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3-Methoxycarbonyl-4-phenyl-2-pyrrolidone in Reactions with Benzalmalonate and Its Analogs

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Abstract—3-Methoxycarbonyl-4-phenyl-2-pyrrolidone reacts with benzalmalonate and related compounds as an N-nucleophile affording adducts as an easily resolvable diastereoisomeric mixture. Structure of the synthesized compounds is studied by IR and ^{1}H, ^{13}C NMR spectroscopy. Structural parameters and configurations of the stereoisomers of one among the series of synthesized compounds was determined by X-ray structural analysis. The pyrrolidone ring of these compounds is shown to be present in an *envelope* conformation. The supramolecular structures in crystal are formed mainly on account of intermolecular hydrogen bonds of C–H···O type and π···π interactions.

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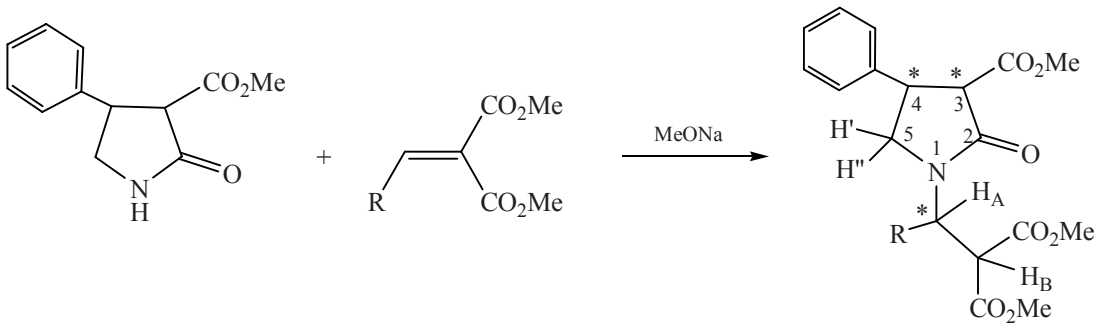
γ-Butyrolactame or 2-pyrrolidone, the product of intramolecular heterocyclization of γ-aminobutyric acid, is a central fragment of a series of drugs. For example, pyrrolidone ring is a fragment of nootropic preparation pyracemate [1] and antiischemic drug phenotropyl (carphedone) [2]; poly-*N*-vinylpyrrolidone is used as a blood plasma substitute, a means for removing toxic substances from organism and for prolongation of action of some pharmaceuticals [1].

As a convenient method for the synthesis of pyrrolidone-containing compounds a reaction of 2-pyrrolidone derivatives with compounds containing activated double bond can be used. Particulary interesting is 3-methoxycarbonyl-4-phenyl-2-pyrrolidone, the reagent that is both CH- and NH-acid simultaneously and a compound having an independent importance as a potentially biologically active substance.

As known, 4-aryl(heteryl)-3-methoxycarbonyl-2-pyrrolidones react as CH-acids at C^3-nucleophilic center of pyrrolidone ring with 2-aryl(heteryl)-1-nitroethenes to form 3-[1-aryl(heteryl)-2-nitroethyl]-3-methoxycarbonyl-4-phenyl-2-pyrrolidones as a mixture of diaseteroisomers [3, 4].

It is logical to suppose that 4-phenylpyrrolidonecarboxylic ester (**I**) can also enter in the reactions with other compounds containing activated multiple bonds, in particularicular, with 2-aryl(heteryl)-1,1-dimethoxycarbonylethenes. There is no data on such reactions in the published sources. We studied reactions of pyrrolidonecarboxylate (**I**) with 2-aryl-1,1-dimethoxycarbonylethenes bearing either an electron-donor, or an electron acceptor group in the *para* position of the benzene ring, and with 1,1-dimethoxycarbonyl-2-(pyridyl-3)ethene.

We found that the reaction of 3-methoxycarbonyl-4-phenyl-2-pyrrolidone (**I**) with 2-aryl(heteryl)-1,1-dimethoxycarbonylethenes (**II–V**) proceeds in the presence of sodium methoxide at room temperature and affords the products of nucleophilic addition, but at the nitrogen atom of pyrrolidone ring rather than at C^3 atom. Probably the preferred attack at the nitrogen atom is defined by its steric accessibility because 2-aryl(heteryl)-1,1-dimethoxycarbonylethenes are sterically more hindered that 2-aryl(heteryl)-1-nitroethenes. Compounds **VIa**, **VIb–XIa**, **XIb** were isolated and then resolved by fractional crystallization into isomers **a** and **b**.



I **II–V** **VIa, VIb–IXa, IXb**

R = C_6H_5 (**II, VIa, VIb**), *p*-O_2N-C_6H_4 (**III, VIIa, VIIb**), *p*-Cl-C_6H_4 (**IV, VIIIa, VIIIb**), pyridyl-3 (**V, IXa, IXb**).

In the studied series of 1,1-dimethoxycarbonylethenes **II–IV** a dependence is clearly seen of the reaction efficiency on the nature of substituent in the benzene ring of electrophilic counterpart and on the ratio of initial reagents **I**, **II–IV**. In particular, the presence of the electron-withdrawing nitro group in the molecule of the initial reagent **III** and the use of pyrrolidonecarboxylate **I** in 1.5-fold excess allowed us to achieve maximal yield (92%) of the target substance **VIIa**, **VIIb** (Table 1).

The study of the structure of 4-phenylpyrrolidonecarboxylate *N*-dimethoxycarbonylethyl derivatives **VIa**, **VIb–IXa**, **IXb** by spectroscopic methods showed the presence in their IR spectra of the absorption bands of pyrrolidone carbonyl groups (1686−1700 cm^{-1}) and ester function (1736−1760 cm^{-1}). Due to the presence of three asymmetric carbon atoms in the molecules of compounds **VI–IX** these com-pounds can exist as mixtures of several diastereomers. Their ^1H and ^{13}C NMR spectra before crystallization contain

Table 1. Melting points, yields and spectral characteristics of compounds **VIa–IXa**, **VIb–IXb**

Comp. no.	Yield, %		mp, °C	IR spectra, ν, cm^{-1}, vaseline oil		^1H NMR spectra, $CDCl_3$														
						Chemical shift, δ, ppm										Spin-spin coupling constants, *J*, Hz				
	total	**a** and **b** isomers		C=O	C=O (CO_2R)	C^3H	C^4H	C^5H'	C^5H''	$\Delta_{H'H''}$	H_A	H_B	Δ_{AB}	CH_3	C_6H_5 (R)	J_{AB}	J_{34}	$J_{4H'}$	$J_{4H''}$	$J_{H'H''}$
VIa	70	38	138–140	1700	1760	3.57	3.81	3.48	3.55	0.07	5.68	4.57	1.11	3.55 3.72 3.79	7.10–7.40	11.91	9.80	8.70	8.70	9.00
VIb		22	114–116	1686	1740	3.53	3.85	3.12	3.78	0.66	5.82	4.54	1.28	3.57 3.75 3.80	7.07–7.37	11.91	9.20	8.65	8.28	8.65
VIIa	92	42	118–120	1700	1760	3.56	3.81	3.47	3.56	0.09	5.65	4.68	0.97	3.59 3.74 3.78	7.25–7.27 (7.56, 8.00)	11.91	9.50	9.20	8.74	9.20
VIIb		35	147–149	1700	1740	3.54	3.88	3.19	3.82	0.63	5.77	4.65	1.12	3.59 3.75 3.82	7.25–7.27 (7.56, 8.20)	11.91	9.20	8.60	8.00	8.60
XIIIa	43	28	134–135	1690	1760	3.56	3.82	3.51	3.57	0.06	5.58	4.57	1.01	3.57 3.73 3.79	7.32 (7.25, 7.28)	11.91	9.30	9.30	8.67	9.30

Table 1. (Contd.)

