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MOLECULAR STRUCTURAL FEATURES OF UNSYMMETRICAL ORTHO ANALOGS OF POPOP

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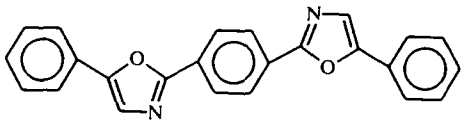
The electronic spectra and structures of sterically hindered molecules of unsymmetrical ortho-analogs of POPOP containing electron donor subsitituents in the oxadiazole part of the molecule have been studied (1-(5'-phenyloxazol-2-yl)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)benzene derivatives (I)). X-Ray structural analysis was carried out on the dimethylamino derivative of I. It was found that the conformation of the molecules of the investigated compounds is determined by the conformation of the starting 2-(5-phenyloxazol-2-yl)benzoic acid and its acid chloride used in the synthesis of the ortho POPOP analogs. In the series of unsymmetrical ortho POPOP analogs there arises a unique possibility for changes in the structure of the oxadiazole part of the molecule to affect the position of the spectral emission almost without affecting the long wavelength absorption band in the process. There were thus prepared efficient organic luminophores having an anomalously large Stokes fluorescence shift.

One of the problems in the physical chemistry of organic luminophores is the preparation of efficiently fluorescing compounds characterized by minimal overlap of absorption and emission spectra and, thus, an increased value of the Stokes fluorescence shift [1]. Its resolution must overcome a number of technical problems concerned with the decreased light output resulting from reabsorption of the emitted light and also the possible absorption by impurities or the products of photodecomposition arising from the use of organic luminophores (e.g., serving as active dye laser agents, in plastic and liquid scintillators, and as tracers and probes in medico-biological research).

From our viewpoint, a promising means of obtaining luminescence with an anomalously large Stokes shift is the use of rapid processes of structural relaxation in the excited state, characteristic for sterically hindered aromatic compounds. Among these we have investigated in this report the ortho analogs of POPOP (1,4-bis(5-phenyloxazol-2-yl)benzene).



In previous work we used x-ray structural analysis to investigate the structure of a series of ortho POPOP analogs in the crystalline state [2]. It was found that these compounds exist in a nonplanar and unsymmetrical conformation characterized by different angles between the planes of the central phenylene and the arylazole fragments in the 1,2 position. Vibrational methods (IR, Raman) [3] and ultraviolet spectroscopy together with quantum chemical calculations [4] have shown that the conformation characterizing the crystalline state is also retained in the solution state. We have also studied the spectro-luminescence properties and the dynamics of the process of structural relaxation (flattening) of the ortho POPOP analogs in the excited state.

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TABLE 1. Atomic Coordinates (Å × 10^4) and Thermal Correction Factors (Å^2 × 10^3) for the Molecule of Compound V

Atom	x	y	z	U(eq)
1	2	3	4	5
O(1)	2923(2)	1551(1)	506(1)	50(1)
O(2)	2317(2)	2149(1)	3005(1)	48(1)
N(1)	4106(3)	2583(2)	-525(2)	63(1)
N(2)	5109(2)	3198(2)	3519(2)	55(1)
N(3)	4799(2)	2170(2)	3883(2)	55(1)
N(4)	-538(3)	-2808(2)	4204(2)	63(1)
C(1)	3299(3)	4017(2)	2484(2)	47(1)
C(2)	3054(3)	5099(2)	3251(3)	58(1)
C(3)	2944(4)	6043(3)	2861(3)	69(1)
C(4)	3084(4)	5900(3)	1704(3)	69(1)
C(5)	3284(3)	4819(3)	919(3)	63(1)
C(6)	3378(3)	3849(2)	1288(2)	51(1)
C(7)	3531(3)	2692(2)	405(2)	50(1)
C(8)	3890(3)	1275(3)	-1086(2)	62(1)
C(9)	3158(3)	634(2)	-466(2)	51(1)
C(10)	2564(3)	-709(2)	-617(2)	52(1)
C(11)	1703(3)	-1062(3)	153(3)	64(1)
C(12)	1139(4)	-2342(3)	-3(3)	74(1)
C(13)	1394(4)	-3283(3)	-935(3)	77(1)
C(14)	2255(4)	-2940(3)	-1696(3)	75(1)
C(15)	2849(3)	-1661(3)	-1537(2)	64(1)
C(16)	3641(3)	3135(2)	3008(2)	44(1)
C(17)	3157(3)	1594(2)	3571(2)	44(1)
C(18)	2167(3)	483(2)	3744(2)	44(1)
C(19)	2977(3)	134(2)	4596(2)	50(1)
C(20)	2093(3)	-939(2)	4758(2)	53(1)
C(21)	351(3)	-1720(2)	4067(2)	47(1)
C(22)	-460(3)	-1354(2)	3228(2)	54(1)
C(23)	435(3)	-270(2)	3079(2)	52(1)
C(24)	-2354(4)	-3541(3)	3550(3)	73(1)
C(25)	240(4)	-3136(3)	5128(4)	77(1)
H(2)	2991(33)	5211(25)	4054(26)	70
H(3)	2827(36)	6820(28)	3463(27)	83
H(4)	3062(35)	6546(29)	1419(26)	83
H(5)	3362(34)	4686(26)	124(27)	75
H(8)	4210(3)	878(3)	-1809(2)	74
H(10)	1501(34)	-397(27)	767(27)	76
H(12)	510(38)	-2551(29)	601(28)	89
H(13)	1046(40)	-4093(32)	-1015(30)	92
H(14)	2440(37)	-3626(30)	-2355(29)	90
H(15)	3430(35)	-1477(27)	-2094(27)	77

