimization of the molecular geometries.

Two important questions remained to be answered: what is the general shape of the eight-membered ring connecting amidinium and carboxylate components and how the original unit charges of both interacting parts are distributed among the atomic centres of the heterocycle. We, therefore decided to investigate a series of simple amidinium carboxylates, using the *ab initio* 3-21G method and also the preparative and spectroscopic procedures.

The simplest model of this interaction seems to be formamidinium formate (*Ia*), not described before. The other representatives could be considered as derivatives of this simple compound formally resulting by C- (*II*), N- (*III*), O- (*IV*) and S-substitu-

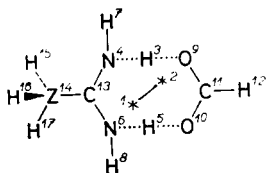
tion (V), respectively. To examine the importance of the carboxylic part, two series of the carboxylates have been investigated: formates (a) and acetates (b).



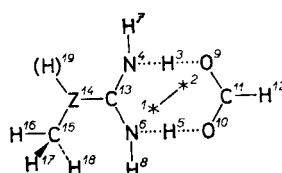
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|---|--|
| <i>I a</i> , X = H; Y = H | <i>III b</i> , X = CH ₃ NH; Y = CH ₃ |
| <i>I b</i> , X = H; Y = CH ₃ | <i>IV a</i> , X = CH ₃ O; Y = H |
| <i>II a</i> , X = CH ₃ ; Y = H | <i>IV b</i> , X = CH ₃ O; Y = CH ₃ |
| <i>II b</i> , X = CH ₃ ; Y = CH ₃ | <i>V a</i> , X = CH ₃ S; Y = H |
| <i>III a</i> , X = CH ₃ NH; Y = H | <i>V b</i> , X = CH ₃ S; Y = CH ₃ |

CALCULATIONS

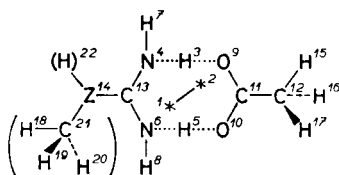
The geometries were fully optimized using the GAUSSIAN 80 program¹⁰ on 3-21G level¹¹ with respect to all degrees of freedom. Optimized geometries of the studied formates (a) and some acetates (b) are summarized in Tables I–III. Schemes 1–3 show the numbering of molecular systems. More telling internal coordinates than the Cartesian ones were used. Dummy atoms *(₁) and *(₂) facilitate the correct description of the cyclic systems.



SCHEME 1



SCHEME 2



SCHEME 3

TABLE I

Geometries of systems Ia and IIa obtained through 3-21G optimization. For numbering of system see Scheme 1

N	Atom	Bond length N—I, pm			I	Bond angle N—I—J, °			J	Dihedral angle N—I—J—K, °			K
		Ia	Ia ^a	IIa		Ia	Ia ^a	IIa		Ia	Ia ^a	IIa	
1	* ^b												
2	* ^b	500.0	500.0	500.0	1								
3	H	119.6	117.4	118.4	1	90.0	90.4	90.4	2				
4	N	107.2	120.2	107.0	3	87.9	89.6	88.2	1	272.4	267.5	271.4	2
5	H	119.2	117.4	118.4	1	90.0	90.4	90.4	2	181.0	181.3	181.2	3
6	N	107.2	120.2	107.0	5	87.9	89.6	88.2	1	-272.4	-267.5	-271.4	2
7	H	99.8	102.2	99.8	4	119.3	124.6	118.5	3	180.0	180.0	180.0	1
8	H	99.8	102.2	99.8	6	119.3	124.6	118.5	5	180.0	180.0	180.0	1
9	O	151.9	120.0	153.0	3	86.8	88.3	87.2	1	92.3	87.5	91.4	2
10	O	151.9	120.0	153.0	5	86.8	88.3	87.2	1	-92.3	-87.5	-91.4	2
11	C	125.8	127.8	125.7	9	119.2	116.7	118.9	3	-0.1	0.3	0.0	1
12	H	108.7	111.1	108.7	11	116.6	115.7	116.6	9	180.2	180.2	180.9	3
13	C	130.1	132.5	130.5	4	120.7	120.6	121.6	3	0.0	-0.6	-0.4	1
14	Z ^c	107.4	109.9	151.1	13	118.1	119.6	119.2	4	179.9	180.4	181.7	3
15	H			108.2 ^d	14			110.1 ^d	13			89.8	4
16	H			108.2 ^d	14			110.1 ^d	13			-30.2	4
17	H			108.2 ^d	14			110.1 ^d	13			209.8	4

^a STO-3G results; ^b dummy atoms used in definition of the geometry; ^c Z = H (Ia), Z = C(H₃) (IIa); ^d optimization presumes equivalence of methyl C—H bonds.

