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X-RAY CRYSTALLOGRAPHIC INVESTIGATION OF 2-N-PHENYLIMINO-3-PHENYL-5-PHENOXYMETHYL-1,3-OXAZOLIDINE

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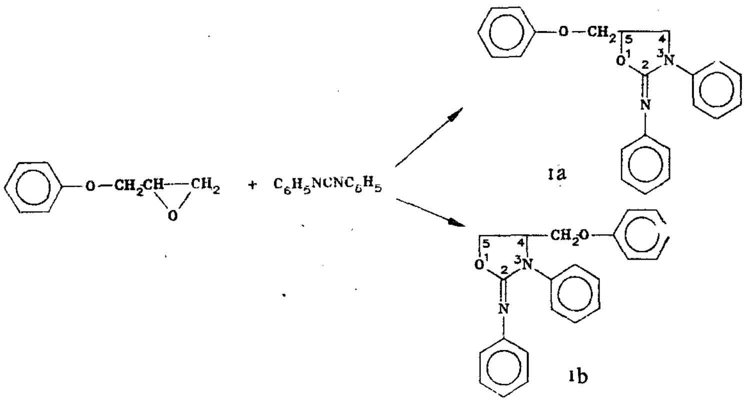
Earlier [1] substituted 2-N-phenyliminooxazolidine (I) was synthesized by the reaction of diphenylcarbodiimide with phenylglycidyl ether. On the basis of the data of elementary analysis, the IR, PMR, and mass spectra, hydrolysis of the reaction product, which led to 2-oxazolidinone, and countersynthesis of the latter, the structure (Ia) with phenyl and phenoxymethyl substituents in the 3- and 5-positions, respectively, was proposed for compound I. However, these data did not exclude the possibility of the formation of the isomeric 3-phenyl-4-phenoxymethyl-2-N-phenylaminooxazolidine (Ib) in this reaction was well:



An x-ray crystallographic investigation that we conducted for an unambiguous establishment of the structure of compound I and analogous heterocyclic fragments of thermostable polymers confirmed the proposed structure of the compound as Ia.

The central oxazolidine ring is noncopolanar. The parameters of folding q_2 = 0.333 Å and φ_2 = 351.4°, calculated by the Kramer—Pople method [2], characterized its conformation as intermediate between an envelope and a half-chair. The $C_{(5)}$ and $C_{(4)}$ atoms emerge —0.274 and 0.109 Å on different sides of the P_1 plane of the other three atoms of the heterocycle (Table 1).

The length of the $C_{(4)}$—$C_{(5)}$ bond 1.525 (6) Å is close to the standard length of the single bond $C(sp^3)$-$C(sp^3)$ 1.537 Å [3]. The $C_{(5)}$-$O_{(1)}$ bond 1.448 (4) Å is slightly lengthened, while the $C_{(4)}$-$N_{(3)}$ bond 1.447 (5) Å is appreciably shortened in comparison with the corresponding standard bond lengths $C(sp^3)$-O 1.426 Å and $C(sp^3)$-N 1.472 Å [3]. On the whole, the distribution of the bond lengths in the oxazolidine ring of compound I corresponds to that observed in the related 3,5-substituted oxazolidinones [4-6], with the exception of a small lengthening of the $C_{(2)}$-$O_{(1)}$ bond to 1.377 (5) Å in comparison with 1.350 Å (average for nine derivatives of 3,5-oxazolidinone [4-6]) and 1.356 Å (in unsubstituted 2-oxazolidinone [7]). The endocyclic valence angles in the heterocycle I agree with those observed in oxazolidinone analogs [4-6]. A comparison of the geometry of the rings in compound I and the above-mentioned analogs and derivatives of oxazolidine, all the carbon atoms of the ring of which are sp^3-hy-

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TABLE 1. Coefficients of the Equations $A_x + B_y + C_z = D$ of Coplanar Fragments and Deviations (Δ) of the Atoms from Them