TABLE 1 (continued)

1	2	3	4	5
$H_{(20)}$	2715(31)	-1114(23)	5366(23)	63
$H_{(22)}$	-1663(33)	-1882(24)	2721(23)	65
$H_{(23)}$	-220(30)	-47(23)	2471(23)	63
$H_{(24A)}$	-2793(45)	-4338(42)	3691(57)	88
$H_{(24B)}$	-2671(46)	-3643(54)	2671(26)	88
$H_{(24C)}$	-3009(38)	-3021(43)	3946(44)	88
$H_{(24D)}$	-2934(40)	-2923(37)	3544(54)	88
$H_{(24E)}$	-2858(44)	-4135(53)	3922(52)	88
$H_{(24F)}$	-2553(45)	-4043(48)	2614(21)	88
$H_{(25A)}$	1505(30)	-2741(58)	5415(53)	93
$H_{(25B)}$	217(84)	-2579(53)	5980(22)	93
$H_{(25C)}$	-335(68)	-4107(26)	4865(43)	93
$H_{(25D)}$	-630(47)	-3632(62)	5399(54)	93
$H_{(25E)}$	684(83)	-2357(41)	5991(21)	93
$H_{(25F)}$	1155(62)	-3429(62)	4897(44)	93

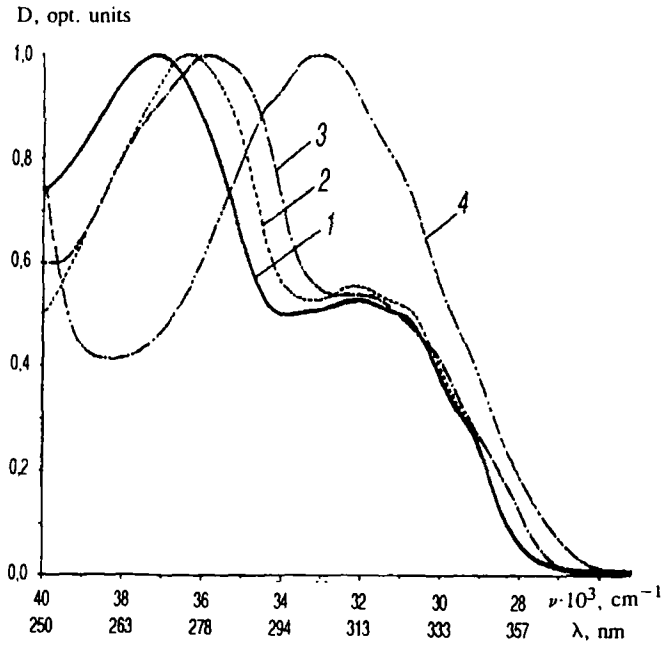


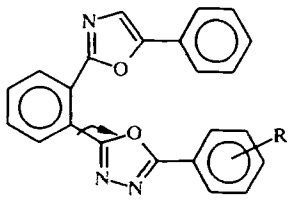
Fig. 1. Absorption spectra of some unsymmetrical ortho POPOP analogs in n-octane: 1) compound III, 2) compound VI, 3) compound IV, 4) compound V (in optical density coordinates versus wave number in thousand cm^{-1}, also given in the corresponding wave number values, nm).