TABLE II
Geometries of systems *IIIa*, *IVa* and *Va* obtained through 3-21G optimization. For numbering of system see Scheme 2

N	Atom	Bond length N—I, pm			I	Bond angle N—I—J, °			J	Dihedral angle N—I—J—K, °			K
		<i>IIIa</i>	<i>IVa</i>	<i>Va</i>		<i>IIIa</i>	<i>IVa</i>	<i>Va</i>		<i>IIIa</i>	<i>IVa</i>	<i>Va</i>	
1	* ^a												
2	* ^a	500·0	500·0	500·0	1								
3	H	129·0	153·0	116·8	1	90·6	92·5	90·9	2				
4	N	106·1	106·2	107·3	3	89·1	89·5	88·2	1	275·1	275·4	273·7	2
5	H	104·6	84·7	118·8	1	91·4	92·8	91·8	2	181·3	185·6	180·2	3
6	N	106·4	108·1	108·7	5	89·2	91·1	87·6	1	-276·0	-275·9	-278·5	2
7	H	99·7	99·9	99·8	4	118·5	120·6	119·0	3	179·8	178·2	183·4	
8	H	99·5	99·4	99·6	6	118·0	118·4	118·3	5	181·7	184·0	188·0	1
9	O	154·8	154·7	152·2	3	87·2	84·9	86·9	1	95·1	95·5	94·7	2
10	O	153·8	148·7	147·9	5	88·5	85·4	89·0	1	-96·1	-96·3	-97·9	2
11	C	125·7	125·5	125·6	9	118·7	118·5	118·8	3	2·0	2·9	4·2	1
12	H	108·8	108·7	108·6	11	116·6	116·9	116·9	9	179·1	179·3	178·3	3
13	C	131·9	130·2	130·0	4	121·2	121·5	120·6	3	-0·3	-1·6	2·6	1
14	Z ^b	135·2	134·1	183·6	13	119·3	115·0	115·9	4	179·4	179·6	175·7	3
15	C	146·3	145·0	189·0	14	123·7	122·5	101·8	13	180·0	179·5	158·8	4
16	H	108·2 ^c	108·0	107·7	15	110·3 ^c	110·7	110·0	14	60·9	61·6	78·3	13
17	H	108·2 ^c	108·1	107·8	15	110·3 ^c	110·5	109·3	14	-60·2	-61·4	-45·1	13
18	H	108·2 ^c	107·6	107·8	15	110·3 ^c	104·8	104·9	14	180·4	180·1	196·8	13
19	H	99·6			14	118·1			13	-0·4			4

^a Dummy atoms used in definition of the geometry; ^b Z = N(H) (*IIIa*), Z = O (*IVa*), Z = S (*Va*); ^c optimization presumes equivalence of methyl C—H bonds.

TABLE III
Geometries of systems *Iib*, *IIIb* and *IVb* obtained through 3-21G optimization. For numbering of system see Scheme 3

