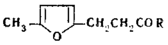
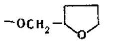
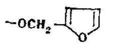
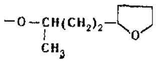
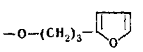
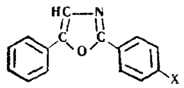
Esters of the Furan Series 

R	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Empirical formula	Found, %		Calculated, %		Yield, %
				found	calculated		C	H	C	H	
	145—146 (3)	1.4850	1.1025	61.93	61.84	$C_{13}H_{18}O_4$	65.59 65.84	7.84 7.67	65.52	7.61	66
	124—124.5 (3)	1.5018	1.1385	60.69	60.90	$C_{13}H_{14}O_4$	67.02 66.91	6.13 6.13	66.65	6.02	73
	182 (7)	1.4761	1.0470	75.55	75.69	$C_{16}H_{24}O_4$	68.66 68.58	8.96 9.00	68.54	8.63	70
	139—140 (3)	1.4915	1.0958	71.89	71.67	$C_{15}H_{18}O_4$	68.86 68.67	7.11 7.19	68.68	6.92	68
$-OCH_2CH=CH_2$	103—104 (7)	1.4780	1.0397	52.87	52.69	$C_{11}H_{14}O_3$	68.12 68.19	7.31 7.42	68.02	7.27	79



EXPERIMENTAL

The furan esters obtained by the method described [1, 2] are colorless or pale yellow liquids with a characteristic odor. Their physical constants and analytical results are given in the table.

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24 November 1966

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DIPOLE MOMENTS AND STRUCTURE OF THE MOLECULES OF SOME OXAZOLE DERIVATIVES

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UDC 547.787:541.67

The values of the dipole moments of 15 substituted, 1, 3-oxazoles are given. The electron density distribution in the molecules of 2, 5-, 2, 4-, and 4, 5-diphenyl-1, 3-oxazoles has been calculated by the LCAO MO method. Their heterocycle does not contain a single π-electron system with the participation in conjugation of the π-electrons of the C=N and C=C bonds and the p-electron pair of the oxygen. A vector calculation permits the detection of a considerable conjugation between substituents and the π-electrons of the heterocycle through phenyl.

An analysis of various properties of the molecules of phenyl-substituted isoxazoles has led to the conclusion that the aromaticity of the isoxazole ring is low and its interaction with the π-electron system of the phenyl rings is very weak [1]. It was desirable to confirm this for phenyl-substituted 1, 3-oxazoles. Table 1 gives the results of measurements of the dipole moments (μ) of a number of substituted 1, 3-oxazoles in benzene as solvent. For some of them (2, 5-, 2, 4-, and 4, 5-diphenyloxazoles) the molecular diagrams and π moments (μ_π) have been calculated by the LCAO MO method in Hückel's approximation; for the compounds with para substituents in the phenyl rings, the observed moment has been compared with that calculated by simple vector combination of the moments of the individual functional groups of the molecule. Calculation of the electron density distribution by the MO method was carried out using Orgel's parameters [3], namely: $\alpha_{(-N=)} = \alpha_C + \beta$; $\alpha_{(-O)} = \alpha_C + 3.2\beta$; $\beta_{(C-O)} = 1,4\beta$; $\beta_{(C-N)} = 1,2\beta$; $\beta_{(N-N)} = \beta$. The inductive influence of the heteroatoms on the carbon atom connected to them was taken into account by