Comp. no.	Yield, %		mp, °C	IR spectra, ν, cm^{-1}, vaseline oil		^{1}H NMR spectra, $CDCl_3$														
	total	**a** and **b** isomers				Chemical shift, δ, ppm										Spin-spin coupling constants, *J*, Hz				
				C=O	C=O (CO_2R)	C^3H	C^4H	C^5H'	C^5H''	$\Delta_{H'H''}$	H_A	H_B	Δ_{AB}	CH_3	C_6H_5 (R)	J_{AB}	J_{34}	$J_{4H'}$	$J_{4H''}$	$J_{H'H''}$
XIIIb		11	120–122	1690	1736	3.55	3.87	3.14	3.81	0.67	5.73	4.53	1.20	3.58 3.74 3.80	7.23 (7.09, 7.23)	11.91	9.30	9.10	8.64	9.10
IXa	82	27	110–112	1700	1760	3.54	3.82	3.51	3.65	0.14	5.57	4.70	0.87	3.55 3.72 3.79	7.25 (7.16, 7.83, 8.58)	11.91	9.24	9.14	8.47	9.14
IXb		37	127–129	1690	1740	3.54	3.87	3.22	3.82	0.60	5.70	4.65	1.05	3.57 3.73 3.79	7.25 (7.10, 7.76, 8.58)	11.91	9.42	8.36	7.75	8.36

Table 2. ^{13}C NMR spectra of diastereomeric compounds **VIa** and **VIb** in $CDCl_3$[a]

Comp. no.	C^2	C^3	C^4	C^5	C^{23}, C^{25}	C^{13}	C^{14}	C^{21}	C^{22}, C^{24}	C^{12}	Ar		
											C^6	C^{15}	C^7–C^{12}, C^{16}–C^{20}
VIa	169.50	56.40	41.96	53.90	52.91	53.40	56.20	52.53	166.68, 167.42	169.00	139.60	135.65	127.00–128.60
VIb	169.62	56.02	41.94	49.79	52.68	53.18	55.52	53.08	166.71, 167.31	168.78	139.23	135.86	127.04–128.12

[a] Numbers of atoms the same as in Figs. 5 and 6.

double sets of proton and carbon signals indicating formation of two diastereomers **a** and **b** in 1 : 1 ratio in all the compounds. Spectral charac-teristics of compounds **VIa**, **VIb–IXa**, **IXb** correspond completely to the assumed structures (Tables 1 and 2). For example, in the ^{1}H NMR spectrum of compounds **VIa** and **VIb** the protons of benzene ring resonate downfield as a multiplet in the region of 7.07–7.40 ppm. The ester methyl groups give rise to singlets at 3.55, 3.72, and 3.79 ppm (**VIa**) and 3.57, 3.75, and 3.80 ppm (**VIb**). Methine protons in dialkoxy-carbonylethyl fragment H_A, H_B resonate as doublets at 5.68 and 4.57 pap (**VIa**) and 5.82 and 4.54 ppm (**VIb**) respectively, therewith the difference in methine H_A and H_B chemical shifts in **VIa** diastereomer (Δ_{AB} 1.11 ppm) is less than that in the diastereomer **VIb** (Δ_{AB} 1.28 ppm). Similar regularity was observed also in the spectra of other compounds **VIIa**, **VIIb–IXa**, **IXb** (Table 1, Figs. 1, 2).

The ring protons form a multispin system and appear as multiplets in the region of 3.1–3.9 ppm where also occur strong signals of methyl groups. To overcome problems arising due to the overlaping of these signals, we applied for reliable assignment the method of two-dimensional heteronuclear NMR spectroscopy. We applied COSY procedure based on the transfer of coherency in the period of mixing. In the 2D-correlation experiment (Figs. 3 and 4) were monitored ^{1}H and ^{13}C NMR spectra, the latter as heteronucleus with proton decoupling. Analysis of the two-dimensional spectra shows that among all the ring protons the proton at the carbon C^4 atom gives a signal at the weakest field, both in **a** and **b** isomers. In the ^{1}H–^{13}C correlation spectrum of compound **VIa** correlations are seen between C^4H proton (δ 3.81 ppm) and C^4 atom (δ 41.96 ppm), C^3H proton (δ 3.57 ppm) and C^3 (δ 56.40 ppm), C^5H' (δ 3.48 ppm) and C^5H'' (δ 3.55 ppm) protons and C^5 atom (δ 53.90 ppm) (Fig. 3).

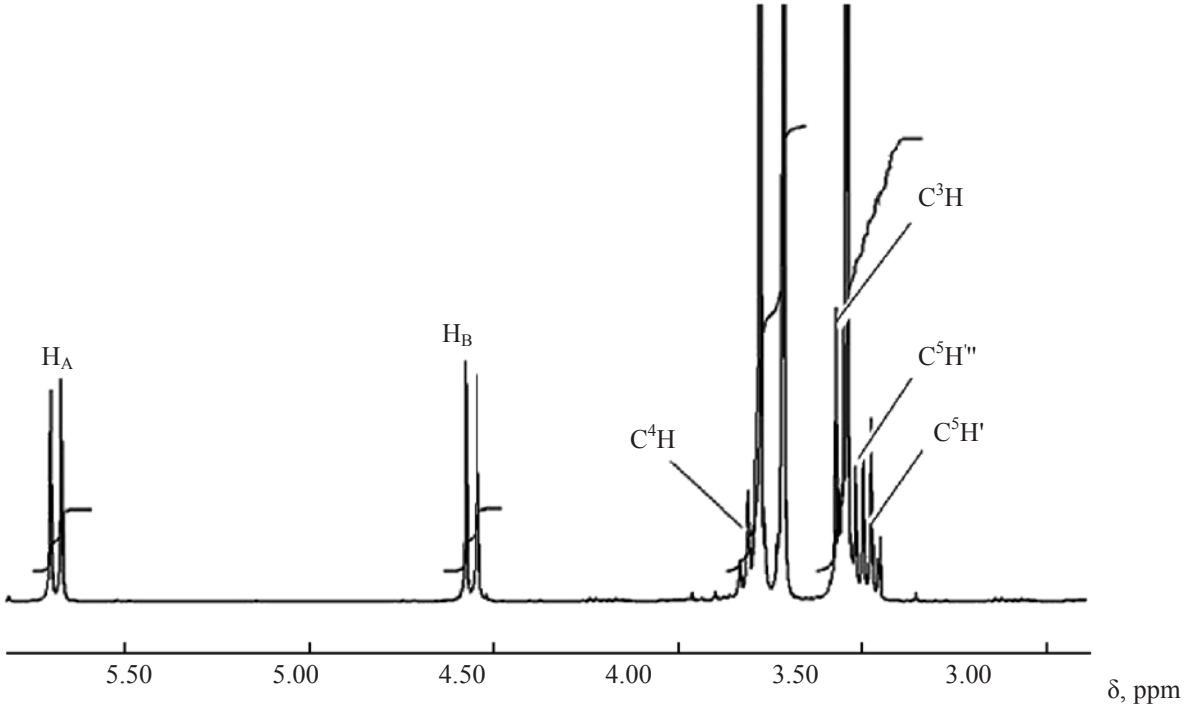


Fig. 1. A fragment of ^{1}H NMR spectrum of compound **VIa** in $CDCl_3$.