N	Atom	Bond length N—I, pm			I	Bond angle N—I—J, °			J	Dihedral angle N—I—J—K, °			K
		<i>Iib</i>	<i>IIIb</i>	<i>IVb</i>		<i>Iib</i>	<i>IIIb</i>	<i>IVb</i>		<i>Iib</i>	<i>IIIb</i>	<i>IVb</i>	
1	* ^a												
2	* ^a	500.0	500.0	500.0	1								
3	H	118.0	128.7	152.5	1	89.9	90.7	92.9	2				
4	N	107.1	106.3	106.6	3	88.3	89.2	89.6	1	271.6	275.6	275.3	
5	H	118.0	104.3	84.3	1	89.9	91.4	93.3	2	181.1	181.2	185.6	
6	N	107.1	106.7	108.7	5	88.3	89.4	91.2	1	-271.6	-276.3	-275.8	
7	H	99.8	99.8	99.9	4	118.8	118.5	120.7	3	180.0	179.0	177.9	
8	H	99.8	99.5	99.9	6	118.8	117.9	118.7	5	180.0	180.8	184.1	
9	O	152.2	154.4	153.3	3	87.2	87.4	84.9	1	91.7	95.4	95.6	
10	O	152.2	152.5	147.2	5	87.2	88.2	85.4	1	-91.7	-96.1	-96.2	
11	C	126.2	126.0	125.9	9	119.7	119.2	119.4	3	-0.1	1.6	2.8	
12	C	151.8	152.3	152.0	11	116.9	117.7	117.7	9	180.1	181.7	181.5	
13	C	130.5	132.0	130.1	4	121.4	121.1	121.4	3	0.1	-0.6	-2.1	
14	Z ^b	151.1	135.2	134.3	13	119.3	119.3	115.1	4	178.5	179.9	179.9	
15	H	108.2 ^c	108.2 ^c	108.0	12	109.5 ^c	109.4 ^c	109.4 ^c	11	121.6	30.0 ^d	30.0 ^d	
16	H	108.2 ^c	108.2 ^c	108.1	12	109.5 ^c	109.4 ^c	109.4 ^c	11	239.4	150.0 ^d	150.0 ^d	
17	H	108.2 ^c	108.3 ^c	107.6	12	109.5 ^c	109.4 ^c	109.4 ^c	11	0.4	270.0 ^d	270.0 ^d	
18	H	108.2 ^c	108.3 ^c	109.0 ^c	14 ^e	110.1 ^c	110.3 ^c	110.7	13 ^f	30.1	60.5	61.2	
19	H	108.2 ^c	108.3 ^c	109.0 ^c	14 ^e	110.1 ^c	110.3 ^c	110.7	13 ^f	150.1	-60.1	-61.7	
20	H	108.2 ^c	108.3 ^c	109.0 ^c	14 ^e	110.1 ^c	110.3 ^c	104.9	13 ^f	270.1	180.0	179.7	
21	C		146.3	145.0	14		123.6	122.3	13		180.1	180.2	
22	H		99.6		14		118.0		13		-0.4		

^a Dummy atoms used in definition of the geometry; ^b Z = C(H₃) (*Iib*), Z = N(H) (*IIIb*), Z = O (*IVb*); ^c optimization presumes equivalence of methyl C—H bonds; ^d fixed values without further optimization; ^e I = 21 for *IIIb*, *IVb*; ^f J = 14 for *IIIb*, *IVb*; ^g K = 13 for *IIIb*, *IVb*.

EXPERIMENTAL

Temperature data are uncorrected. Melting points were determined on a Boetius apparatus. The spectra were measured on a Bruker AM 400 spectrometer (^1H and ^{13}C NMR) in $(\text{CD}_3)_2\text{SO}$ solutions related to tetramethylsilane. Experimental parameters were: for ^1H NMR 400.13 MHz, 64 K data points, digital resolution 0.2 Hz/point, pulse width 4 μs ; for ^{13}C NMR 100.61 MHz, 64 K data points, digital resolution 1 Hz/point, used ATP (Attached Proton Test) technique, pulse sequence.

Formamidineum formate (Ia) and acetate (Ib): Attempts to obtain compound *Ia* directly from both components failed, therefore, another preparation of this not yet described compound was elaborated starting from *Ib*. Compound *Ib* was prepared by the application of the procedure¹². Ethylorthoformate (30 g) treated with glacial acetic acid and gaseous ammonia yielded 16.9 g (80%) of formamidineum acetate (*Ib*). Aqueous solution (0.2 mol l⁻¹) of 1 g formamidineum acetate (*Ib*) was passed through a column containing 30 g (dry weight) of ion exchanger Amberlite IRA-401 (100–200 mesh) in formate cycle. Formamidineum formate (*Ia*) was collected, evaporated to dryness resulting in colorless hygroscopic crystals and submitted to elemental analysis. Yield quantitative.

Acetamidineum formate (IIa) and acetate (IIb): Compounds *IIa* and *IIb* were prepared similarly as *Ia* on Amberlite IRA-401 in the formate and acetate cycle, respectively, from the commercially available acetamidineum chloride.

Methylguanidineum formate (IIIa) and acetate (IIIb): Methylguanidineum chloride was prepared by the reaction of 8.4 g (0.1 mol) of dicyandiamide and 13.5 g (0.2 mol) of methylammonium chloride¹³. Hygroscopic chloride (14.0 g, 64%) was obtained which was converted to formate (*IIIa*) and acetate (*IIIb*) as described for *Ia*.