Table 1

Dipole Moments of Oxazoles

Compound	α	β	$P_{2\infty}$	P_{E+A}	$P_{expt.}$	$\mu_{obs.}$ D	$\mu_{calc.}$ D	$\Delta\mu=\mu_{obs.}-\mu_{calc.}$
2,5-Diphenyl-1,3-oxazole	4.35	0.404	123.32	71.38	51.96	1.55	—	—
2,4-Diphenyl-1,3-oxazole	3.41	0.644	105.90	71.38	34.52	1.29	—	—
4,5-Diphenyl-1,3-oxazole	5.95	0.688	141.92	71.38	70.54	1.85	—	—
5-Biphenylyl-1-phenyl-1,3-oxazole	6.53	0.713	175.58	96.94	78.64	1.95	1.84	+0.11
2-Biphenylyl-5-phenyl-1,3-oxazole	5.25	0.819	153.49	96.94	56.55	1.65	1.70	−0.05
2-p-methoxyphenyl-5-phenyl-1,3-oxazole	5.86	0.573	154.29	71.95	76.34	1.92	2.12	−0.20
2-p-Nitrophenyl-5-phenyl-1,3-oxazole	37.70	1.080	616.46	76.80	539.66	5.11	4.62	+0.49
5-p-Nitrophenyl-2-phenyl-1,3-oxazole	18.56	0.832	344.26	76.80	267.46	3.56	2.99	+0.57
2-p-Bromophenyl-5-phenyl-1,3-oxazole	4.57	0.593	152.29	79.54	72.75	1.87	2.41	−0.54
2-p-Methoxyphenyl-5-p-nitrophenyl-1,3-oxazole	36.53	1.300	602.79	83.37	519.42	4.96	—	—
2-Bromomethyl-5-phenyl-1,3-oxazole	10.86	1.060	208.06	57.92	150.14	2.68	—	—
2-α-Bromoethyl-5-phenyl-1,3-oxazole	9.34	1.003	194.78	62.77	132.01	2.52	—	—
4-Iodo-2,5-diphenyl-1,3-oxazole	8.60	1.803	186.78	84.60	102.18	2.22	—	—
4-Bromo-2,5-diphenyl-1,3-oxazole	7.43	1.083	178.49	79.54	98.95	2.15	—	—
5-Iodo-2,4-diphenyl-1,3-oxazole	4.02	1.610	126.32	84.60	41.72	1.42	—	—

Table 2

Total Charges and Moments of the Diphenyloxazoles

Position of the substituents in 1,3-diphenyl-oxazole	Total charges on the			μ_{π}, D	μ_{σ}, D	μ_{total}, D	μ_{obs}, D
	hetero-cycle	phenyl in position 2(4)	phenyl in position 5(4)				
-2.5	−0.0280	0.0320	−0.0039	3.36	0.94	1.35	1.55
-2.4	−0.0303	0.0331	−0.0021	3.63 φ=0°	0.79 φ=133°	1.69	1.29
-4.5	0.0055	−0.0023	−0.0028	3.32 φ=8°	0.64 φ=133°	1.43	1.85

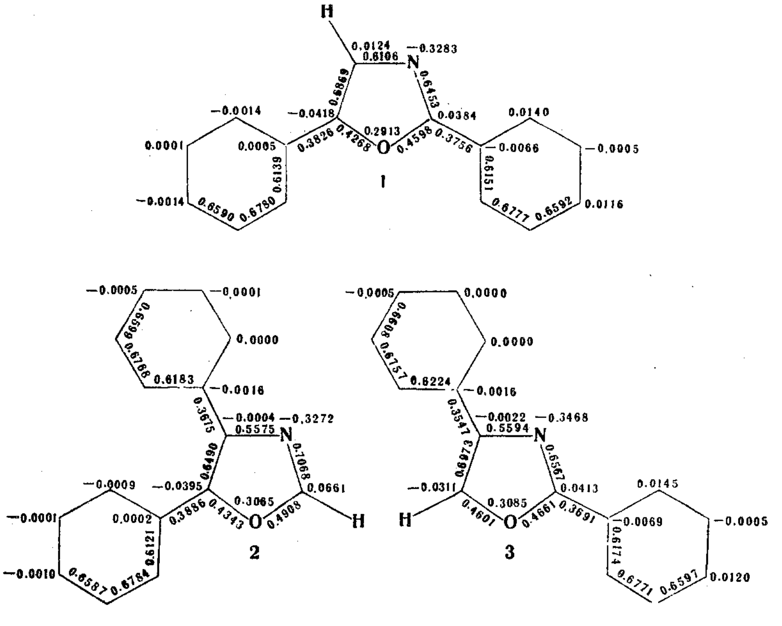


Fig. 1. Molecular diagrams of the diphenyloxazoles: 1) 2,5-diphenyl-1,3-oxazole; 2) 4,5-diphenyl-1,3-oxazole; 3) 2,4-diphenyl-1,3-oxazole.

