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EFFECT OF THE AGGREGATE STATE ON THE CONJUGATION IN THE 2-(2'-QUINOLYL)BENZOXAZOLE SYSTEM

N. A. Klyuev, P. B. Kurapov, G. G. Aleksandrov, and I. I. Grandberg

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It was demonstrated by x-ray diffraction analysis, electronic spectroscopy, and mass spectrometry that the phase state and a decrease in the temperature of the solution have a substantial effect on the dihedral angle between the planes of the rings and the conjugation in the 2-(2'-quinolyl)benzoxazole molecule. The molecule is planar in the crystalline state, in the gas phase, and in solution at low temperature. The conjugation is maximal in these cases. The conjugation decreases when the compound is dissolved, and this is reflected in the character of the electronic absorption and emission spectra.

It is known [1] that the magnitude of the activation barrier (ΔE) for the conformers of bisheterocyclic analogs of biphenyl in the general case amounts to only 2-12 kcal/mole. Under these conditions the position of the equilibrium between the conformers is sensitive to various external factors [1, 2]. In particular, the magnitude of the dihedral angle between the planes of the aryl or hetaryl rings of a system with a structure of the biphenyl type and, consequently, the conjugation between them may depend on the aggregate state of the compound, the temperature, and the polarity of the solvent.

In order to study the effect of external factors on the conjugation in the 2-(2'-quinolyl)benzoxazole system (I) we obtained the electronic absorption and emission spectra of I at various temperatures in solutions and in the solid phase and made a detailed study of the character of the fragmentation of I under the influence of electron impact (the gas phase). We also determined the conformation of the I molecules in the crystal by means of x-ray diffraction analysis (XDA).

Thus in the case of a specific compound we have for the first time by means of various physicochemical methods traced how the aggregate state of the sample and the temperature of the solutions affect the conjugation in a system with a structure of the biphenyl type.

According to the XDA data, the 2-(2'-quinolyl)benzoxazole molecule is virtually planar in the crystal. The dihedral angle between the planes of the rings is only 1.1°. The maximum deviation of the C_9 and C_{13} atoms from the middle of the plane drawn through all of the nonhydrogen atoms is 0.03-0.04 Å, respectively (Tables 1 and 2 and Fig. 1). Thus in the solid phase the hetaryl rings of I constitute a planar system represented by the S-trans isomer. Maximum conjugation between the rings leads to a decrease in the length of the interannular C_7-C_8 bond (Fig. 1), which is 1.48(1) Å; this is 0.025 Å shorter than the central bond in biphenyl [3]. Sesqui character of the interannular bond was previously predicted for similar bisheterocyclic systems on the basis of the results of quantum-chemical calculations [4]. The principal geometrical parameters

K. A. Timiryazev Moscow Agricultural Academy, Moscow 127550. All-Union Scientific-Research Institute of Antibiotics, Moscow 113105. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 775-779, June, 1982. Original article submitted August 4, 1981.

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TABLE 1. Bond Angles in the 2-(2'-Quinolyl)benzoxazole Molecule

Atoms	Angles, deg	Atoms	Angles, deg
$C_1C_2C_3$	122 (1)	$C_7C_8C_9$	119,0 (8)
$C_2C_3C_4$	121 (1)	$N_2C_8C_9$	124,7 (8)
$C_2C_1C_6$	117 (1)	$C_7C_8N_2$	116,3 (8)
$C_3C_4C_5$	115 (1)	$C_8C_9C_{10}$	120,0 (9)
$C_4C_5C_6$	125 (1)	$C_9C_{10}C_{11}$	118,1 (8)
$C_5C_6C_1$	119 (1)	$C_{10}C_{11}C_{12}$	118,4 (8)
C_4C_5O	127,4 (9)	$C_{11}C_{12}N_2$	123,6 (8)
$C_1C_6N_1$	131,4 (9)	$C_{10}C_{11}C_{13}$	123,6 (8)
$C_5C_6N_1$	110,0 (8)	$C_{12}C_{11}C_{13}$	117,9 (8)
$C_6N_1C_7$	102,5 (8)	$C_{11}C_{12}C_{16}$	121,7 (8)
C_6C_5O	107,4 (8)	$N_2C_{12}C_{16}$	114,7 (8)
N_1C_7O	117,3 (8)	$C_{11}C_{13}C_{14}$	119,0 (9)
C_5OC_7	102,8 (7)	$C_{13}C_{14}C_{15}$	121,6 (9)
C_8C_7O	119,1 (8)	$C_{14}C_{15}C_{16}$	121,6 (9)
$N_1C_7C_8$	123,6 (9)	$C_{15}C_{16}C_{12}$	118,2 (9)
$C_8N_2C_{12}$	115,1 (7)		