O-Methylisouronium formate (IVa) and acetate (IVb): O-Methylisouronium methylsulfate was prepared by the reaction of 6 g (0.1 mol) urea and 12.6 g (0.1 mol) dimethylsulfate¹⁴. 16.5 g (89%) of viscous liquid was obtained and characterized as picrate (m.p. 186–7°C, ref.¹⁴ 184°C; for $\text{C}_8\text{H}_9\text{N}_5\text{O}_8$ calculated 31.69% C, 2.99% H, 23.10% N; found 31.61% C, 3.03% H, 22.92% N). Formate (*IVa*) and acetate (*IVb*) were prepared from methylsulfate by the same manner as for *Ia*.

S-Methylisothiuronium formate (Va) and acetate (Vb): S-Methylisothiuronium sulfate was prepared from thiourea and dimethylsulfate¹⁵ in a 81% yield and converted to carboxylates *Va* and *Vb* on the ion exchanger, as described for *Ia*.

RESULTS AND DISCUSSION

Molecular structures optimization: The structures obtained by *ab initio* 3-21G full optimization exhibit a certain degree of nonplanarity; the angle contained by the planes of amidinium and carboxylate fragments for *Ia* amounts to 177.3°. This feature is conserved also for other studied structures and is more pronounced from *II* to *V* (see Tables I–III). Slightly nonplanar molecular shapes of amidinium–carboxylate fragments were also found by X-ray diffraction of benzamidineum pyruvate¹⁶.

The N–H_a distances approach those of normal covalent N–H bonds while H_a–O distances are somewhat longer and slightly sensitive to the nature of substituent X. Geometrical characteristics of H-bonds are not influenced when formates (*a*)

are changed for acetates (*b*). Molecules *III–V* lacking a plane of symmetry exhibit non-significant geometry differences between $N'-H_a-O'$ and $N''-H_a-O''$ bonded systems.

STO-3G molecular energy optimization was also performed for *Ia* to compare the effect of the chosen basis set. The results differ considerably from the 3-21G ones (see Table I and Fig. 1), e.g. the STO-3G procedure predicts incorrectly that the $N-H_a$ and the H_a-O distance are equal.

The positive results of the reported calculations^{3–9} and especially of our presented 3-21G *ab initio* total molecular energy optimizations indicate the occurrence of a correct minima on the corresponding potential energy hypersurfaces for various amidinium-carboxylate nuclear systems. Calculation of the stabilization energy is a problem not correctly solved yet^{17,18}. Due to the incompatibility of the basis sets for the dimer and monomers, respectively, stability of the dimer is overestimated. A simple difference between total energy of the dimer and the monomers is physically not fully justified. Just for illustration, nevertheless, this simple process applied to compound *Ia* leads to high stabilization energy (3-21G)

$$E = E_{IV} - (E_{VI} + E_{VII}) = 648.5 \text{ kJ mol}^{-1}.$$

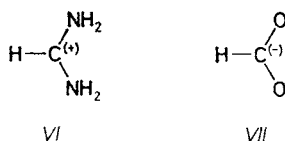
Hence, species *Ia*, *b–Va*, *b* may be considered as identifiable or even isolable really existing covalent compounds.

To confirm this presumption all compounds *I–V* were prepared in the formate (*a*) and acetate (*b*) series. As a matter of fact all compounds have been isolated as crystalline substances possessing well defined and relatively high melting points. These phase transition temperatures, given in Table IV, do not, however, exhibit characteristic changes, due to variations of the molecular structure. After confirming that the general shape of the hydrogen bonded system is very similar for all investigated compounds *Ia*, *b–Va*, *b* the second question remains to be answered.

Charge distribution for compound *Ia* is shown in Fig. 1. Two features are of interest: although the electronic structure has been usually treated as if the $N'-C_{(1)}-N''$ system is positively and the $O'-C_{(1')} - O''$ system negatively charged, the calculations exhibit charge alternation among all atomic centres of the eight-membered ring involving the hydrogen-bonded system. Especially strong negatively charged nitrogens, as well as positive charges at carboxylic and amidinium carbons, are typical for the charge distribution. Charge distribution for respective subsystems *VI* and *VII* is depicted in Fig. 2. The effect of molecular structure variations on charge distribution is very weak and this general feature is valid also for compounds *II–V*.