One of the conclusions arising from the results obtained in [2-4] inferred the presence in the ortho POPOP molecules of two quasi planar fragments (diphenyloxazole and azolylphenyl), mutual conjugation of which in the ground state is disturbed through steric hindrance. On crossing to the excited state the conjugation in the molecules of the compounds discussed is partially restored and this results in a significant lowering of the energy of the fluorescence state and to the observation of anomalously high Stokes emission shift values (7000-9000 cm^{-1}). It is characteristic that, as in the case of several unsymmetrical ortho POPOP analogs discussed in [2-4], the diphenyloxazole fragment emerges as the quasiplanar fragment with the more extended π-conjugated system. (Here and subsequently the designation unsymmetrical ortho POPOP analogs implies different heterocycles, e.g., oxazole and oxadiazole, in contrast to symmetrical ortho POPOP analogs which contain

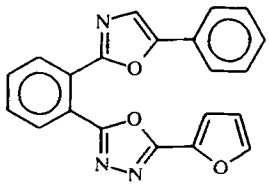
identical heterocycles). The proposed reason for this [2] is the large energetic favorability of the conjugated oxaxole ring with two neighboring benzene nuclei when compared with the analogous conjugation for the oxadiazole ring.

In order to confirm the indicated proposal a series of quantum chemical calculations were performed via the AM1 method [5] to investigate the difference in conjugation energies for the heterocycles with benzene rings added at positions 2 and 5. For the model compounds 2,5-diphenyloxazole (PPO, I) and 2,5-diphenyl-1,3,4-oxadiazole (PPD, II), their geometry was initially optimized. Both benzene rings were simultaneously moved out of the heterocyclic plane by an angle from 20-90°C, with the difference between the calculated heat of formation of the optimized and planar conformation serving as a measure of the conjugation energy. The calculations showed that the conjugation of the oxadiazole ring with the neighboring benzene rings is more energetically favored than is the oxazole ring case but the difference in calculated conjugation energies is small (up to 0.3 kCal/mole), i.e., the result as a whole conflicts with the proposal given [2] for explaining the structural features of the ortho POPOP analogs.

In our work a further attempt has been made to examine the extent of the effect of electronic factors on the structure of the molecules of the unsymmetrical ortho POPOP analogs. Hence several derivatives (III-VI) were studied with electron donor substitutents in the oxadiazole part of the molecule. The synthesis of III, VI has been reported in [2-4].



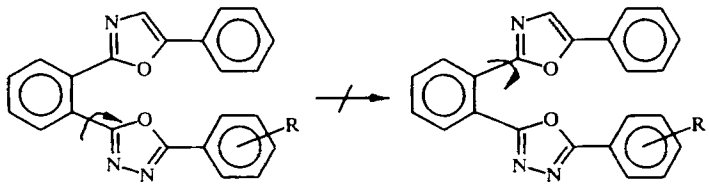
III–V



VI

III R = H; IV R = OMe; V R = NMe_2

It has been proposed that introduction of electron donor substituents should lead to an increase in the order of the single bonds in the oxadiazole part of the molecule and, in the final analysis, to make the substituted diphenyloxadiazole fragment basically a planar part of the molecule while the oxazole fragment should deviate from its plane.



However, our measurements of the electronic absorption spectra for the compounds synthesized have pointed rather to retention of the conformation of the molecules in the series studied than to a change in conformation due to the effect of the introduced substituents (Fig. 1). The electronic absorption spectra of the ortho POPOP analogs can be considered as a specific superposition of the spectra of the individual molecular fragments [4], mutual conjugation of which is disturbed by steric hindrance. Hence the long wave transition in the spectra of these compounds proves to be localized on the fragment with a more extended conjugated system (PPO) and, hence, the S_0-S_2 transition is localized on the fragment with the less conjugated π-system, displaced from the plane of the first fragment [4]. As evident from the data in Fig. 1, the long wavelength absorption band position remains almost unchanged and the structural change in the oxadiazole part of the molecule has an effect only on the position of the shorter wavelength band (even when the strongly electron donor dimethylamino substituent is present). Similar behavior is only possible in the case of a similar type of S_0-S_1 transition in the spectra of ortho POPOP analogs and, therefore, with retention of a planar diphenyloxazole fragment in all the investigated compounds.

