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Tetrahedron Letters 45 (2004) 5291–5294

Tetrahedron Letters

Synthesis and scintillating efficiencies of 2,5-diarylthiazoles with intramolecular hydrogen bond

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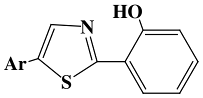
Received 20 January 2004; revised 29 January 2004; accepted 4 May 2004

Abstract—A series of 2,5-diarylthiazole derivatives exhibiting an intramolecular hydrogen bond has been synthesized. The scintillation efficiency of each member of the series has been determined relative to 2,5-diphenyloxazole. Introduction of an OH group in *ortho* positions of 2,5-diphenyloxazole and 2,5-diphenylthiazole has led to a red shift of the fluorescence spectra due to intramolecular hydrogen bond, as supported by quantum chemical calculations.

The search for novel organic luminophores possessing desired spectral properties is both fundamentally and practically important. Luminophores created by derivatizing 2,5-diaryloxazole exhibit the necessary optical characteristics and are used in a variety of scientific and technological applications. 2,5-Diaryloxazole derivatives show excellent luminescence and can be tuned to emit over the whole visible spectrum. Applications of 2,5-diaryloxazoles range from solid-phase synthesis and peptide chemistry,[1,2] monitoring of protein activity[3] and potassium signaling[4] to radioanalytical chemistry[5] and biomolecule sensing.[6] Synthesis and spectral-luminescent properties of 2,5-diaryloxazole and its derivatives have been studied in detail.[7–15] At the same time, the thiazole analogues of diaryloxazoles have only been barely investigated,[12,16] and already have found applications in fiber-optic biosensing of nucleic acids.[17] It is expected that replacement of the oxygen atom in the oxazole cycle with a sulfur atom to form a thiazole cycle raises molecular polarizabilities and introduces interesting novel spectral-luminescent properties. Formation of an intramolecular hydrogen bond (IHB) in these compounds promotes luminescence intensity and results in abnormally large Stokes shifts that are essential for practical applications of the luminophores.

The current communication investigates the luminescence characteristics of 2,5-diarylthiazoles with IHBs formed between the nitrogen atom of the azole heterocycle and the OH group in the *ortho*-position of the 2-phenyl fragment



The compounds were synthesized according to the following scheme (Scheme 1).

10% solution of sodium carbonate was added portionwise to a mixture of 0.011 mol of salicyloyl chloride **II** in benzene (20 mL) and 0.01 mol of α-aminoarylacetophenone hydrochloride **I** in water (25 mL) at vigorous stirring at 20–25 °C at pH 7–8. After 30 min, the precipitate formed was filtered off, washed with water and dried. The amide **III** was then boiled with P_2S_5 in $CHCl_3$ (35 mL) with stirring for 20 h. Water (50 mL) was added to a cooled reaction mixture and left to stand at room temperature for 5 h. The chloroform layer was separated, washed with water until pH of the aqueous solution became neutral, and evaporated. The resulting oily product was boiled with 10% ethanolic KOH for 2 h, poured into water (100 mL) and neutralized with HCl to a slightly acidic pH. The formed precipitate was

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Keywords: Thiazole; Electronic spectra; Scintillation; Hydrogen bond.

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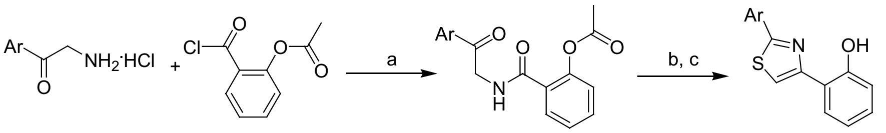
0040-4039/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2004.05.012



I II III IV

Scheme 1. Reagents and conditions: (a) Na_2CO_3, C_6H_6, 20 °C, 30 min; (b) P_2S_5, $CHCl_3$, 20 h, Δ; (c) 10% ethanolic KOH, H_2O, 2 h, Δ.

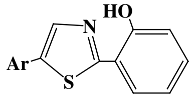
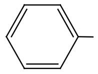
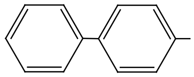
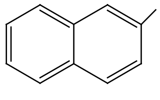
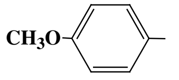
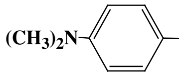
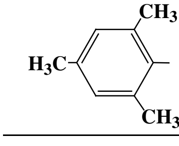
filtered off, washed with water and dried. Purification of the final products **IV** was achieved by chromatography on Silochrom C-120 with heptane.