The frontier orbitals localization for compound *Ia* is depicted in Fig. 3. From Fig. 3 it may be seen that HOMO is localized on the carboxylate while LUMO on the amidinium parts, respectively. The frontier MOs of *Ia* seem to be the super-

position of analogous MOs of formamidinium cation *VI* and formate anion *VII*, as proved by the independent 3-21G calculations of the individual fragments.



On the other hand, the next lower MO (HOMO-1) is delocalized in both parts of the molecule. This MO is evidently responsible for a covalent structure and stability of amidinium carboxylates and exhibits a nodal plane on $\text{C}_{(1)}$, disabling a substituent effect transmission from X to the counter molecular part. Only two other bonding MOs delocalized over the whole molecular system could be found: HOMO-8 and

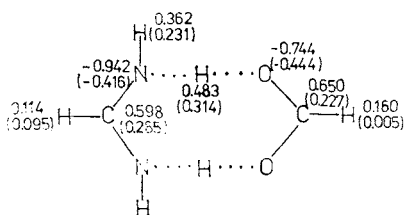


FIG. 1

Charge distribution for compound *Ia* calculated by 3-21G and STO-3G (in parentheses) methods

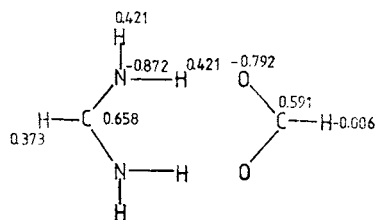


FIG. 2

Charge distribution for subsystems *VI* and *VII* calculated by 3-21G method

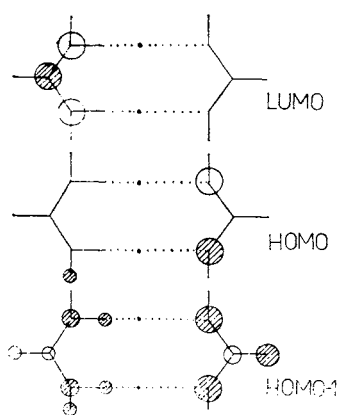


FIG. 3

Schematic description of several molecular orbitals of compound *Ia*. The diameters of the circles correspond to the expansion coefficients of the respective atomic orbitals

HOMO-10. Thus, only 4 electrons from 48 might contribute to the substitution effect transmission.

The values of frontier orbital energies for compounds *Ia*–*Va* (Table V) exhibit the same properties – HOMOs are not altered and only LUMOs differ, depending on substitution. Energies of HOMO-1 are close to those of HOMOs and may be considered as the criterion for the stability of the supermolecule.

The predicted absence of the electronic substitution effect was checked experimentally. ^{13}C NMR spectra (Table VI) show an absence of measurable substitution

TABLE IV
Melting points and elemental analyses for compounds *Ia, b*–*Va, b*

Compound	M.p., °C	Formula (M.w.)	Calculated/Found		
			%C	%H	%N
<i>Ia</i>	98–99	$\text{C}_2\text{H}_6\text{N}_2\text{O}_2$ (90.082)	26.67	6.71	31.10
			26.76	6.55	31.06
<i>Ib</i>	172–173 ^a	$\text{C}_3\text{H}_8\text{N}_2\text{O}_2$ (104.109)	34.61	7.75	26.91
			34.38	7.67	27.19
<i>IIa</i>	214–215 ^g	$\text{C}_3\text{H}_8\text{N}_2\text{O}_2$ (104.109)	34.61	7.75	26.91
			34.72	7.77	26.74
<i>IIb</i>	197–199 ^{b,h}	$\text{C}_4\text{H}_{10}\text{N}_2\text{O}_2$ (118.136)	40.67	8.53	23.71
			40.23	8.53	23.44
<i>IIIa</i>	121–122 ^{c,g}	$\text{C}_3\text{H}_9\text{N}_3\text{O}_2$ (119.124)	30.25	7.62	35.27
			30.45	7.73	35.04
<i>IIIb</i>	125–127 ⁱ	$\text{C}_4\text{H}_{11}\text{N}_3\text{O}_2$ (133.151)	36.08	8.33	31.56
			35.78	7.97	31.28
<i>IVa</i>	135–137	$\text{C}_3\text{H}_8\text{N}_2\text{O}_3$ (120.108)	30.00	6.71	23.32
			29.99	6.46	23.36
<i>IVb</i>	125–127 ^g	$\text{C}_4\text{H}_{10}\text{N}_2\text{O}_3$ (134.135)	35.81	7.51	20.88
			35.90	7.20	21.25
<i>Va</i>	151–152 ^j	$\text{C}_3\text{H}_8\text{N}_2\text{O}_2\text{S}^e$ (136.169)	26.46	5.92	20.57
			26.42	5.87	20.48
<i>Vb</i>	147–148 ^{d,j}	$\text{C}_4\text{H}_{10}\text{N}_2\text{O}_2\text{S}^f$ (150.196)	31.99	6.71	18.65
			31.94	6.71	18.69