TABLE 2. Coordinates of the Atoms ($\cdot 10^4$) and Their Anisotropic Temperature Factors in the Form $T=\exp[-1/4(B_{11}h^2a^{*2}+\ldots+2B_{23}klb^*c^*)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O	7876 (7)	430 (3)	1128 (10)	5,7 (4)	5,3 (3)	6,1 (4)	−0,3 (3)	0,4 (3)	−0,3 (3)
N_1	7782 (9)	−162 (4)	−1907 (10)	5,8 (5)	4,4 (3)	6,7 (4)	−0,5 (4)	−0,2 (4)	−0,4 (4)
N_2	9601 (8)	1379 (4)	−291 (10)	4,7 (5)	5,1 (4)	5,8 (4)	−0,1 (4)	0,4 (3)	−0,4 (3)
C_1	6099 (12)	−1056 (5)	−815 (17)	6,4 (7)	4,9 (5)	8,5 (7)	−0,8 (5)	−0,7 (5)	0,3 (5)
C_2	5395 (12)	−1236 (5)	828 (23)	6,5 (7)	4,8 (5)	9,9 (7)	−1,2 (5)	−1,8 (6)	1,6 (6)
C_3	5465 (10)	−861 (6)	2649 (18)	4,9 (6)	6,2 (5)	10,2 (8)	−1,4 (5)	−0,3 (5)	2,1 (5)
C_4	6290 (11)	−291 (5)	2928 (15)	5,4 (6)	6,5 (5)	7,0 (6)	−0,5 (5)	0,0 (5)	0,6 (5)
C_5	6980 (11)	−118 (4)	1271 (17)	4,4 (6)	4,1 (5)	6,9 (6)	−0,5 (5)	−0,2 (5)	0,8 (5)
C_6	6947 (11)	−479 (5)	−561 (16)	5,2 (6)	4,9 (5)	5,8 (5)	0,2 (5)	−0,3 (5)	0,2 (5)
C_7	8262 (10)	361 (4)	−822 (17)	4,6 (6)	4,7 (5)	6,2 (6)	0,1 (5)	−0,2 (5)	1,0 (5)
C_8	9211 (9)	869 (4)	−1590 (15)	5,0 (6)	5,1 (5)	5,4 (5)	1,5 (5)	0,2 (4)	−0,5 (4)
C_9	9613 (10)	794 (4)	−3590 (16)	5,0 (6)	5,4 (5)	6,7 (6)	0,3 (5)	0,4 (5)	1,2 (4)
C_{10}	10535 (10)	1245 (5)	−4301 (12)	5,2 (6)	6,7 (5)	5,3 (5)	1,5 (5)	0,4 (4)	−1,0 (4)
C_{11}	11002 (10)	1795 (4)	−2995 (15)	4,3 (5)	5,9 (5)	5,2 (5)	1,4 (5)	0,4 (4)	−0,3 (4)
C_{12}	10525 (10)	1842 (4)	−1035 (16)	4,0 (5)	5,0 (5)	6,0 (6)	0,5 (5)	0,6 (4)	−0,8 (4)
C_{13}	11990 (10)	2299 (5)	−3544 (14)	5,2 (6)	6,8 (5)	6,8 (5)	0,6 (5)	1,1 (5)	1,5 (5)
C_{14}	12379 (10)	2815 (4)	−2152 (19)	5,9 (6)	5,0 (5)	8,5 (6)	−0,2 (5)	0,6 (5)	1,0 (5)
C_{15}	11876 (12)	2851 (5)	−241 (18)	6,5 (7)	5,9 (5)	7,9 (6)	−0,8 (5)	1,5 (5)	−0,2 (5)
C_{16}	10936 (11)	2382 (5)	357 (13)	6,5 (6)	5,3 (5)	6,4 (5)	−0,3 (5)	1,7 (4)	−0,8 (4)