X-Ray structural analysis of compound V fully supports the conclusions above. Table 1 shows the atomic coordinates and equivalent thermal corrections (isotropic corrections for hydrogen atoms), Tables 2-4 show bond lengths and some valence and dihedral angles, and Fig. 2 the atomic numbering scheme for the molecule of compound V with ellipsoidal thermal vibrations (probability level 50%). It was found that the configuration of the discussed molecule was very close to that found by us for the ortho POPOP molecule [3]. If one defines the plane of the central benzene ring as P_1, the plane of the oxazole ring P_2, the terminal benzene ring connected to the oxazole as P_3, the oxadiazole ring as P_4, and the final benzene ring con-

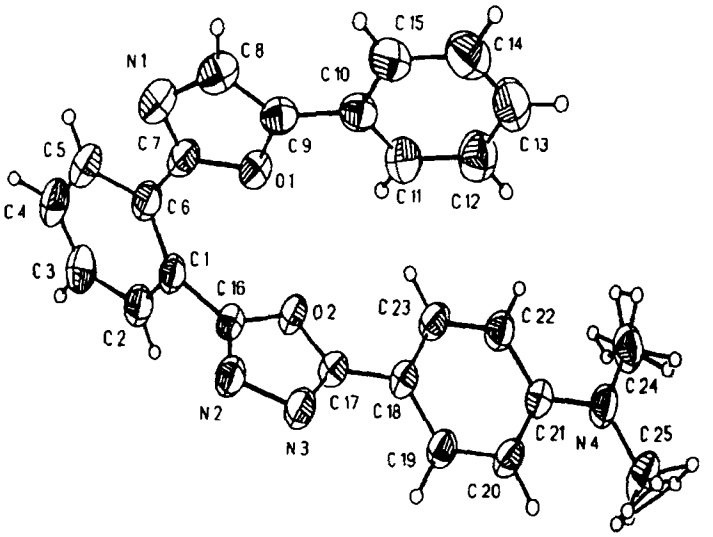


Fig. 2. Atomic numbering scheme and ellipsoidal thermal vibrations for the molecule of compound V.

nected to it as P_5 then the angles between these planes are: $P_1 \wedge P_2 = 25.2(1)$, $P_2 \wedge P_3 = 5.0(2)$, $P_1 \wedge P_3 = 29.6(1)$; $P_1 \wedge P_4 = 82.1(1)$, $P_4 \wedge P_5 = 17.4(2)°$. The RMS deviations of the individual atoms from the $P_{1...5}$ plane (calculated by the method of least squares) are respectively, 0.010, 0.003, 0.006, 0.004, and 0.006 Å. In rather broad terms, the molecule can be regarded as consisting of two quasi coplanar fragments ($P_1 + P_2 + P_3$) and ($P_4 + P_5$) (mean square deviation of 0.26 and 0.13 Å) with an angle of 88.55(5)°. As in the case of ortho POPOP, in V the steric hindrance in reflected in some lengthening of the intercyclic bonds of the central fragment when compared with the intercyclic bonds of the outer benzene rings as well as an increase in the valence angles $C_6-C_1-C_{16}$ and $C_1-C_6-C_7$ which are less in the case discussed than in ortho POPOP. This can be explained in the molecule of V by a greater twisting of the oxadiazole ring relative to the central fragment than for the corresponding rotational angle for the unconjugated oxazole ring in ortho POPOP (66.9°). The intramolecular contact $O_1 \ldots O_2$ of 3.01 Å, characterizing steric hindrance, is significantly greater in V than in ortho POPOP (2.85 Å). Shortening of the intermolecular contacts on packing of molecule V is not observed.

Overall the data obtained point to a similar molecular conformation in the series of unsymmetrical ortho POPOP analogs. Thus the structure of the compounds discussed is controlled not by electronic factors nor by a difference in the conjugation energies of the heterocycles occurring in the composition of their molecules but, rather, by some other circumstances.

An explanation for the reported phenomenon is given in our publication [6] where we discussed a similar example of the steric hindrance of a bisoxadiazole derivative having an o,o'-biphenyl fragment in the molecule. With the aid of results calculated in the AM1 regime and of x-ray structural analytical data, it was shown that this compound directly after synthesis is obtained in an energetically less favored conformation and can be converted to a more energetically favored conformation by refluxing in a high boiling solvent for many hours. It is possible that the molecular conformation of the azole heterocyclic compounds (whose synthesis occurs via formation from acyclic intermediate products) is fully controlled by the conformation of the starting material, i.e., no change in conformation occurs in the cyclization process.