Plane	A	B	C	D	Δ
P_1	−0,7637	0,2184	−0,6074	−24,82	$O_{(1)}$ 0; $C_{(2)}$ 0; $N_{(3)}$ 0; $C_{(4)}$ 0,109; $C_{(5)}$ −0,274; $N_{(6)}$* 0,014; $C_{(21)}$* −0,296
P_2	0,1287	0,9168	−0,3779	2,9559	$C_{(7)}$ −0,006; $C_{(8)}$ 0,001; $C_{(9)}$ 0,006; $C_{(10)}$ −0,007; $C_{(11)}$ 0; $C_{(12)}$ 0,006; $N_{(6)}$* −0,151
P_3	−0,6426	−0,4015	−0,6526	−22,20	$C_{(21)}$ 0,002; $C_{(22)}$ −0,011; $C_{(23)}$ 0,011; $C_{(24)}$ −0,003; $C_{(25)}$ −0,006; $C_{(26)}$ −0,006; $N_{(3)}$* −0,027
P_4	0,5079	−0,2359	−0,8285	12,7017	$C_{(15)}$ −0,006; $C_{(16)}$ 0,012; $C_{(17)}$ −0,004; $C_{(18)}$ −0,014; $C_{(19)}$ 0,016; $C_{(20)}$ −0,004; $O_{(14)}$* −0,063
P_5	0,4100	−0,4099	0,8148	9,1643	$C_{(13)}$ 0; $O_{(14)}$ 0; $C_{(15)}$ 0
P_6	−0,8435	0,0969	−0,5283	−27,17	$C_{(2)}$ 0; $C_{(4)}$ 0; $C_{(21)}$ 0; $N_{(3)}$* 0,077

Two-faced angles between planes: P_1/P_2 70.6°; P_1/P_3 36.9°; P_1/P_4 86.3°; P_4/P_5 11.5°.

*Atoms not included in the calculation of the equations of the plane.

bridized [8, 9], reveals a substantial shortening in the first bonds with the participation of the sp^2-hybridized $C_{(2)}$ atom, as well as an increase in the endocyclic angle at it by 4-6°, just as should have been expected. At the same time, in oxazolidine derivatives the corresponding bond lengths are close to the standards for $C(sp^3)-O$ and $C(sp^3)-N$, while the OCN angles are 102.4-105.4°.

The conformation of the $N_{(3)}$ atom of the heterocycle is close to planotrigonal: The sum of the bond angles at it is 359.1°, the deviation of $N_{(3)}$ from the plane of the three neighboring atoms is 0.077 Å. The shortening of the $N_{(3)}-C_{(21)}$ bond to 1.402 (5) Å in comparison with the standard $N-C_{arom}$ bond length 1.43 Å [3] is evidently due to a certain interaction of the unshared pair of the $N_{(3)}$ atom with the π-system of the phenyl ring A (Fig. 1), despite the rather substantial rotation (36.9°) of the latter relative to the plane P_1 of the heterocycle. Stronger p-π interaction (coplanarity of the heterocycle and the A ring) is evidently prevented by steric repulsion between the $N_{(6)}$ and $C_{(26)}$ atoms (the distance $N_{(6)} \ldots C_{(26)}$ 3.018 (5) Å is shortened in comparison with the sum of the van der Waals radii of C and N, 3.20 Å [10]). Probably these same steric factors are responsible for the increase in the angles $N_{(6)}C_{(2)}N_{(3)}$ to 126.4 (4)°, $C_{(2)}N_{(3)}C_{(21)}$ to 126.7 (3)° and $N_{(3)}C_{(21)}C_{(26)}$ in comparison with the adjacent exocyclic angles [123.7 (4), 122.8 (3) and 118.4 (4)°, respectively].

A definite analogy in the structure is traced in a comparison of oxazolidine I with phenyliminothiazolidines [11]. The lengths of the endo- and exocyclic bonds $C_{(2)}-N_{(3)}$ 1.378 (5) Å and $C_{(2)}=N_{(6)}$ 1.272 (5) Å, differ substantially (the latter is close to the length of the purely double bond C=N 1.255 Å [12]) and are in good agreement with average values 1.368 and 1.267 Å of the corresponding bond lengths in imino-tautomers of thiazolidines [11]. In these cases the endocyclic angles at $C_{(2)}$ actually coincide: 109.9 (3)° in compound I with the average values (110.1°) in the indicated tautomers [11].