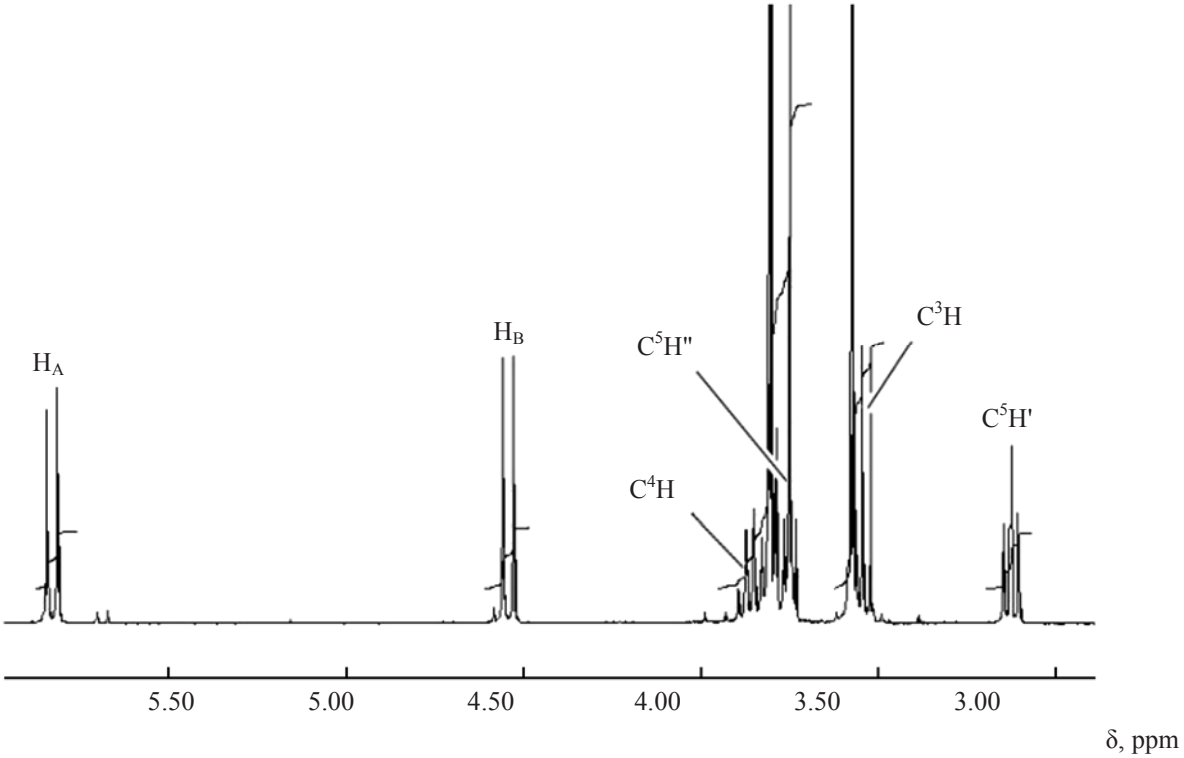


Fig. 2. A fragment of ^{1}H NMR spectrum of compound **VIb** in $CDCl_3$.

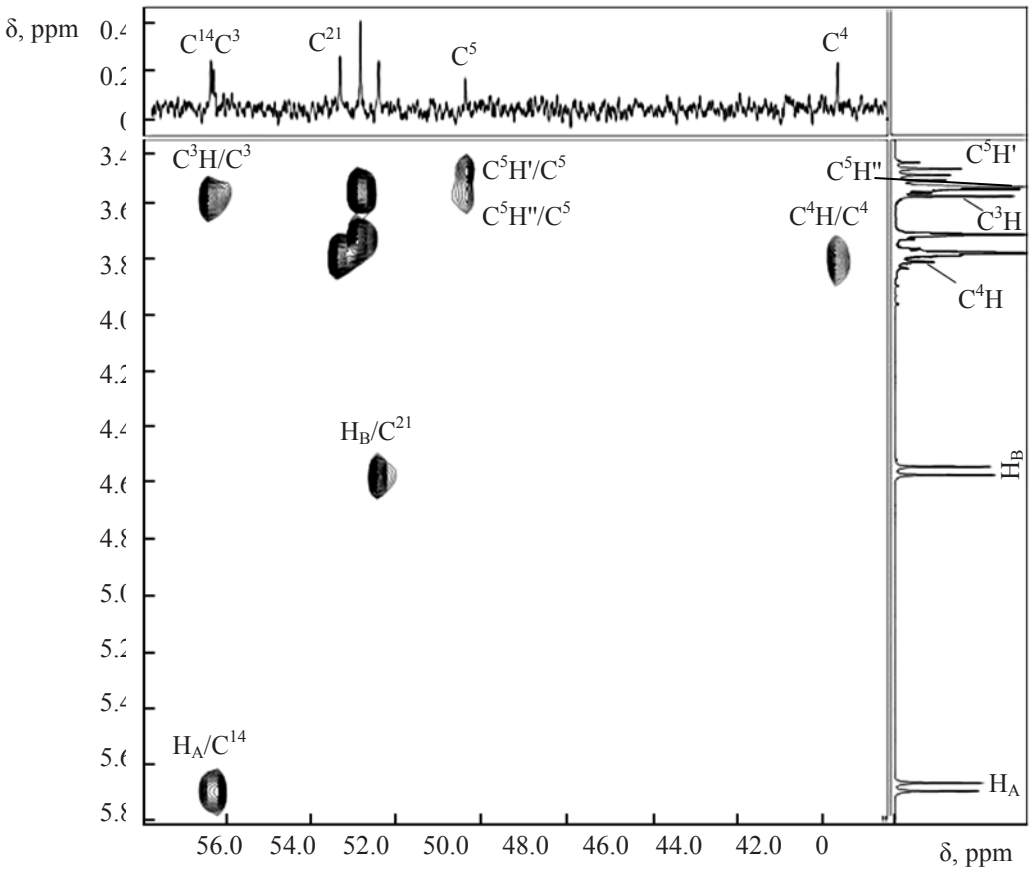


Fig. 3. A fragment of 2D (^{1}H–^{13}C) of compound **VIa** in $CDCl_3$.