The unsymmetrical ortho POPOP analogs covered in our report were obtained by treatment of the acid chloride of 2-(5-phenyloxazol-2-yl)benzoic acid (ortho-COOH-PPO, VII) with substituted benzhydrazides and subsequent cyclization of the formed products with phosphorus oxychloride [2, 3]. The starting carboxylic acid VII exists in a single possible conformation (not counting an optical isomer) which is stabilized by an intramolecular hydrogen bond. As follows from the calculations reported by us with AM1 method optimization of the geometry, the diphenyloxazole fragment of acid VII is almost planar but the steric hindrance arising in the molecule is minimized via rotation of the carboxyl group by up to 65°. This significantly weakens (but does not rupture) the intramolecular hydrogen bond (N...O length = 2.76 Å). Formation of the acid chloride leads to a further deviation of the COCl group from the plane of the diphenyloxazole fragment in the molecule (to more than 80°) since the hydrogen bond which tends to turn the acid group into the molecular plane is absent in this compound. Rotation of the 2-phenyl radical around the single bond joining it to the oxazole ring is unlikely since the given rotation is significantly

TABLE 2. Bond Lengths (d) in the Molecule of Compound V

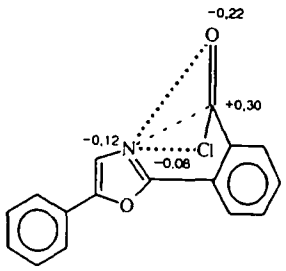
Bond	d, Å	Bond	d, Å
$O_{(1)}$—$C_{(7)}$	1,358(3)	$C_{(5)}$—$C_{(6)}$	1,397(3)
$O_{(1)}$—$C_{(9)}$	1,374(3)	$C_{(6)}$—$C_{(7)}$	1,460(3)
$O_{(2)}$—$C_{(17)}$	1,366(2)	$C_{(8)}$—$C_{(9)}$	1,353(3)
$O_{(2)}$—$C_{(16)}$	1,366(2)	$C_{(9)}$—$C_{(10)}$	1,452(3)
$N_{(1)}$—$C_{(7)}$	1,286(3)	$C_{(10)}$—$C_{(15)}$	1,385(4)
$N_{(1)}$—$C_{(8)}$	1,386(3)	$C_{(10)}$—$C_{(11)}$	1,390(4)
$N_{(2)}$—$C_{(16)}$	1,273(3)	$C_{(11)}$—$C_{(12)}$	1,377(4)
$N_{(2)}$—$N_{(3)}$	1,413(2)	$C_{(12)}$—$C_{(13)}$	1,371(4)
$N_{(3)}$—$C_{(17)}$	1,285(3)	$C_{(13)}$—$C_{(14)}$	1,376(5)
$N_{(4)}$—$C_{(21)}$	1,376(3)	$C_{(14)}$—$C_{(15)}$	1,376(4)
$N_{(4)}$—$C_{(25)}$	1,432(3)	$C_{(17)}$—$C_{(18)}$	1,449(3)
$N_{(4)}$—$C_{(24)}$	1,438(4)	$C_{(18)}$—$C_{(23)}$	1,385(3)
$C_{(1)}$—$C_{(2)}$	1,385(3)	$C_{(18)}$—$C_{(19)}$	1,395(3)
$C_{(1)}$—$C_{(6)}$	1,399(3)	$C_{(19)}$—$C_{(20)}$	1,377(3)
$C_{(1)}$—$C_{(16)}$	1,479(3)	$C_{(20)}$—$C_{(21)}$	1,400(3)
$C_{(2)}$—$C_{(3)}$	1,387(4)	$C_{(21)}$—$C_{(22)}$	1,399(3)
$C_{(3)}$—$C_{(4)}$	1,374(4)	$C_{(22)}$—$C_{(23)}$	1,381(3)
$C_{(4)}$—$C_{(5)}$	1,372(4)		