The phenyl ring B (Fig. 1) has a cisoid arrangement relative to the $O_{(1)}$ atom of the heterocycle (Z-isomer). The appreciable twisting of the double bond (torsion angle $O_{(1)}C_{(2)}N_{(6)}-C_{(7)}$ 7.9°; Table 2) can be explained by steric hindrances. The twisting of the $C_{(2)}=N_{(6)}$ bonds, as well as the substantial rotation of the B ring (its plane P_2, two-faced angle P_1/P_2 70.6°), increase the $O_{(1)} \ldots C_{(8)}$ distance to the normal van der Waals 3.095 (5) Å. In this case there is virtually no conjugation possible between the phenyl ring B and the unshared pair of the $N_{(6)}$ atom, which is indicated by the bond length $C_{(7)}-N_{(6)}$, close to the length of the single bond $C_{arom}-N$, 1.43 Å.

The $O_{(14)}$ atom is situated synclinally with respect to the $O_{(1)}$ and $C_{(4)}$ atoms of the heterocycle (torsion angles relative to the $C_{(5)}-C_{(13)}$ bond are −55.7 and 59.9°) and is at a distance from them of 2.698 (4) and 2.878 (5) Å, respectively, which are close to the normal van der Waals values of 2.8 and 3.1 Å [10]; however, they remain somewhat shorter. Similar information is frequently encountered in 5-phenoxymethyl-substituted oxazolidinones [4-6]. In this case it explains the fact that compound I does not isomerize to the corresponding imidazolidone [1], although such isomerization is characteristic of unsubstituted and 5-phenyl-substituted 2-N-phenyliminooxazolidines in which the $O_{(1)}$ atoms is sterically unshielded [13].

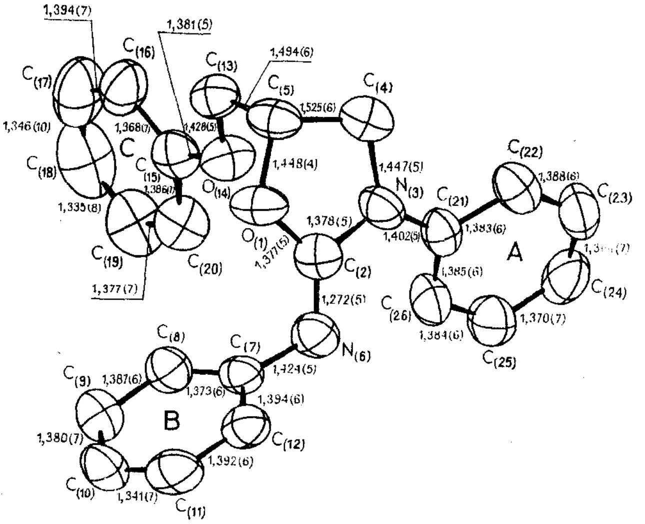

Fig. 1. Bond lengths in the 2-N-phenylimino-3-phenyl-5-phenyloxymethyl-1,3-oxazolidine molecule.

TABLE 2. Torsional Angles τ in Compound Ia

Angle	τ, deg	Angle	τ, deg
$O_{(1)}C_{(5)}C_{(4)}N_{(3)}$	23,2 (4)	$O_{(1)}C_{(5)}C_{(13)}O_{(14)}$	−55,7 (4)
$C_{(5)}C_{(4)}N_{(3)}C_{(2)}$	−17,5 (4)	$O_{(1)}C_{(2)}N_{(6)}C_{(7)}$	7,9 (4)
$C_{(4)}N_{(3)}C_{(2)}O_{(1)}$	4,6 (4)	$N_{(3)}C_{(2)}N_{(6)}C_{(7)}$	−173,0 (6)
$N_{(3)}C_{(2)}O_{(1)}C_{(5)}$	11,5 (4)	$C_{(5)}C_{(13)}O_{(14)}C_{(15)}$	−175,3 (5)
$C_{(2)}O_{(1)}C_{(5)}C_{(4)}$	−21,7 (4)	$C_{(13)}O_{(14)}C_{(15)}C_{(16)}$	11,9 (5)
$C_{(4)}C_{(5)}C_{(13)}C_{(14)}$	59,9 (4)	$C_{(13)}O_{(14)}C_{(15)}C_{(20)}$	−169,8 (5)