The absorption and fluorescence spectra of the compounds under study were measured with the 'Specord M-40' spectrophotometer and 'Hitachi' spectrofluorimeter, respectively, in a 1 cm cuvette in 10^{-5} mol/L solutions. The EPR spectra were obtained relative to the trimethylsilane external etalon with the 'Brukker-500' apparatus at the 500 MHz frequency. The IR spectra within the 700–4000 cm^{-1} range were measured with the UR-20 spectrophotometer in KBr matrices. The element analysis for the sulfur and nitrogen contents was carried out by the Shenniger and Dumas–Pregdtl techniques, respectively.[18] The product melting points, yields and element analysis data are given in Table 1.

The geometric and electronic structure of the compounds under study was investigated by the all-valence semiempirical AM1 approach,[19] and by molecular mechanics with the VESCF description of the π-electron conjugation effects using the MMX-M force field[20] implemented in the PCModel software packet. The electronic spectra were computed by the INDO/S semiempirical quantum chemical approach in the Ridley–Zerner parameterization (ZINDO/S)[21] including 12 × 12 configuration interaction singles (CIS). The value of the $\kappa_{\pi-\pi}$ constant was taken equal 0.615 found earlier[22] to reproduce the correct order of the singlet electronic terms of different orbital origins.

In order to establish the presence of IHB between the hydrogen atom of the OH group located in the *ortho*-position of the benzene ring and the nitrogen atom of the azole heterocycle, the IR spectra of the compounds under study were investigated in both solid state and CCl_4 solution. The 10^{-3} mol/L solution is particularly convenient for the studies; the concentration is sufficiently low to make formation of intermolecular hydrogen bonds unlikely and, at the same time, sufficiently high to allow for investigation of the electronic absorption and luminescence spectra. Practically no absorption at the frequency of the free OH group is observed in the IR spectra. At the same time, intense absorption in the range of 3110–3145 cm^{-1} is seen. This band is absent in similar thiazole compounds without the ortho OH group. A number of bands with significant

Table 1. Melting temperature (*T*), reaction yield (%) and element analysis data for the synthesized compounds

 Ar	Yield (%)	*T* (°C)	Element analysis				
			Obtained (%)		Formula	Calculated (%)	
			S	N		S	N
	73	89–90	12.84	5.43	$C_{15}H_{11}NOS$	12.65	5.53
	61	178–179	9.77	4.31	$C_{21}H_{15}NOS$	9.73	4.26
	66	134–135	10.62	4.53	$C_{19}H_{13}NOS$	10.56	4.62
	52	111–112	11.47	4.96	$C_{16}H_{13}NO_2S$	11.31	4.95
	67	124–125	10.80	9.20	$C_{17}H_{16}N_2OS$	10.81	9.45
	59	59–60	10.78	4.60	$C_{18}H_{17}NOS$	10.85	4.75

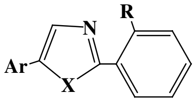
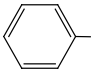
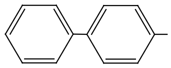
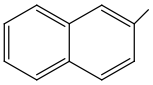
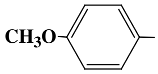
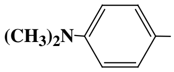
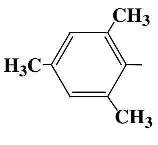
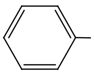
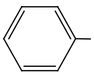
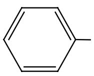
absorption intensity are observed in the frequency range below 2870 cm^{-1} characteristic of the NH$^+$ group. The data testify for a very strong IHB resulting in formation of a quasiaromatic six-member cycle. The hydrogen atom is substantially displaced towards the nitrogen atom. The proton can tunnel between the oxygen and hydrogen atoms resulting in a mixture of the original structure and the structure with the proton attached to the nitrogen. Similar IR spectra are observed in the solid state, where the spectral features are wider. A minor band in the range from 3400 to 3500 cm^{-1} appears indicating the presence in the solid phase of a small amount of intermolecular H-complexes.