Similar correlations are typical for the second isomer (**VIb**): in the spectrum cross peaks are observed between the proton C^4H (δ 3.85 ppm) and C^4 atom (δ 41.94 ppm), C^3H proton and (δ 3.53 ppm) C^3 atom (δ 56.02 ppm), C^5H' (δ 3.12 ppm) and C^5H'' (δ 3.78 ppm) protons and C^5 atom (δ 49.79 ppm) (Fig. 4.). The proton C^4H is coupled (Table 1) with the proton C^3H (J_{34} 9.80 Hz in compound **VIa**, J_{34} 9.20 Hz in compound **VIb**) and with methylene protons C^5H', C^5H'' ($J_{4H'}$ 8.70, $J_{4H''}$ 8.70 Hz in **VIa**, $J_{4H'}$ 8.65, $J_{4H''}$ 8.28 Hz in **VIb**).

The correlation spectra demonstrate most clearly the difference in the appearance of methylene protons C^5H' and C^5H'' of pyrrolidone ring. In the diastereomer **a** the signals of H' and H" are closer while in diastereomer **b** they are reciprocaly more distant (Figs. 3 and 4). For example, in the spectrum of **VIa** the difference of C^5H' and C^5H'' chemical shifts ($\Delta_{H'H''}$ 0.07 ppm) is much less than in the spectrum of diasetreomer **VIb** ($\Delta_{H'H''}$ 0.66 ppm), and similar pattern occurs in the spectra of the whole series of the synthesized compounds (Table 1). Obviously, this criterion can also be used as analytical index for the identification of diastereomers. Thus, the difference characteristics Δ_{AB} and $\Delta_{H'H''}$ can be recommended as tests at the analysis of spectra of diastereoisomeric mixtures **VIa–IXa** and **VIb–IXb** and related structures.

An important information on the structure of synthesized compounds is obtained at the study of two compounds, the diastereomers **VIa** and **VIb**, by X-ray structural analysis.

Compounds **VIa** and **VIb** form monoclinic crystals of space groups $P2_1/n$ (**VIa**) and $P2_1/c$ (**VIb**) with one independent molecule in the asymmetric part of the unit cell (Figs. 5 and 6, Tables 3–6). Both compounds crystallize as a racemate with the following configurations of three asymmetric carbon atoms C^3, C^4, and C^{14}: **VIa**, 3S, 4R, 14R; **VIb**, 3R, 4S, 14R. Conformations of heterocycles in these molecules are close to C^4-*envelope* with dihedral angles between planar fragments $C^5N^1C^2C^3$ and $C^3C^4C^5$ 153.2° 149.5°

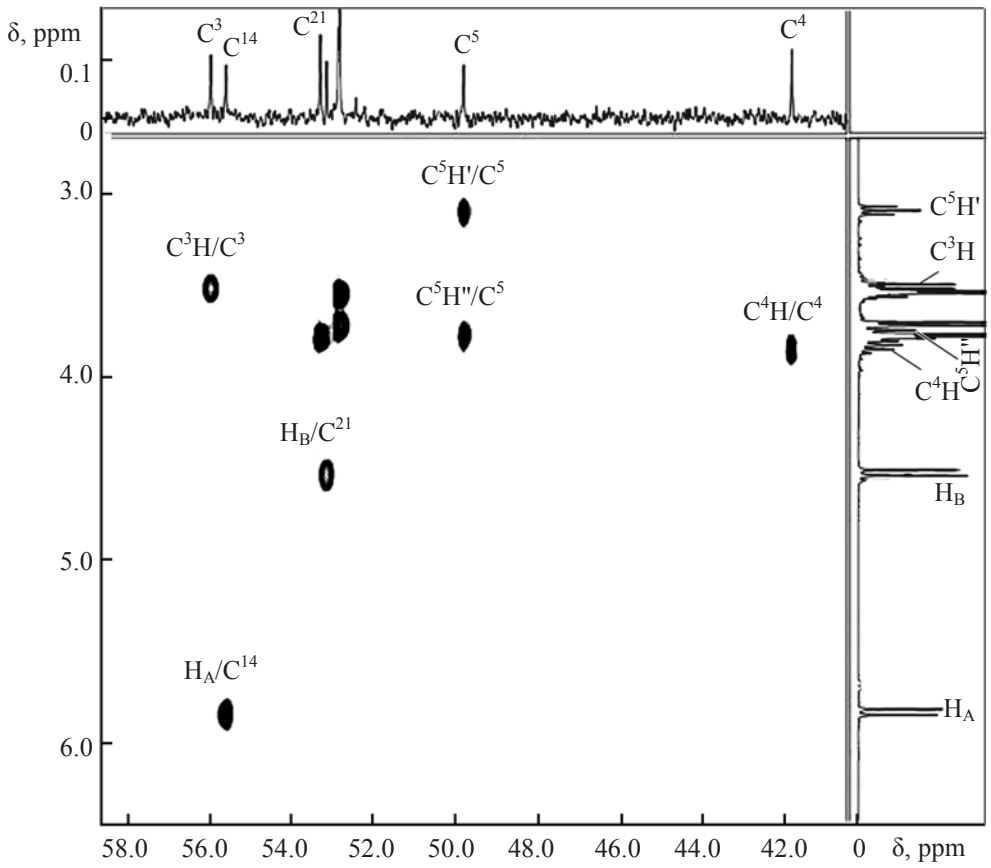


Fig. 4. A fragment of 2D ($^{1}H–^{13}C$) of compound **VIb** in $CDCl_3$.

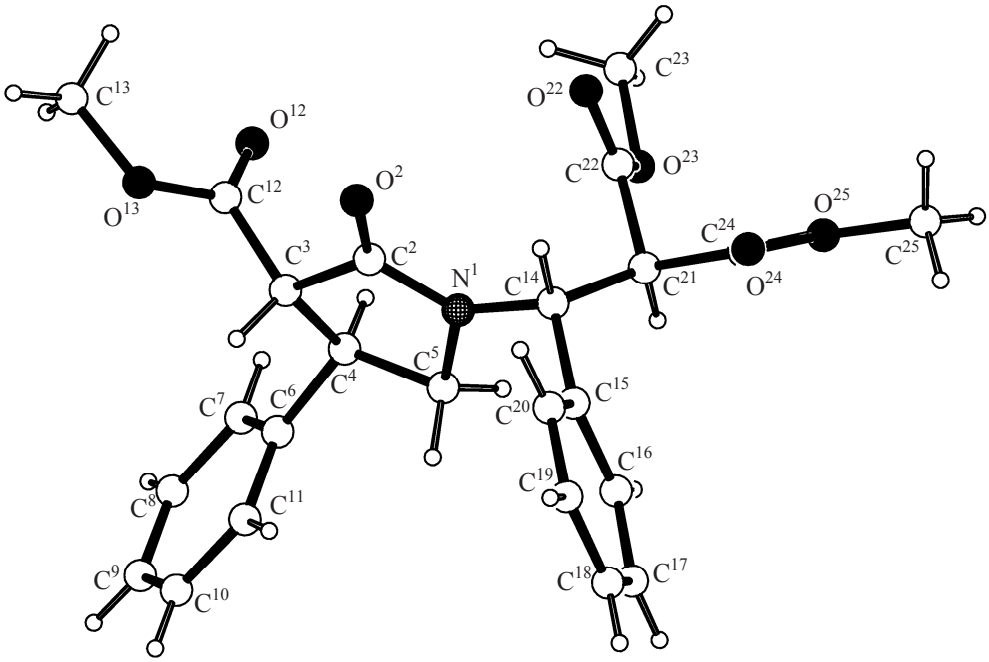


Fig. 5. Molecular geometry of compound **VIa** in crystal. Configuration of asymmetric atoms rel (3*S*, 4*R* and 14*R*).