Steric factors induce some distortions of the phenoxymethyl fragment, normal for $ROCH_2$-substituted aromatic compounds [14]. These distortions consist of an inequality of the exocyclic angles $O_{(14)}C_{(15)}C_{(16)}$ 124.8 (4) and $O_{(14)}C_{(15)}C_{(20)}$ 114.5 (4) at the ipso-atom $C_{(15)}$ and rotation of the methylenoxy group around the $O_{(14)}$—$C_{(15)}$ bond through an angle of 11.5° and are explained by repulsion of the CH_2 group from the closest H atom of the phenyl ring.

The shortening of the C—C bond lengths in all three benzene rings [average values for the A, B, and C rings 1.379 (7), 1.378 (7) and 1.368 (8) Å, respectively] in comparison with the standard value 1.397 Å [3] is due to the substantial thermal vibrations of these rings. In this case the values of the valence angles in the phenyl rings remain as usual: the average value for each ring is 120.0 (4)°.

The crystal is constructed from discrete molecules, and no shortened intermolecular contacts are detected.

EXPERIMENTAL

Crystals of substance I, produced by evaporation from solution in isopropanol, are rhombic, a = 36.535(3), b = 10.2431(7), c = 9.7945(3) Å, M = 344, d_{calc} = 1.25 g/cm³, Z = 8. $C_{22}H_{20}N_2O_2$, space group Pbca.

The parameters of the unit cell and the intensities of 2155 independent reflections were measured at room temperature (20 ± 2°C) on a Hilger-Watts four-circle automatic diffractometer (λCuK_{α}, graphite monochromator, $\theta \leq 68°$, $\theta/2\theta$-scan). In subsequent calculations we used 1679 reflections with $F^2 > 2.2\sigma$.

The structure was delineated by a direct method according to the MULTAN program and refined by the method of least squares in a block-diagonal approximation, first isotropically to R = 0.151 and then anisotropically to R = 0.100. Then all the hydrogen atoms were detected in the differential series and included in a refinement with fixed B_{iso} = 5 Å². The final value of the discrepancy factor R = 0.057 (R_W = 0.061). All the calculations were performed on an Eclipse S-200 computer according to the INEXTL programs [15]. The coordinates of the nonhydrogen atoms and their temperature factors are cited in Table 3, the coordinates of the

TABLE 3. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Equivalent Isotropic Temperature Factors $B_{iso}^{equiv} = 1/3\Sigma_i\Sigma_j B_{ij} a^*_i a^*_j (\vec{a}_i\vec{a}_j)$ of Compound Ia