^a Ref.¹² 162–164°C; ^b ref.¹⁹ 189–191°C; ^c ref.²⁰ 116–119°C; ^d compound described²¹ without reference to m.p.; ^e calcd. 23.54%S, found 23.34%S; ^f calcd. 21.35%S, found 21.26%S. Cryst. from ^g ethanol, ^h ethanol/acetone, ⁱ ethanol/ether, ^j ethanol/water.

chemical shifts in agreement with the above discussed MO treatments. As we proved²² by experiments with compounds of type *I*, where X and/or Y are substituted aromates, molecules of the discussed type are not dissociated into both partners in hexadeuterio-dimethylsulfoxide solutions. A comparison of chemical shifts of carboxylic carbon C_(1') in series of formates (*a*) and acetates (*b*) shows a strong similarity. Differences in chemical shifts of the methyl group in acetates (*b*), ranging in the order of CH₃O > > CH₃S > H > CH₃ > CH₃NH, are not attributable to the similar order of

TABLE V

Energies of the frontier orbitals calculated for compounds *Ia*–*Va* by 3–21 G method. (1 a.u. = = 2 625.5 kJ/mol)

Compound	Energy (a.u.)		
	HOMO	HOMO-1	LUMO
<i>Ia</i>	–0.36425	–0.37152	0.15498
<i>IIa</i>	–0.35883	–0.36638	0.15653
<i>IIIa</i>	–0.35113	–0.36081	0.20627
<i>IVa</i>	–0.36297	–0.37285	0.19300
<i>Va</i>	–0.36978	–0.37495	0.13392

TABLE VI

NMR spectra of compounds *Ia, b*–*Va, b*

Compound	¹³ C NMR shifts, ppm				¹ H NMR shifts ppm		
	C ₍₁₎	X	C _(1')	Y	H _a + H _b (4 H)	X	Y
<i>Ia</i>	158.22		167.60		9.52	7.81 (1 H)	8.46 (1 H)
<i>Ib</i>	158.35		175.53	24.38	8.59	7.78 (1 H)	1.68 (3 H)
<i>IIa</i>	168.21	18.43	167.59		9.71	2.08 (3 H)	8.43 (1 H)
<i>IIb</i>	168.14	18.51	176.21	24.96	9.92	2.03 (3 H)	1.65 (3 H)
<i>IIIa</i>	158.45	27.44	167.58		7.85	2.65 (3 H)	8.43 (1 H)
<i>IIIb</i>	158.39	27.16	175.80	25.04	8.08	8.74 (1 H)	2.64 (3 H)
						8.08 (1 H)	1.64 (3 H)
<i>IVa</i>	162.79	56.34	167.21		8.46	3.86 (3 H)	8.39 (1 H)
<i>IVb</i>	162.50	55.42	175.21	23.65	8.58	3.79 (3 H)	1.73 (3 H)
<i>Va</i>	170.07	13.04	167.58		9.90	2.49 (3 H)	8.37 (1 H)
<i>Vb</i>	168.68	12.77	175.99	23.99	9.10	2.42 (3 H)	1.73 (3 H)

various known substituent constants. The ^{13}C NMR shifts difference of carbons $\text{C}_{(1)}$ of compounds *Va* and *Vb* is not easily explainable and might be caused by the relative instability of compound *Vb* that tends to undergo decomposition into methylmercaptane. Nevertheless, a comparison of the H-bonds by ^1H NMR (Table VI) again shows a similarity of the hydrogen bonded systems.

CONCLUSIONS

MO calculations, as well as the NMR data of compounds *I*–*V* proved, that regardless of the differences in their counter parts forming stable molecules *I*–*V* the properties of the hydrogen bonded system remain very similar. Alternation of the charges within the systems are of importance. These facts will be of interest as far as our effort to investigate some redox bioreactions is concerned where active centre models of different chemical nature could be applied.

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