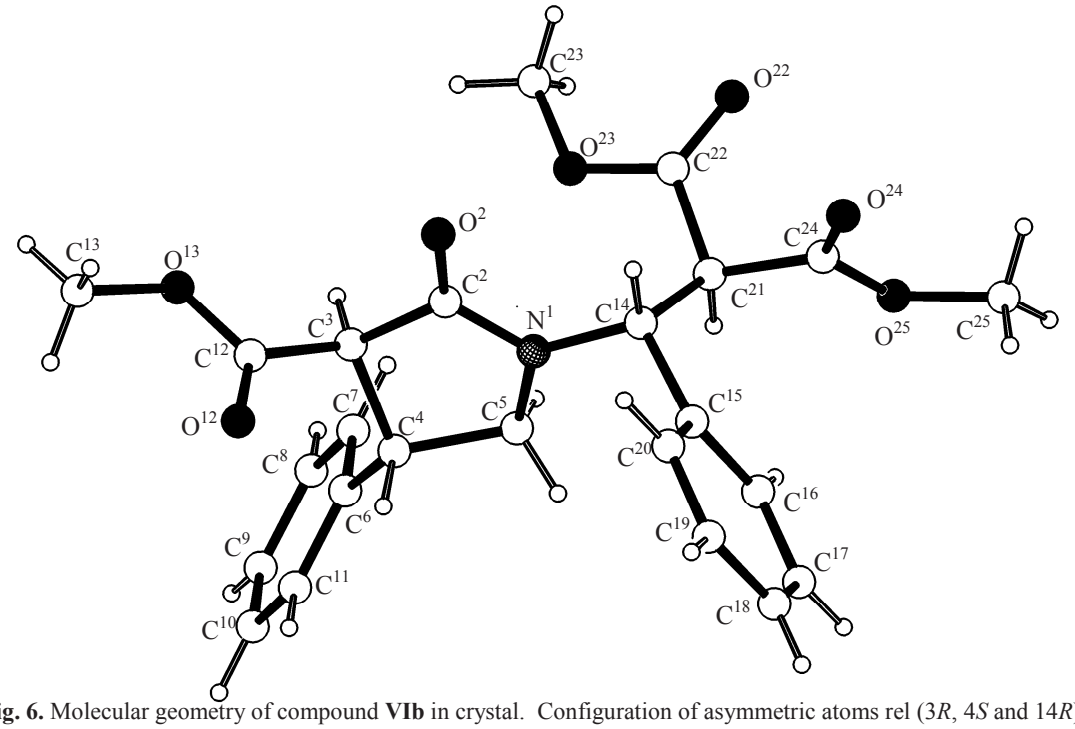


Fig. 6. Molecular geometry of compound **VIb** in crystal. Configuration of asymmetric atoms rel (3*R*, 4*S* and 14*R*).

Table 3. Bond lengths (*d*) in the molecules of diastereomers**VIa** and **VIb**

Bond	Compound **VIa**	Compound **VIb**
N^1–C^2	1.353(2)	1.341(3)
N^1–C^5	1.467 (2)	1.465(3)
N^1–C^{14}	1.467 (2)	1.461(3)
C^2–O^2	1.219(2)	1.217(3)
C^2–C^3	1.522(2)	1.536(3)
C^3–C^4	1.533(2)	1.539(3)
C^3–C^{12}	1.503 (2)	1.510(3)
C^4–C^5	1.534(2)	1.549(3)
C^4–C^6	1.517 (2)	1.506(3)
C^{12}–O^{12}	1.191(2)	1.195(3)
C^{12}–O^{13}	1.317(2)	1.306(3)
C^{13}–O^{13}	1.441(2)	1.447(4)
C^{14}–C^{15}	1.513(2)	1.526(3)
C^{14}–C^{21}	1.535(2)	1.549(3)
C^{21}–C^{22}	1.518(2)	1.527(4)
C^{21}–C^{24}	1.520 (2)	1.528(3)
C^{22}–O^{22}	1.183 (2)	1.197(4)
C^{22}–O^{23}	1.324 (2)	1.314(4)
C^{23}–O^{23}	1.449(2)	1.448(4)
C^{24}–O^{24}	1.185(2)	1.192(3)
C^{24}–O^{25}	1.309 (2)	1.328(3)
C^{25}–O^{25}	1.444(2)	1.451(4)

for **VIa** and **VIb** respectively, atom C^4 is deviated from the plane of the four-atomic fragment by 0.43 Å (**VIa**) and 0.49(3) Å (**VIb**). Two of the three bonds at the nitrogen atom N^1 are leveled while the third bond is significantly shortened: in **VIa** the bond lengths are N^1–C^5 1.467(2) Å, N^1–C^{14} 1.467(2) Å, N^1–C^2 1.353(2) Å; in **VIb** they are N^1–C^5 1.465(4) Å, N^1–C^{14} 1.461(4) Å, and N^1–C^2 1.341(4) Å.

In the crystal of compound **VIa** occur intermolecular interactions of different type, the most significant are hydrogen bonds of C–H···O type and interactions of π···π type. On account of the realization of the intermolecular hydrogen bonds C^3–H^3...$O^{25'}$ and C^5–H^{52}...$O^{2''}$ in the crystal chains are formed along the screw second order axes (Fig. 7). Parameters of the hydrogen bonds are listed in Table 5. Also, there are two intramolecular C–H···O hydrogen bonds between hydrogen atoms H^4 and H^{14} at the asymmetric carbon atoms and oxygen atoms O^{12} and O^2 in carbonyl groups of heterocyclic and methoxycarbonyl fragments of the molecule, respectively.