TABLE 3. Some Valence Angles (ω) in the Molecule of Compound V

Angle	ω, deg	Angle	ω, deg
$C_{(7)}$—$O_{(1)}$—$C_{(9)}$	105,3(2)	$C_{(15)}$—$C_{(10)}$—$C_{(11)}$	119,0(2)
$C_{(17)}$—$O_{(2)}$—$C_{(16)}$	102,5(2)	$C_{(15)}$—$C_{(10)}$—$C_{(9)}$	120,2(2)
$C_{(7)}$—$N_{(1)}$—$C_{(8)}$	104,5(2)	$C_{(11)}$—$C_{(10)}$—$C_{(9)}$	120,8(2)
$C_{(16)}$—$N_{(2)}$—$N_{(3)}$	106,4(2)	$C_{(12)}$—$C_{(11)}$—$C_{(10)}$	120,3(3)
$C_{(17)}$—$N_{(3)}$—$N_{(2)}$	106,2(2)	$C_{(13)}$—$C_{(12)}$—$C_{(11)}$	120,2(3)
$C_{(21)}$—$N_{(4)}$—$C_{(25)}$	121,5(2)	$C_{(12)}$—$C_{(13)}$—$C_{(14)}$	119,9(3)
$C_{(21)}$—$N_{(4)}$—$C_{(24)}$	120,4(2)	$C_{(13)}$—$C_{(14)}$—$C_{(15)}$	120,4(3)
$C_{(25)}$—$N_{(4)}$—$C_{(24)}$	117,5(2)	$C_{(14)}$—$C_{(15)}$—$C_{(10)}$	120,2(3)
$C_{(2)}$—$C_{(1)}$—$C_{(6)}$	119,7(2)	$N_{(2)}$—$C_{(16)}$—$O_{(2)}$	112,7(2)
$C_{(2)}$—$C_{(1)}$—$C_{(16)}$	118,5(2)	$N_{(2)}$—$C_{(16)}$—$C_{(1)}$	126,5(2)
$C_{(6)}$—$C_{(1)}$—$C_{(16)}$	121,5(2)	$O_{(2)}$—$C_{(16)}$—$C_{(1)}$	120,7(2)
$C_{(3)}$—$C_{(2)}$—$C_{(1)}$	120,6(2)	$N_{(3)}$—$C_{(17)}$—$O_{(2)}$	112,2(2)
$C_{(4)}$—$C_{(3)}$—$C_{(2)}$	119,5(3)	$N_{(3)}$—$C_{(17)}$—$C_{(18)}$	128,5(2)
$C_{(5)}$—$C_{(4)}$—$C_{(3)}$	120,7(2)	$O_{(2)}$—$C_{(17)}$—$C_{(18)}$	119,4(2)
$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	120,6(2)	$C_{(23)}$—$C_{(18)}$—$C_{(19)}$	118,0(2)
$C_{(5)}$—$C_{(6)}$—$C_{(1)}$	118,7(2)	$C_{(23)}$—$C_{(18)}$—$C_{(17)}$	122,5(2)
$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	118,8(2)	$C_{(19)}$—$C_{(18)}$—$C_{(17)}$	119,5(2)
$C_{(1)}$—$C_{(6)}$—$C_{(7)}$	122,5(2)	$C_{(20)}$—$C_{(19)}$—$C_{(18)}$	121,2(2)
$N_{(1)}$—$C_{(7)}$—$O_{(1)}$	113,8(2)	$C_{(19)}$—$C_{(20)}$—$C_{(21)}$	120,9(2)
$N_{(1)}$—$C_{(7)}$—$C_{(6)}$	128,0(2)	$N_{(4)}$—$C_{(21)}$—$C_{(22)}$	121,0(2)
$O_{(1)}$—$C_{(7)}$—$C_{(6)}$	118,1(2)	$N_{(4)}$—$C_{(21)}$—$C_{(20)}$	121,5(2)
$C_{(9)}$—$C_{(8)}$—$N_{(1)}$	110,0(2)	$C_{(22)}$—$C_{(21)}$—$C_{(20)}$	117,6(2)
$C_{(8)}$—$C_{(9)}$—$O_{(1)}$	106,4(2)	$C_{(23)}$—$C_{(22)}$—$C_{(21)}$	121,0(2)
$C_{(8)}$—$C_{(9)}$—$C_{(10)}$	136,1(2)	$C_{(22)}$—$C_{(23)}$—$C_{(18)}$	121,3(2)
$O_{(1)}$—$C_{(9)}$—$C_{(10)}$	117,5(2)		

retarded by steric hindrance. Evidently, there is also observed some electrostatic stabilization of the same conformation of the acid chloride due to attraction of unlike charges on the heterocyclic nitrogen atom and the carbon atom of the COCl group and also repulsion of like charges on the nitrogen atom of the oxazole ring and the oxygen and chlorine atoms of the acid chloride (charge distributions according to the AM1 method).