The spectral–luminescent characteristics of the compounds under study and related model compounds were investigated in toluene solution and are summarized in Table 2. Compared to 2,5-diaryloxazole, the absorption spectra of its thiazole analogue show a bathochromic displacement of the long-wave absorption bands without essential changes in the band intensities.

The absorption spectra of 2,5-diphenylazoles with the ortho OH group exhibit two bands. For oxazole, the shorter and longer wavelength absorption bands have maxima at $\lambda_{max} = 300$ and 330 nm, respectively. For thiazole, these bands are at 320 and 352 nm. The combination of the shorter and longer wavelength bands can be explained by the presence in these molecules of two absorbing molecular fragments. The shorter wavelength transitions are identical with those of unsubstituted 2,5-diphenylazoles and, therefore, are localized on the 2,5-diphenylazole fragment. The longer wavelength transition appears upon introduction of the ortho OH group and is localized on the six-member cycle involving the IHB.

Expansion of the 5-aryl radical by replacement of the phenyl with the 4-biphenyl or 2-naphthyl fragments is accompanied by red shifts of the absorption spectra. The bathochromic effect grows with increasing electron donor properties of the substituent entered at the 5-aryl radical.

Table 2. Spectral luminescent and scintillating characteristics of the synthesized and model compounds

			Absorption $\lambda_{Макс}$, nm ($\varepsilon \times 10^{-4}$)	Fluorescence $\lambda_{Макс}$, nm (η)	$\Delta\nu$ (cm^{-1})	Scintillating efficiency (%)	
Ar	**R**	**X**				Toluene	1-Methyl-naphthalene
Synthesized compounds							
	OH	S	320 (1.3) 352 (2.4)	525 (0.2)	9400	60	95
	OH	S	362 (3.6)	525 (0.2)	8600	50	85
	OH	S	362 (3.0)	525 (0.3)	8500	55	85
	OH	S	358 (2.5)	520 (0.2)	8700	55	90
	OH	S	373 (2.3)	485 (0.3)	4800	60	96
	OH	S	345 (2.0)	520 (0.2)	9750	70	100
Model compounds							
	H	O	310 (2.6)	365 (0.5)	4700	—	—
	OH	O	300 (1.5) 330 (2.9)	483 (0.2)	9600	—	—
	H	S	326 (4.1)	394 (0.2)	5300	—	—

Without exception, all compounds under study fluoresce in solution and solid state. Introduction of the OH group in the ortho position of the 2,5-diphenyloxazole molecule red shifts the fluorescence spectra. The red shift in the thiazole compounds is more significant than in oxazoles and can be as large as 130 nm. The increased fluorescence red shift observed with thiazoles is mostly likely due to the presence of the vacant d-orbital in the sulfur atom. The fluorescence spectra of the compounds under investigation contain a single well-defined band with the maximum around 520 nm. The chromophore fragment containing the IHB is responsible for both the long wavelength absorption and fluorescence bands. It is important to note that the fluorescence quantum yields of oxazole and thiazole compounds are similar, with some thiazoles having even more intense luminescence than oxazoles. The 'heavy' atom effect that tends to quench fluorescence must be weakened in this case. The abnormally large Stokes' shifts observed with the compounds under study reach nearly 9000 cm^{-1} and are associated with the large amounts of energy involved in shifting the proton along the hydrogen bond coordinate in both the ground and excited electronic states. Interestingly, the fluorescence maximum in the *N*,*N*-dimethylaniline compound (Table 2) is displaced hypochromicly, while its Stokes' shift is decreased, indicating that the NH_2 group has a stronger influence on the spectra than the IHB.

The synthesized thiazole compounds reported in this communication exhibit long wavelength luminescence, abnormally large Stokes' shifts and good radiation resistance compared to the corresponding oxazoles and, therefore, can be applied for liquid phase scintillation. The resulting long wavelength, high intensity, radiation-resistant scintillators are suitable in particular for gamma spectroscopy, identification of ionized particles in low energy regimes, and scintillation detection of radiation over large areas.

Acknowledgements

The authors are grateful to Dr. V. A. Kuksa for useful comments on the manuscript. The financial support of NSF, CAREER Award CHE-0094012 is gratefully acknowledged. O.V.P. is a Camille and Henry Dreyfus New Faculty and an Alfred P. Sloan Fellow.

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