The tota packing of the molecules of compound **VIa** in the crystal can be represented as parallel packing of the above-describes H-bound molecular chains in a hexagonal mode (Fig. 8). Therewith, the π···π interactions appearing between electron systems

Table 4. Bond angles (ω, deg) in the molecules of diastereomers **VIa** and **VIb**

Angle	Compound **VIa**	Compound **VIb**	Angle	Compound **VIa**	Compound **VIb**
$C^2N^1C^5$	113.2(1)	113.9(2)	$C^{12}O^{13}C^{13}$	117.1(2)	116.9(3)
$C^2N^1C^{14}$	121.8(1)	123.4(2)	$N^1C^{14}C^{15}$	112.1(1)	108.7(2)
$C^5N^1C^{14}$	123.9(1)	122.4(2)	$N^1C^{14}C^{21}$	109.0(1)	112.2(2)
$O^2C^2N^1$	126.6(1)	126.6(2)	$C^{15}C^{14}C^{21}$	113.8(1)	112.5(2)
$O^2C^2C^3$	125.6(1)	125.5(2)	$C^{22}C^{21}C^{24}$	107.1(1)	106.9(2)
$N^1C^2C^3$	107.8(1)	107.9(2)	$C^{22}C^{21}C^{14}$	109.9(1)	117.2(2)
$C^2C^3C^4$	104.9(1)	103.2(2)	$C^{24}C^{21}C^{14}$	111.8(1)	108.9(2)
$C^{12}C^3C^2$	111.9(1)	111.9(2)	$O^{22}C^{22}O^{23}$	124.6(2)	123.8(3)
$C^{12}C^3C^4$	113.3(1)	114.0(2)	$O^{22}C^{22}C^{21}$	123.7(2)	123.0(3)
$C^6C^4C^3$	112.3(1)	116.4(2)	$O^{23}C^{22}C^{21}$	111.7(1)	113.0(2)
$C^6C^4C^5$	116.2(1)	113.7(2)	$C^{22}O^{23}C^{23}$	115.2(2)	116.4(3)
$C^3C^4C^5$	103.2(1)	102.6(2)	$O^{24}C^{24}O^{25}$	124.4(1)	125.5(2)
$N^1C^5C^4$	103.1(1)	102.8(2)	$O^{24}C^{24}C^{21}$	125.3(1)	124.3(2)
$O^{12}C^{12}O^{13}$	123.6(1)	122.6(3)	$O^{25}C^{24}C^{21}$	110.2(1)	110.2(2)
$O^{12}C^{12}C^3$	124.8(1)	124.5(2)	$C^{24}O^{25}C^{25}$	118.1(1)	115.8(3)
$O^{13}C^{12}C^3$	111.6(1)	112.8(2)			

of phenyl substituents in the molecules belonging to neighboring chains stabilize this packing as a whole and thus lead to the formation of 3D supramolecular structure (the shortest distance between the ring planes is 3.73 Å, the distance between the ring centers is 4.22 Å, dihedral angle is 0º). However, the bulky substituents at the heterocycle restrict the appearance in the crystal of the most dense packing: the value of calculated

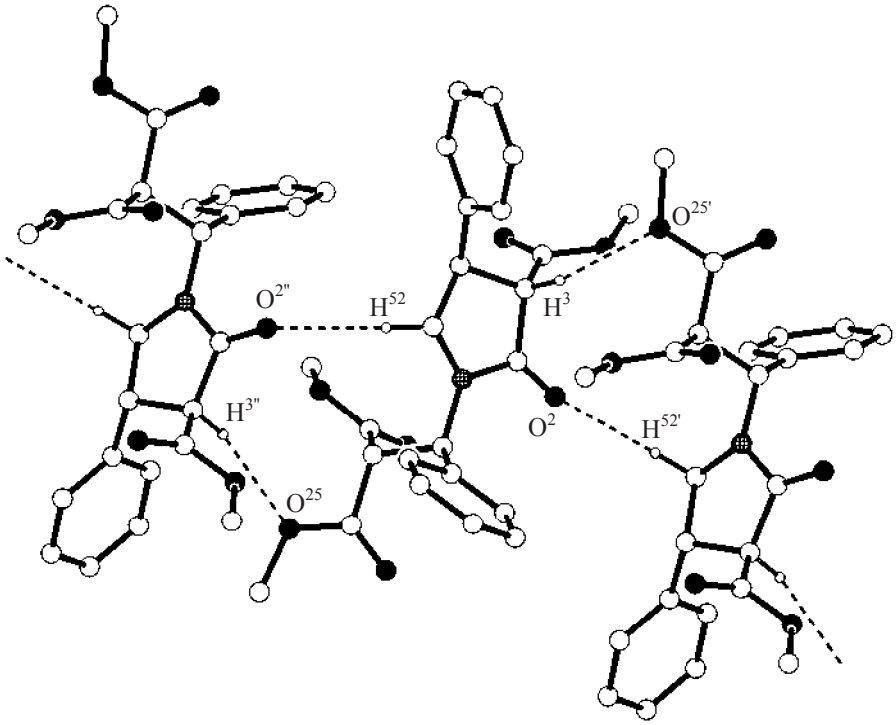


Fig. 7. Systems of hydrogen bond of C–H···O type in the crystal of compound **VIa**. Only hydrogen atoms involved in hydrogen bonding (dashed lines) are depicted.

Table 5. Parameters of hydrogen bonds in the crystal of compound **VIa**

D–H···A	D–H, Å	H···A, Å	D···A, Å	DHA, deg	Symmetry operations
Intermolecular H-bonds					
C^3–H^3···$O^{25'}$	0.98	2.43	3.339(2)	154	3/2 – *x*, 1/2 + *y*, 1/2 – *z*
C^5–H^{52}···$O^{2''}$	0.97	2.51	3.453(2)	165	3/2 – *x*, –1/2 + *y*, 1/2 – *z*
Intramolecular H-bonds					
C^4–H^4···O^{12}	0.98	2.49	2.901(2)	105	–
C^{14}–H^{14}···O^2	0.98	2.44	2.866(2)	106	–

Table 6. Parameters of hydrogen bonds in the crystal of compound **VIb**

D–H···A	D–H, Å	H···A, Å	D···A, Å	DHA, deg	Symmetry operations
Intermolecular H-bonds					
C^4–H^4···$O^{12'}$	0.98	2.50	3.280(4)	137	1 – *x*, 1 – *y*, 2 – *z*
C^8–H^8···$O^{13''}$	0.93	2.59	3.257(4)	129	*x*, 1/2 – *y*, –1/2 + *z*
C^{21}–H^{21}···$O^{2''}$	0.98	2.47	3.233(3)	135	*x*, 1/2 – *y*, –1/2 + *z*
C^5–H^{51}···$O^{2''}$	0.97	2.52	3.435(4)	158	*x*, 1/2 – *y*, –1/2 + *z*
Intramolecular H-bonds					
C^{14}–H^{14}···O^2	0.98	2.48	2.883(3)	105	

packing factor of the crystal is extremely low, only 65.2%.

The supramolecular structure of the crystal of compound **VIb** is formed mainly on account of existence of C–H···O type hydrogen bonds. Each molecule of compound **VIb** in the crystal is involved into seven intermolecular hydrogen bonds, four as donor and three as acceptor (the oxygen atom O^2 is involved in the formation of a bifurcate H-bond). The hydrogen bonds parameters are listed in Table 6. Three H-bonds, C^8-H^8···$O^{13''}$, C^{21}-H^{21}···$O^{2''}$ and C^5-H^{51}···$O^{2''}$, lead to the formation of chains along 0*c* axis. The H-bond C^4-H^4···$O^{12'}$ connects the molecular chains in the crystallographic direction 0*b*, thus the total effect of these bonds leads to the formation of 2D supramolecular structure as infinite layer of H-bound molecules in the *b*0*c* plane (Fig. 9). Therewith, an intramolecular C–H···O hydrogen bond exists (Table 6) between H^{14} hydrogen atom at the asymmetric carbon atom and O^2 oxygen atom in the heterocycle carbonyl group.