the auxiliary induction parameter $\delta_X = 0.1\ \Sigma\ (\alpha_X - \alpha_C)$. The molecular diagrams obtained are given in Fig. 1,

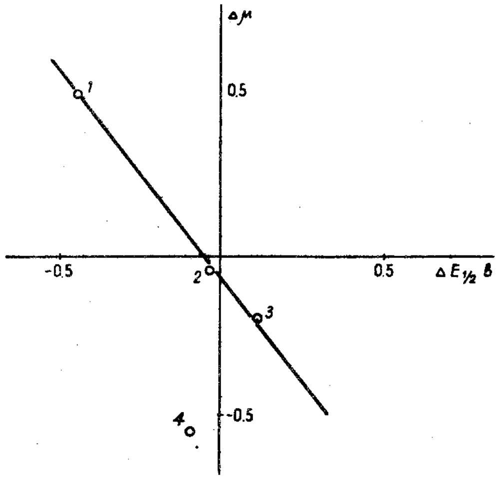
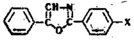


Fig. 2. $\Delta\mu$ as a function $\Delta E_{1/2}$ for compounds of type  with X = 1) NO_2; 2) C_6H_5; 3) OCH_3; 4) Br.

and the values of the total charges on the phenyl rings and the heterocycle, μ_π, μ_σ, and μ_{total}, equal to the vector sum of μ_σ and $\mu_\pi/1.6$ [3] are given in Table 2.

As can be seen, the introduction of phenyl groups into the oxazole molecule causes a considerable change in the charge distribution on the various atoms of the heterocycle (Fig. 1). As compared with unsubstituted oxazoles [3], for which the electron density distribution has been calculated by means of the same parameters of the Coulomb and resonance integrals, particularly for the 2,4-diphenyl derivative, a negative charge arises on the nitrogen and the positive charge on the oxygen falls somewhat.

The excess charge (total over all the atoms) of the heterocycle in the case of 2,4- and 2,5-diphenyloxazoles proves to be negative with a considerable absolute value, while in the case of 4,5-diphenyloxazole, conversely, it is positive and extremely small. It is evident that in the first two the heterocycle is an electron acceptor with respect to the phenyl groups. At the same time, in their electronic effect the phenyl groups differ considerably according to whether they are connected with the carbon atoms of the C═N or C═C bonds of the heterocycle. The former exhibit a considerable positive total charge and the latter an extremely negative total charge. Apparently, phenyl groups attached to the carbon atom of a C═N bond react appreciably, and phenyl groups attached to a C═C bond react extremely feebly, with the π-electrons of the heterocycle. In neither case does the effect of one of the phenyl groups extend over all the atoms of the heterocycle and through the heterocycle to the atoms of the other phenyl group but it is limited to the atoms adjacent to the atoms of the corresponding carbon atom (mainly the nitrogen in the case where the phenyl groups are attached to C═N and C—N bonds or carbon in the case of the C═C bond). This means that in the oxazoles considered, as in the isoxazoles and oxadiazoles [2], the heterocycle does not contain a single π-system with the participation in conjugation of the π-electrons of the C═N and C═C bonds and the pair of p-electrons of the oxygen.

The values of μ_{total} calculated from the charges on the atoms at μ_σ are fairly close to the observed figures (Table 2). The deviation does not exceed ±0.4 D and is only slightly higher than 1,3-oxazole itself [3]. As in the case of the diphenyloxadiazoles [2], because of the existence of a steric effect, 4,5-diphenyl-1,3-oxazole exhibits the greatest deviation of μ_{total} from μ_{obs}.