of the I molecule are in good agreement with the analogous parameters in other heterocyclic compounds. The length of the C_7-N_1 double bond [1.30(1) Å] in the oxazole fragment is close to the length of the standard C=N bond (1.29 Å) [5] and to the length found in 2-methyl-4-nitroimidazole [1.308(3) Å] [6]; the length of the C–O bonds [1.36(1) and 1.39(1) Å] is comparable to the standard length of the $C_{sp^2}-O$ bond (1.36 Å) [5].

The bond lengths and angles of I are presented in Fig. 1 and Table 1.

It is known [7-10] that a more planar orientation of the hetaryl rings in systems with structures of the biphenyl type promotes an increase in the fluorescence intensity and leads to a bathochromic shift of the long-wave absorption band in the UV spectrum. In fact, 2-(2'-quinolyl)benzoxazole luminesces strongly in the crystalline state; the luminescence maximum is shifted ~35 nm to the red region as compared with the solution (Table 3). The long-wave band in the absorption spectrum of I due to a $\pi-\pi^*$ transition also experiences a bathochromic shift on passing from the solution to the crystal (Table 3). The low fluorescence intensity and the shorter-wave absorption spectrum of I in solution as compared with the crystal constitute evidence that the planarity of the I molecule is disrupted when the compound is dissolved.

It may be assumed that appreciable stabilization will not be observed in solutions at 20°C (under the usual experimental conditions) because of the low ΔE value. However, freezing the solution to 77°K leads to a sharp increase in the luminescence quantum yield ($\varphi = 0.84$) and a bathochromic shift of the long-wave absorption and emission bands (Table 3). Consequently, lowering the temperature of the solution leads to stabilization of the more planar conformer, i.e., the conjugation effect begins to prevail over the steric factors, which act in the opposite direction.

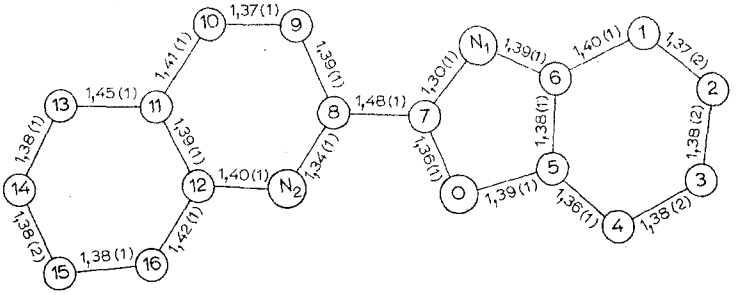

Fig. 1. Bond lengths (Å) in the 2-(2'-quinolyl)benzoxazole molecule.

TABLE 3. Electronic Spectra of 2-(2'-Quinolyl)benzoxazole

No.	Solvent	Temp., °K	Absorption		Emission	
			λ_{max}, nm	lg ε	λ_{max}, nm	φ
1	Crystal	293	333 348 364	—	433	0,25*
2	Ethanol	293	244 256 282 321 333 348	4,22 4,01 4,10 4,15 4,17 4,04	—	≪0,1
3	Dioxane	293	243 255 273 281 305 318 331 346	4,43 4,22 4,29 4,47 4,29 4,37 4,39 4,32	363 379 397	<0,1
4	Cyclohexane	293	224 255 280 309 329 345	4,32 4,32 4,47 4,39 4,44 4,44	—	≪0,1
5	Ethanol–ether (2:1)	293	257 282 321 333 349	4,00 4,08 4,12 4,15 4,05	—	—
6	Ethanol–ether (2:1)	77	258 276 286 310 321 331 324 335 352	—	364 375 396 420	0,84

* The emission intensity is presented relative to salicylalazine as the standard.