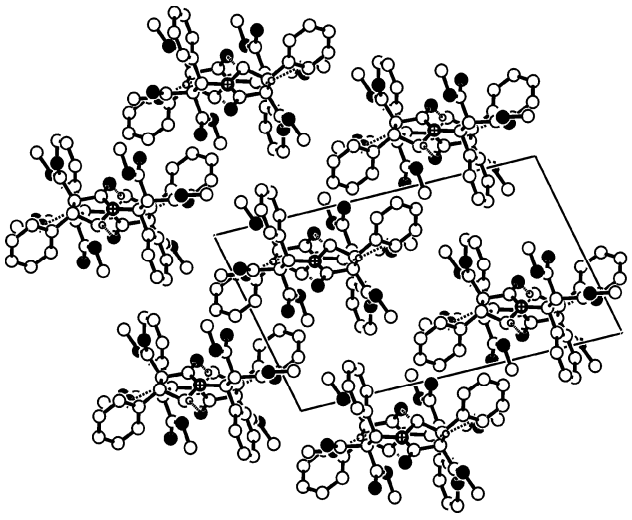


Fig. 8. Packing of molecules of compound **VIa** in crystal, view along crystallographic axis 0*b*. Only the hydrogen atoms involved into hydrogen bonding are depicted.

The whole packing of the molecules of compound **VIb** in the crystal can be represented as a parallel packing of H-bound molecular layers along the crystallographic direction 0*c* (Fig. 10). Between the parallel layers no significant interactions is detected, except the ordinary van der Waals forces. Despite the presence of aromatic fragments in **VIb** molecule the contacts between the π-electronic systems of aromatic rings are not revealed. Mutual positions of molecules does not result in the most dense packing in the crystal, and calculated value of packing coefficient for the crystal is also as low as 67.0%.

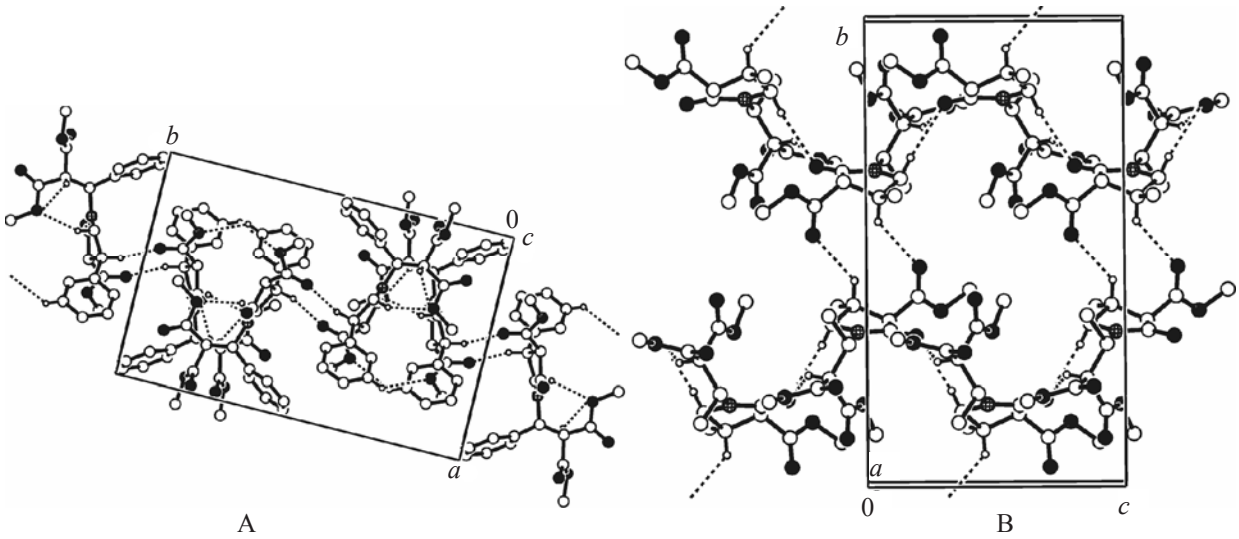


Fig. 9. Two projections of the system of C–H···O hydrogen bonds in the crystal of compound **VIb**. Only hydrogen atoms involved into hydrogen bonding (dashed lines) are depicted. A–view along 0*c* axis, B–view along 0*a* axis, phenyl substituents are omitted.

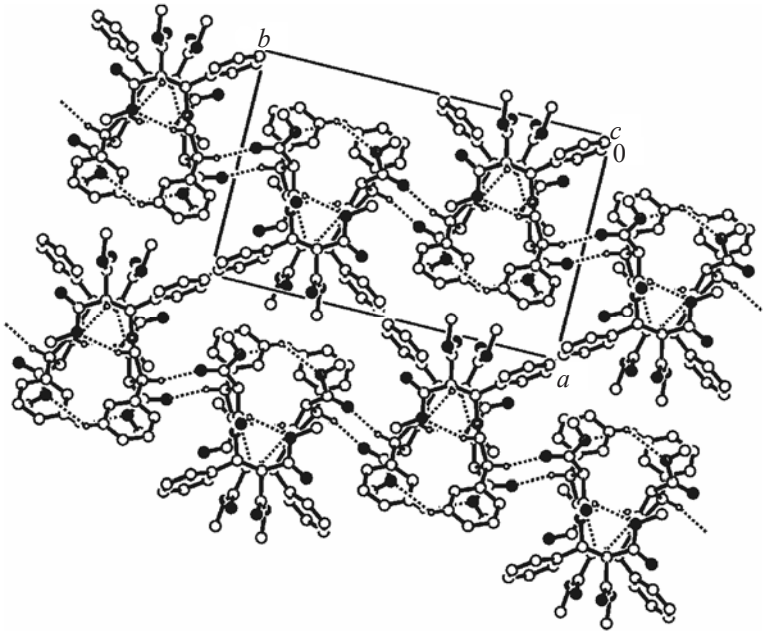


Fig. 10. Packing of molecules of compound **VIb** in crystal. View along crystallographic axis 0*c*.

As a result of our investigation, on the basis of reactions of 3-methoxycarbonyl-4-phenyl-2-pyrrolidone with 2-aryl(heteryl)-1,1-dimethoxycarbonylethenes we developed preparative method for the synthesis of ethyl]-3-methoxycarbonyl-4-phenyl-2-pyrrolidones **VIa–IXa** and **VIb–IXb**. By IR and ^{1}H, ^{13}C NMR spectroscopy (with application of COSY experiment) and X-ray structural analysis structures of the compounds were reliably elucidated. Synthesized compounds **VIa–IXa** and **VIb–IXb** can be used for the synthesis of new derivatives of γ-aminobutyric acid and α-pyrrolidone, and can also be recommended for the study of their pharmacological properties.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were registered on a JNMR JNN ECX400A instrument [400 MHz (^{1}H),

100.52 MHz (^{13}C)] using chloroform-*d* as a solvent. The vibration spectra were registered on a InfraLUM FT-02 spectrophotometer from mulls in minerale oil.