Atom	x	y	z	B_{iso}^{eq} (Å^2)
$O_{(1)}$	8601 (1)	1823 (2)	2078 (3)	4,75 (8)
$C_{(2)}$	8395 (1)	859 (4)	2685 (4)	4,3 (1)
$N_{(3)}$	8203 (1)	1370 (3)	3774 (3)	4,58 (9)
$C_{(4)}$	8262 (1)	2766 (4)	3841 (4)	4,5 (1)
$C_{(5)}$	8602 (1)	2956 (4)	2961 (4)	4,4 (1)
$N_{(6)}$	8385 (1)	−316 (3)	2266 (4)	4,8 (1)
$C_{(7)}$	8633 (1)	−699 (4)	1220 (4)	3,9 (1)
$C_{(8)}$	9002 (1)	−777 (4)	1474 (4)	4,6 (1)
$C_{(9)}$	9236 (1)	−1278 (5)	489 (5)	5,4 (1)
$C_{(10)}$	9096 (1)	−1706 (5)	−740 (5)	5,8 (1)
$C_{(11)}$	8736 (1)	−1620 (5)	−999 (4)	5,6 (1)
$C_{(12)}$	8495 (1)	−1113 (4)	−35 (4)	4,6 (1)
$C_{(13)}$	8953 (1)	3001 (4)	3741 (4)	4,6 (1)
$O_{(14)}$	8982 (1)	1781 (3)	4438 (3)	5,03 (8)
$C_{(15)}$	9298 (1)	1531 (4)	5163 (4)	4,6 (1)
$C_{(16)}$	9560 (1)	2441 (5)	5467 (5)	6,0 (1)
$C_{(17)}$	9854 (1)	2041 (7)	6274 (6)	8,0 (2)
$C_{(18)}$	9887 (2)	806 (7)	6728 (5)	8,4 (2)
$C_{(19)}$	9635 (2)	−79 (6)	6382 (5)	7,0 (2)
$C_{(20)}$	9332 (1)	255 (5)	5617 (5)	5,5 (1)
$C_{(21)}$	8030 (1)	665 (4)	4817 (4)	4,2 (1)
$C_{(22)}$	7744 (1)	1251 (5)	5510 (4)	5,1 (1)
$C_{(23)}$	7568 (1)	584 (5)	6553 (5)	5,9 (2)
$C_{(24)}$	7683 (1)	−630 (5)	6932 (5)	6,2 (2)
$C_{(25)}$	7969 (1)	−1214 (5)	6264 (5)	5,5 (1)
$C_{(26)}$	8142 (1)	−574 (4)	5199 (4)	4,9 (1)

TABLE 4. Coordinates of Hydrogen Atoms ($\times 10^3$) of Compound Ia

Atom	x	y	z
$H_{(4A)}$	833 (1)	304 (3)	476 (3)
$H_{(4B)}$	807 (1)	322 (3)	349 (3)
$H_{(5)}$	857 (1)	369 (3)	245 (4)
$H_{(8)}$	89 (1)	486 (3)	261 (4)
$H_{(9)}$	949 (1)	−136 (3)	66 (3)
$H_{(10)}$	925 (1)	−203 (3)	−125 (3)
$H_{(11)}$	863 (1)	−186 (3)	−171 (3)
$H_{(12)}$	825 (1)	−104 (3)	−14 (3)
$H_{(13A)}$	916 (1)	310 (3)	321 (3)
$H_{(13B)}$	895 (1)	373 (3)	437 (3)
$H_{(16)}$	954 (1)	323 (3)	515 (3)
$H_{(17)}$	999 (1)	270 (3)	641 (3)
$H_{(18)}$	1007 (1)	56 (3)	724 (3)
$H_{(19)}$	966 (1)	−98 (3)	677 (3)
$H_{(20)}$	913 (1)	−42 (3)	546 (3)
$H_{(22)}$	767 (1)	208 (3)	527 (3)
$H_{(23)}$	736 (1)	99 (3)	685 (3)
$H_{(24)}$	756 (1)	−109 (3)	754 (3)
$H_{(25)}$	806 (1)	−210 (3)	650 (3)
$H_{(26)}$	834 (1)	−91 (3)	480 (3)