In the examined 2-(2'-quinolyl)benaoxazole system both rings are π-deficient systems, and in this case, as demonstrated in [11, 12], conjugation between the rings will be realized through the mutual π-electron-donor character of the hetaryl fragments. π-Electron depletion of the rings and, as a consequence, an increase in the double bond character of the interannular C_7-C_8 bond should lead to a decrease in the basicity of the nitrogen atoms of the pyridine type. This effect is actually observed for I. The decrease in the basicity of the nitrogen atom of the quinoline ring in this case is 2.65 pH units (see the experimental section).

In the gas phase the molecular ion (M^+) of I is planar, and the conjugation in the system is significant. The following experimental data constitute evidence for this; the high stability of M^+ to electron impact (W_M = 19.2% of the total ion current); the observed elimination of hydrogen, which leads to condensation of the rings in the bishetaryl system through the formation of a four-membered ring (the N_1-C_9 bond) [4], which is possible only under the conditions of a planar S-trans conformation of the molecular ion; the absence in the mass spec-

trum of ions that characterize cleavage of the interannular bond in the I molecule, viz. benzoxazole (m/z 118) and quinoline (m/z 128) cations (see the experimental section).

Under conditions of dissociative ionization and in the case of the apparent absence of isomerization processes in both the molecule and the molecular ion (M^+) the structure of M^+ corresponds, according to the Franck–Condon principle, to the unexcited ground state of the starting molecule (the ionization time is 10^{-15}–10^{-17} sec, while the lifetime of the ion is 10^{-7} sec [13]).

Thus the set of data that we obtained constitutes evidence that the phase state and a decrease in the temperature of the solution have a substantial effect on the dihedral angle between the planes of the rings and the conjugation in the 2-(2'-quinolyl)benzoxazole molecule. The I molecule is planar in the crystal and the gas phase, and the conjugation here is maximal. This leads to an increase in the double bond character of the interannular bond, a bathochromic shift of the long-wave absorption band in the UV spectrum, and intense luminescence. The conjugation decreases when the compound is dissolved, probably due to solvolysis and the low ΔE value, which leads to free rotation of the rings relative to one another; this is accompanied by a hypsochromic shift of the long-wave absorption band in the UV spectrum and quenching of the luminescence. A decrease in the temperature of the solution promotes stabilization of the more planar conformer and an increase in the conjugation; this has a substantial effect on the character of the electronic absorption and emission spectra.

EXPERIMENTAL

The x-ray diffraction studies were made by means of a Sintex-Pl automatic diffractometer with λ CuK_α emission, an Ni filter, $\theta/2\theta$ scanning, $2^\circ \geq 2\theta \geq 110^\circ$, and 776 independent nonzero reflections with $F^2 \geq 36$. The structure was decoded by direct methods and was refined by the method of least squares in the anisotropic* total matrix approximation to R = 0.090. The bond lengths and angles and the coordinates of the atoms and their anisotropic temperature factors are presented in Fig. 1 and Tables 1 and 2. The I crystals were monoclinic with $a = 9.327(3)$, $b = 20.072(5)$, $c = 6.407(3)$ Å, $\beta = 98.26(3)^\circ$, ρ (calc.) = 1.38 g-cm^{-3}, Z = 4, and space group $P2_1/n$.

A spectral luminescence study at 293°K was carried out with a Hitachi EPS-3T spectrophotometer equipped with a G-3 fluorescence adapter. The spectra at 77°K were obtained by means of a special device for recording low-temperature spectra. A 10^{-5} mole/liter solution of quinine bisulfate in 0.1 N sulfuric acid ($\varphi = 0.55$) was used as the standard in the determination of the relative quantum yields [a solution of benzophenone ($\varphi = 0.71$) was used as the standard at low temperatures [14]]. The luminescence spectra of powders were recorded by means of an ISP-51 spectrophotometer and an FÉP-1 photoelectronic adapter, in which the photomultiplier was replaced by an FÉU-51. The luminescence was excited by the light of a PRK-2 mercury-quartz lamp (with a USF-4 light filter in the region of the mercury line at 336 nm). The spectra are given with allowance for all of the corrections for the sensitivity of the apparatus; the slit width was 0.01 mm, and the standard was salicylalazine (light-yellow monogen). The pK_a values were determined by spectrophotometry in 50% ethanol (hydrochloric acid served as the oxonium ion donor). The pH was measured with an OR-401/1 titration pH meter with glass and calomel electrodes. The pK_a of the conjugate acid of I was 1.35 ± 0.02. For comparison, the pK_a of quinoline was 3.99 in 50% ethanol.