In all probability, in the case of ortho POPOP analogs (as in the work reported by us [6]), a change in conformation occurs neither at the stage of reaction of the acid chloride of VII with the corresponding benzhydrazide nor at the stage of closing the oxadiazole ring. As a result, and independently of the structure of the oxadiazole part of the unsymmetrical ortho POPOP analogs, the molecules of the studied compounds present a planar, diphenyloxazole fragment and an oxadiazolylphenyl fragment deviating from its plane by an angle of 70-80°.



From what has been said, there emerges one conclusion which is extremely important for the spectro-luminescence properties of ortho POPOP analogs. Since the S_0-S_1 transition in the absorption spectra of these compounds is localized on the diphenyloxazole fragment, the structural changes in the oxadiazole part of the molecule have almost no effect on its energy because of the disturbance to conjugation caused by steric hindrance. The excited state of ortho POPOP results in well defined flattening of their molecules leading, at least, to partial restoration of conjugation [4]. Hence subsitituents in the oxadiazole part of the molecule begin to show an effect on the structural relaxation energy of the excited state leading to its lowering and correspondingly to an increased Stokes shift (Table 5). An even more clearly defined effect is seen in polar solvents.

Hence the series of unsymmetrical ortho POPOP analogs can be thought of as a novel class of efficient organic luminophores, characterized by an anomalously large Stokes fluorescence shift, values of which depend on the nature of the introduced substituent. There is thus realized a unique possibility for a selective effect through a change in the molecular structure on the position of the fluorescence spectrum almost without an associated change in the position of the long wavelength absorption. The example quoted is important from a practical viewpoint since the absorption of the ortho POPOP molecule in the excited state is not accompanied by marked fluorescence quenching [4].

EXPERIMENTAL

Electronic absorption spectra were measured on Specord M-40 and Hitachi U-3210 spectrophotometers and fluorescence spectra on a Hitachi F-4010 spectrometer. Quantum fluorescence yields were determined relative to quinine bisulfate in 1N sulfuric acid (φ_f = 0.546 [7]) with the inclusion of a quadratic correction for differences in refractive indices for ethanol and the measured solution.

X-Ray structural investigation was carried out on an automatic, four circle Siemens P3/PC diffractometer with molybdenum irradiation and graphite monochromator (λ = 0.71073 Å) for an approximately isometric crystal of size 0.4 mm ($2\theta/\theta$-scanning in the range 2θ between 5 and 55° at a speed of 4 to 30 deg/min and scanning interval 2°), ratio of the measurement time of the background to time of the reflex 0.40, two control reflexes for each of 98 intensities. In all, 2747 intensities were measured, of which 2560 independent (R_{int} = 1.60%) were used for solving and refining the structure. For calculations of the intensity in F_{hkl}, absorption was not taken into account; Lorentz and polar factors were included. Crystallographic data: $C_{25}H_{20}N_4O_2$, M_r =408.5, T = 293 K, triclinic, space group P-1, cell parameters: a = 8.627(3), b = 11.890(3), c = 12.057(3) Å, α = 111.46(2), β = 100.27(2), γ = 107.58(2)°, V = 1037.5(5) Å^3, Z = 2, ρ_{calc} = 1.307 g/cm^3, μ(MoKα) 0.085 mm^{-1}. The structure was solved by a direct, full matrix F^2_{hkl}, least squares method using the SHELXL program in the anisotropic approximation for C, N, and O atoms and isotropic for hydrogen atoms. Disordered hydrogen atoms in the dimethylamino group were located by difference Fourier synthesis and refined by connection to the corresponding carbon atoms. Structural confidence factors: R_1 = 4.43, R_2 = 11.52 for 2541 reflections with $I_{hkl} > 4\sigma(I)$ (correspondingly 4.43 and 12.41% throughout the group of reflections), S = 1.031, maximum and minimum electron density in the final difference synthesis 0.185 and −0.115 e/Å^3. The SHELXTL PLUS program package [8] was used for solution of the structure and preparation of the illustration.

Synthesis of 1-(5-phenyloxazol-2-yl)-2-(5-aryl-1,3,4-oxadiazol-2-yl)benzenes IV and V (general method). To a solution of the hydrazide of p-methoxy or p-dimethylaminobenzoic acid (0.02 mole) in water (50 ml) there was added a solution of an equimolar amount of 2-(5-phenyloxazol-2-yl)benzoyl chloride in benzene (40 ml). A saturated solution of sodium carbonate was added with stirring to give a weakly basic medium. The product was stirred for 1-1.5 h and the precipitate filtered, washed with water, and dried. The condensation product was refluxed for 2 h in phosphorus oxychloride (50 ml) and poured onto ice with stirring. The precipitate was filtered, washed with water, and recrystallized from ethanol.