TABLE 5. Bond Angles ω in Compound Ia

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$C_{(2)}O_{(1)}C_{(5)}$	108,5 (3)	$N_{(6)}C_{(7)}C_{(12)}$	119,3 (3)	$C_{(16)}C_{(17)}C_{(18)}$	122,1 (5)
$O_{(1)}C_{(2)}N_{(3)}$	109,9 (3)	$C_{(8)}C_{(7)}C_{(12)}$	119,7 (4)	$C_{(17)}C_{(18)}C_{(19)}$	119,5 (6)
$O_{(1)}C_{(2)}N_{(6)}$	123,7 (4)	$C_{(7)}C_{(8)}C_{(9)}$	120,0 (4)	$C_{(18)}C_{(19)}C_{(20)}$	121,5 (5)
$N_{(3)}C_{(2)}N_{(6)}$	126,4 (4)	$C_{(8)}C_{(9)}C_{(10)}$	119,7 (4)	$C_{(15)}C_{(20)}C_{(19)}$	118,7 (4)
$C_{(2)}N_{(3)}C_{(4)}$	109,6 (3)	$C_{(9)}C_{(10)}C_{(11)}$	120,5 (4)	$N_{(3)}C_{(21)}C_{(22)}$	118,4 (4)
$C_{(2)}N_{(3)}C_{(21)}$	126,7 (3)	$C_{(10)}C_{(11)}C_{(12)}$	121,1 (4)	$N_{(3)}C_{(21)}C_{(26)}$	122,5 (4)
$C_{(4)}N_{(3)}C_{(21)}$	122,8 (3)	$C_{(7)}C_{(12)}C_{(11)}$	118,9 (4)	$C_{(22)}C_{(21)}C_{(26)}$	119,2 (4)
$N_{(3)}C_{(4)}C_{(5)}$	102,8 (3)	$C_{(5)}C_{(13)}O_{(14)}$	106,3 (3)	$C_{(21)}C_{(22)}C_{(23)}$	119,9 (4)
$O_{(1)}C_{(5)}C_{(4)}$	103,5 (3)	$C_{(13)}O_{(14)}C_{(15)}$	118,1 (3)	$C_{(22)}C_{(23)}C_{(24)}$	120,4 (4)
$O_{(1)}C_{(5)}C_{(13)}$	109,4 (3)	$O_{(14)}C_{(15)}C_{(16)}$	124,8 (4)	$C_{(23)}C_{(24)}C_{(25)}$	120,2 (5)
$C_{(4)}C_{(5)}C_{(13)}$	114,5 (3)	$O_{(14)}C_{(15)}C_{(20)}$	114,5 (4)	$C_{(24)}C_{(25)}C_{(26)}$	120,0 (4)
$C_{(2)}N_{(6)}C_{(7)}$	118,3 (4)	$C_{(16)}C_{(15)}C_{(20)}$	120,6 (4)	$C_{(21)}C_{(26)}C_{(25)}$	120,3 (4)
$N_{(6)}C_{(7)}C_{(8)}$	120,7 (4)	$C_{(15)}C_{(16)}C_{(17)}$	117,5 (5)		

H atoms in Table 4. A general view of the molecule with bond lengths is presented in Fig. 1, and the bond angles are given in Table 5.

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HYDROGENATION OF HETEROCYCLIC COMPOUNDS USING POLYMER-CONTAINING CATALYSTS

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The hydrogenation of a series of oxygen- and nitrogen-containing compounds: furan, sylvan, benzofuran, certain dioxa-compounds, and pyridine, was investigated under mild conditions in the presence of polymer-containing catalysts based on metals of group VIII. The catalysts used were soluble complexes of Pt, Pd, and Rh with various polymers and copolymers. The greatest activity was exhibited by rhodium complexes with carboxyl-containing polymers.

Despite the increased interest of researchers in metallocomplex catalysts, there are comparatively few studies devoted to the hydrogenation of heterocyclic compounds on the indicated catalysts. The hydrogenation of heterocyclic compounds on catalysts prepared using polymer macroligands has practically not been studied.

In this work we investigated the hydrogenation of a series of oxygen- and nitrogen-containing heterocyclic compounds in the presence of catalysts prepared on the basis of complexes of metals of group VIII (Rh, Pd, Pt, and Ni) with polymer macroligands: copolymers of styrene with maleic acid (I), a copolymer of maleic acid with methyl methacrylate (II), polyacrylic acid (III), and polyvinylpyrrolidone (IV). Hydrogenation was conducted at atmospheric pressure and a temperature of 20-60°C.

Rhodium and palladium catalysts exhibited high activity and selectivity in the hydrogenation of furan compounds (Table 1). At the same time, platinum and nickel catalysts were ineffective. A platinum catalyst showed low activity in the hydrogenation of benzofuran. It is interesting to note that the activity series in the hydrogenation of benzofuran with palladium,

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