The observed dipole moment of the isoxazole molecule is almost twice that of the oxazole molecule [3]. Apparently, the resultant moment of the molecules of these compounds is determined mainly, as in the case of the oxadiazole [2] by the value and direction of the

C=N and C—O—C (in the oxazoles) or C—O—N (in the isoxazoles) group moments. In oxazole, the moments of these groups have opposite directions and in isoxazole they are in the same direction. If a moment of 2.47 D is assumed for the C=N bond [2] and moments of 0.8, 0.45, 0.5, and 0.4 D, respectively, for the C—O, C—N, N—O, and C—H bonds, then for oxazole and isoxazole by vector addition we obtain, respectively, 1.35 and 3.90 as compared with the observed values of 1.4 and 2.8 D.

The moment of 2,5-diphenyl-1,3-oxazole was calculated vectorially from the moments of the $\mu_{\overrightarrow{C=N}}$, $\mu_{\overrightarrow{C-O}}$, $\mu_{\overleftarrow{C-H}}$, $\mu_{C_{ar-2}\overleftarrow{-}C_{het}}$ and $\mu_{C_{ar-5}\overrightarrow{-}C_{het}}$, bonds equal, respectively, to 2.47, 0.8, 0.4, 0.4, and 0.4 D; the angles between all the bonds in the heterocycle were taken as the same and equal to the angle in a regular pentagon. The calculated moment proved to be 1.29 D (as compared with the observed 1.55 D) with an angle of inclination of the vector of this moment to the nominal axis of symmetry of the molecule passing through the oxygen atom and the center of the C_4—N bond of 32°. The calculated values of the moments of the derivatives with para substituents in the phenyl group are given in Table 1. In the calculation, values of the moments of substituted benzenes C_6H_5X with $X = NO_2$, C_6H_5, Br, and OCH_3 equal, respectively, to 4.00, 0.4, 1.52, and 1.31 D were used and the angle of inclination at $X = OCH_3$ was taken as 67°. As can be seen from Fig. 2, the values of $\Delta\mu = \mu_{obs} - \mu_{calc}$ correlate satisfactorily, except for X = Br, with $\Delta E_{1/2}$ — the increase in the polarographic reduction potential of a nitro or carbonyl group under the influence of X [4, 5], which shows the existence of appreciable conjugation between the electrons of the substituent X through the phenyl group with the π-electrons of the heterocycle.

The authors express their thanks to Yu. A. Kruglyak for cooperation and help in carrying out the calculations on the EVM-20 computer in the Institute of Cybernetics of the Academy of Sciences of the Ukrainian SSR.

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3 January 1967 Lenin Khar'kov Polytechnic Institute

THIONYLAMIDES AND THIONYLAMIDINES OF CARBOXYLIC ACID

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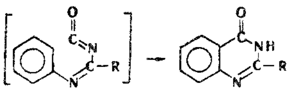
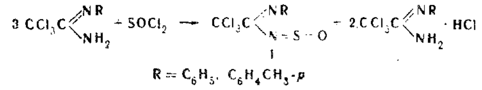
Amidines of carboxylic acids react with thionyl chloride to form thionylamidines which are converted spontaneously into 2H-1,2,4-benzothiadiazine 1-oxides. Carbimidic esters react with thionyl chloride to give thionylamides as final products.

In preceding communications [1, 2] we have shown that isocyanates of carbimidic acids are converted into 4-quinazolones at the moment of their formation.



It was of interest to study the properties of the thionylamidines, the sulfur analogs of the isocyanates of carbimidic acids. The thionylamidines were obtained with quantitative yields by the reaction of amidines of carboxylic acid with thionyl chloride in carbon tetrachloride at 50° C.



I

$R = C_6H_5, C_6H_4CH_3\text{-}p$

Compounds I consist of orange-colored crystalline substances with low melting points, readily soluble in organic solvents and readily hydrolyzed by atmospheric moisture to the initial amidines. The IR absorption spectra of compounds I have a strong band in the 1260 cm^{-1} region which is ascribed to the —N=S=O group [3, 4]. On being stored in a closed vessel at room temperature, compound I ($R = C_6H_5$) is converted spontaneously after 2–4 days into 2H-1,2,4-benzothiadiazine-1-oxide (cf. [5, 6]).