TABLE 4. Some Torsional Angles (θ) in the Molecule of Compound V

Angle	θ, deg	Angle	θ, deg
$C_{(16)}—C_{(1)}—C_{(6)}—C_{(7)}$	9,80(0,33)	$N_{(3)}—C_{(17)}—C_{(18)}—C_{(23)}$	-162,01(0,23)
$C_{(5)}—C_{(6)}—C_{(7)}—N_{(1)}$	23,14(0,36)	$O_{(2)}—C_{(17)}—C_{(18)}—C_{(23)}$	17,87(0,31)
$C_{(1)}—C_{(6)}—C_{(7)}—N_{(1)}$	-157,71(0,23)	$N_{(3)}—C_{(17)}—C_{(18)}—C_{(19)}$	16,94(0,35)
$C_{(5)}—C_{(6)}—C_{(7)}—O_{(1)}$	-153,06(0,21)	$O_{(2)}—C_{(17)}—C_{(18)}—C_{(19)}$	-163,17(0,19)
$C_{(1)}—C_{(6)}—C_{(7)}—O_{(1)}$	26,08(0,32)	$C_{(25)}—N_{(4)}—C_{(21)}—C_{(22)}$	-175,19(0,25)
$C_{(8)}—C_{(9)}—C_{(10)}—C_{(15)}$	6,01(0,40)	$C_{(24)}—N_{(4)}—C_{(21)}—C_{(22)}$	-4,34(0,36)
$O_{(1)}—C_{(9)}—C_{(10)}—C_{(15)}$	-176,49(0,19)	$C_{(25)}—N_{(4)}—C_{(21)}—C_{(20)}$	4,79(0,38)
$C_{(8)}—C_{(9)}—C_{(10)}—C_{(11)}$	-173,89(0,26)	$C_{(24)}—N_{(4)}—C_{(21)}—C_{(20)}$	175,64(0,24)
$O_{(1)}—C_{(9)}—C_{(10)}—C_{(11)}$	3,61(0,30)		
$C_{(2)}—C_{(1)}—C_{(16)}—N_{(2)}$	-94,15(0,28)		
$C_{(6)}—C_{(1)}—C_{(16)}—N_{(2)}$	79,85(0,30)		
$C_{(2)}—C_{(1)}—C_{(16)}—O_{(2)}$	84,21(0,26)		
$C_{(6)}—C_{(1)}—C_{(16)}—O_{(2)}$	-101,78(0,25)		

TABLE 5. Absorption and Fluorescence Spectral Data for Some Unsymmetrical Ortho POPOP Analogs in Octane

Compound	Substituent	Spectral parameters*				
		$\nu_a^{(2)}/\lambda_a^{(2)}$	$\nu_a^{(1)}/\lambda_a^{(1)}$	ν_f/λ_f	$\Delta\nu_{ST}$	φ
III	H	37420/267	31720/315	24440/409	7280	0,57
VI	(2-furyl)	36680/273	31760/315	24300/411	7450	0,55
IV	OCH_3	36920/276	31440/318	23850/419	7600	0,55
V	$N(CH_3)_2$	34130/293	30880/324	23150/432	7730	0,59

*$\nu_a^{(1,2)}$, $\lambda_a^{(1,2)}$) position of the two long wavelength transitions in the absorption spectra from separation data for the experimental spectra via combination of its separate bands (cm^{-1}, nm); ν_f, λ_f) position of the fluorescence spectra (cm^{-1}, nm); $\Delta\nu_{ST}$) Stokes shift (cm^{-1}); φ) quantum fluorescence yield.

1-(5-Phenyloxazol-2-yl)-2-[5-(4'-methoxyphenyl-1,3,4-oxadiazol-2]-yl)benzene (IV). Yield 48%. mp 143-145°C. Found, %: N 10.5. $C_{24}H_{17}N_3O_3$. Calculated, %: N 10.6.

1-(5-Phenyloxazol-2-yl)-2-[5-(4'-dimethylaminophenyl)-1,3,4-oxadiazol-2-yl]benzene (V). Yield 32%. mp 137-139°C. Found, %: N 13.7. $C_{25}H_{20}N_4O_2$. Calculated, %: N 13.7.

Spectroscopic measurements for the compounds synthesized were made on materials purified chromatographically on aluminium oxide (eluent hot benzene) and then by additional recrystallization from heptane.

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