Crystals of **VIa**, $C_{24}H_{25}NO_7$, molecular weight 439.45, monoclinic. At 23°C, a = 10.7921(4), b = 11.8349(4), c = 18.5705(6) Å, β = 103.705(1)°, V = 2304.4(1) Å^3, d_{calc} = 1.267 g cm^{-3} , Z = 4, space group $P2_1/n$. Unit cell parameters and intensities of 17484 independent reflexes (R_{int} = 0.0306) of which 3910 have $I \geq 2\sigma$ were measured at temperature 23°C on an automatic four-circle diffractometer Bruker Kappa Apex II equipped with a flat CCD detector (CuK_α, graphite monochromator, l 1.54178 Å, ω/2θ-scanning, measurement range: $-12 \leq h \leq 12$, $-14 \leq k \leq 13$, $-19 \leq l \leq 22$, 4.35° ≤ θ ≤ 69.99°). Extinction was accounted for semiempiricaly using SADABS program [5] (μCu 7.77 cm^{-1}).

Crystals of **VIb**, $C_{24}H_{25}NO_7$, molecular weight 439.45, monoclinic. At 23°C, a = 12.250(2), b = 18.151(4), c = 10.543(2) Å, β = 106.889(2)°, V = 2243.1(8) Å^3, d_{calc} = 1.301 g cm^{-3}, Z = 4, spatial group $P2_1/c$. Unit cell parameters and intensities of 31031 reflexes of which 4144 were independent (R_{int}= 0.0199], of which 3489 have $I \geq 2\sigma$, were measured at 23°C on an automatic diffractometer Bruker Smart Apex II with flat CCD detector (MoK_α, graphite monochromator, l 0.71073 Å, ω-scanning, measuring range: $-15 \leq h \leq 15$, $-22 \leq k \leq 22$, $-12 \leq l \leq 13$, 2.07° ≤ θ ≤ 26.00°). Extinction was accounted for semi-empirically with SADABS program [5] (μMo 0.96 cm^{-1}).

Stuctures **VIa** and **VIb** were solved by the direct method and refined by the least-squares method, initially isotropically and then in anisotropic approximation (for all non-hydrogen atoms) with the programs SHELXTL [6] and WinGX [7]. Coordinates of hydrogen atoms are calculated on the basis of stereochemical criteria and then refined using *rider* models.

Final values of divergence factors R = 0.0418, R_w = 0.1052, on 3910 independent reflexes with $F^2 \geq 4\sigma$, Goodness-of-fit equals to 1.045, number of refined parameters is 293 in **VIa**; R = 0.0937, R_W = 0.2321 on 3489 independent reflexes with $F^2 \geq 4\sigma$, Goodness-of-fit equals to 1.029, number of refined parameters is 292 in the structure **VIb**. Data acquisition, processing and refinement of parameters of unit cells are carried out using APEX2 program [8]. Analyses of intermolecular interactions and images of the molecules are obtained using PLATON program [9]. Atomic coordinates of the structures and their temperature parameters are deposited in the Cambridge Crystallographical Database (http://www.ccdc.cam.ac.uk; deposite nos. CCDC 691926 and 691927, respectively).

Syntheses of 3-methoxycarbonyl-4-phenyl-2-pyrrolidone **I** and 2-aryl(heteryl)-1,1-dimethoxycarbonylethenes **II–V** were carried out along the procedures in [10] and [11, 12], respectively.

1-(2,2-Dimethoxycarbonyl-1-phenylethyl)-3-methoxycarbonyl-4-phenyl-2-pyrrolidones (VIa, VIb). To a solution prepared from 11 ml of methanol, 0.41 g (0.018 mol) of sodium was added 3.94 g (0.018 mol) of 3-methoxycarbonyl-4-phenyl-2-pyrrolidone (**I**) in 10 ml of methanol and then at stirring was added a suspension of 2.64 g (0.012 mol) of 1,1-dimethoxycarbonyl-2-phenylethene (**II**) in 18 ml of methanol. The reaction mixture was stirred for 5 h at 20ºC and then it was poured on crushed ice containing concentrated hydrochloric or glacial acetic acid in an amount equal to the used sodium. The precipitate formed was filtered off and dried in air. 4.74 g (70%) of compound **VI** was obtained. By fractional crystallization from aqueous methanol (2:1) were isolated isomers **VIa** and **VIb**. Yield of **VIa** 2.00 g (38 %), mp 138–140°C. Found, %: C 65.32, H 5.89, N 3.25. $C_{24}H_{25}NO_7$. Calculated, %: C 65.60, H 5.70, N 3.19. Yield of **VIb** 1.16 g (22 %), mp 114–116°C. Found, %: C 65.67, H 5.71, N 3.13. $C_{24}H_{25}NO_7$. Calculated, %: C 65.60, H 5.70, N 3.19.

Compounds **VIIa–IXa** and **VIIb–IXb** were prepared by the same procedure.

1-[2,2-Dimethoxycarbonyl-1-(4'-nitrophenyl)-ethyl]-3-methoxycarbonyl-4-phenyl-2-pyrrolidones (VIIa, VIIb). Total yield 92%. Yield of **VIIa** 42 %, mp 118–120°C. Found, %: C 59.50, H 4.99, N 5.78. $C_{24}H_{24}N_2O_9$. Calculated, %: C 59.43, H 5.02, N 5.76. Yield of **VIIb** 35%, mp 147–149°C. Found, %: C 59.48, H 4.98, N 5.77. $C_{24}H_{24}N_2O_9$. Calculated, %: C 59.43, H 5.02, N 5.76.

1-[2,2-Dimethoxycarbonyl-1-(4'-chlorophenyl)-ethyl]-3-methoxycarbonyl-4-phenyl-2-pyrrolidones (VIIIa, VIIIb). Total yield 43%. Yield of **VIIIa** 28%, mp 134–135°C. Found, %: C 60.82, H 5.11, N 2.97. $C_{24}H_{24}NO_7Cl$. Calculated, %: C 60.82, H 5.07, N 2.96. Yield of **VIIIb** 11 %, mp 120–122°C. Found, %: C 60.83, H 5.10, N 2.96. $C_{24}H_{24}NO_7Cl$. Calculated, %: C 60.82, H 5.07, N 2.96.

1-[2,2-Dimethoxycarbonyl-1-(pyridyl-3')ethyl]-3-methoxycarbonyl-4-phenyl-2-pyrrolidones (IXa,

IXb). Total yield 82 %. Yield of **IXa** 27 %, mp 110–112°C. Found, %: C 62.00, H 5.35, N 6.48. $C_{23}H_{24}N_2O_7$. Calculated, %: C 62.73, H 5.45, N 6.36. Yield of **IXb** 37 %, mp 127–129^{0}C. Found, %: C 62.01, H 5.33, N 6.48. $C_{23}H_{24}N_2O_7$. Calculated, %: C 62.73, H 5.45, N 6.36.

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