The mass-spectrometric study was carried out under standard conditions [9, 13] with a Varian MAT-311A spectrometer. Mass spectrum of I (m/z): 43 (13.6), 51 (10.0), 57 (16.8), 63 (23.4), 64 (18.1), 75 (10.4), 76 (4.8), 77 (14.6), 92 (4.4), 101 (27.2), 102 (8.2), 123 (11.5), 128 (7.2), 217 (3.5), 218 (5.8), 220 (13.6), 245 (18.3), 246 (100.0), 247 (17.4).

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REGIOSELECTIVE METHYLATION OF 1-BENZYL-$\Delta^{9,10}$-OCTAHYDRO-4-QUINOLONE*

G. V. Grishina, I. F. Leshcheva, N. M. Sergeev, V. M. Potapov, and A. I. Vovk

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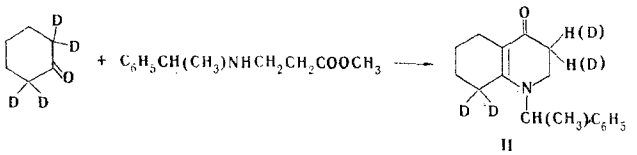
The methylation of 1-benzyl-$\Delta^{9,10}$-octahydro-4-quinolone with methyl iodide in the presence of lithium diethylamide in tetrahydrofuran is a regioselective electrophilic substitution reaction, and, depending on the reaction conditions, takes place in the 3 or 8 position of the quinolone system. Deuteration under the same conditions takes place only in the 3 position.

Regioselective electrophilic substitution has been observed for N-substituted $\Delta^{9,10}$-octahydro-4-quinolone [1]. To ascertain the possibility of carrying out functional and asymmetric electrophilic substitution we investigated the effect of various factors on the direction of methylation of 1-benzyl-$\Delta^{9,10}$-octahydro-4-quinolone in the presence of strong bases.

We observed electrophilic substitution in a study of the ^{13}C NMR spectrum of the deutero derivative of 1-(1-phenylethyl)-$\Delta^{9,10}$-octahydro-4-quinolone (II). The synthesis of deuterated derivative II was carried out in order to assign the signals in the ^{13}C NMR spectrum of II (Table 1), since only the signals related to the C_2, C_3, C_4, C_9, and C_{10} atoms could be previously assigned by means of the literature data [2] and data from the spectra with incomplete decoupling of the protons. Deutero derivative II was obtained by condensation of 2,2,6,6-d_4-cyclohexanone with methyl 2-[N-(1-phenylethyl)amino]propionate:



II

In conformity with the scheme, it was assumed that the reaction proceeds with the formation of enamino ketone II, which contains deuterium atoms only in the 8 position. However, in the spectrum of deutero derivative II we observed a sharp decrease in the intensities of the two signals at 26.9 and 35.3 ppm.

For a more detailed analysis of the composition of the isotopomers we measured the triple ^{13}C-{^1H, ^2H} NMR spectra (see [3] for the method used to carry out these experiments).† It is apparent from the spectrum presented in Fig. 1 that three signals of unequal intensity were observed at 26.9 and 35.3 ppm. In conformity with the ^{13}C α-isotopic shifts (−0.35 ppm) due to replacement of hydrogen by deuterium [4], these signals can

*Communication 1 from the series "Methylated cis-enamino ketones."

†The triple {$^{13}C-^1H$, ^2H} NMR spectra were measured with the participation of Yu. K. Grishin and V. A. Chertkov.

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 780-784, June, 1982. Original article submitted November 2, 1981.

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