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Structure and Luminescence of Thietane-Containing 1,2,4-Triazoles

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Abstract—New thietane-containing 1,2,4-triazole derivatives were synthesized, and their structure was determined by ^{13}C and ^{1}H NMR spectroscopy and mass spectrometry. The electronic absorption spectra of the new compounds in the ultraviolet and visible regions and their photoluminescence and luminescence excitation spectra were analyzed, and photoluminescence quantum yields were estimated.

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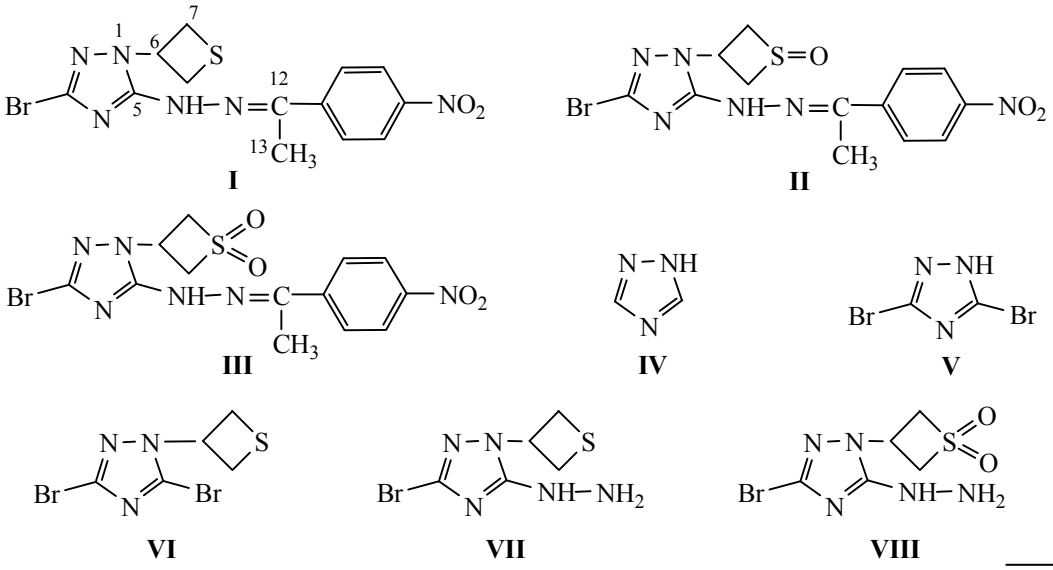
1,2,4-Triazoles and their derivatives are fairly extensively studied due to new possibilities for their application both in medicine as biologically active substances [1–3] and in optoelectronics [4–10]. 1,2,4-Triazoles were also proposed as extractants for transuranium elements [11]. Much attention is also given to coordination compounds of 1,2,4-triazoles with transition metals. As a rule, 1,2,4-triazoles are coordinated to metal ions through the endocyclic nitrogen atoms. Such ligands make it possible to construct polymer matrices and cluster polynuclear structures with silver, copper, cadmium, zinc, iron, and iridium ions. 1,2,4-Triazole derivatives were also introduced into polymer chain [12]. Studies in this field are usually aimed at creating electroluminescent devices (e.g., organic light-emitting diodes). Triazoles are also used as catalysts for peroxyoxalate chemiluminescence [13], as well as in immunochemiluminescence assay [14].

Luminescence spectra of 1,2,4-triazoles and their derivatives cover almost the entire visible region of the spectrum. Variation of complexing metal ions, phase state, substituents in the triazole ring, and polymer matrix nature make it possible to change the emission color over a wide range, from the blue region to red.

Introduction into triazole ring of various substituents, in particular oxothietane fragment, could considerably extend the potential of the resulting compounds as biologically active substances and ligands for complex formation. As substituents we tried thietane rings containing sulfur atom in different oxidation states (i.e., as sulfide, sulfoxide, and sulfone moieties) and benzylidenehydrazines. These fragments were selected taking into account that thietane-containing benzimidazoles and xanthines are known to exhibit immunotropic, antimicrobial, and antiviral activity [15, 16] and affect liver monooxygenase system [17, 18] and that heterocyclic ylidenehydrazines are structural fragments of such medical agents as ftivazide, furagin, etc. [2].

In the present work we examined the structure of compounds **I–VII** and their luminescence properties which ensure their quantitative determination even at very small concentration, e.g., in biological liquids while studying their pharmacokinetics. The purity of compounds **I–VII** was checked by HPLC, and their structure was confirmed by IR, ^{1}H and ^{13}C NMR, and mass spectra. The NMR spectra of **I–VII** lacked signals assignable to quaternary ammonium salts or other impurities. The NMR spectra of **I–III** were analyzed, and signals therein were assigned, by comparing with the spectra of model 3,5-dibromo-1-

† Deceased.



I **II** **III** **IV** **V** **VI** **VII** **VIII**

(thietan-3-yl)-1,2,4-triazole (**VI**) and 3-bromo-5-hydrazino-1-(1,1-dioxo-λ^6-thietan-3-yl)-1,2,4-triazole (**VIII**).

The ^{13}C NMR spectrum of **VIII** contains two singlets at δ_C 127.84 and 140.81 ppm due to C^3 and C^5 in the triazole ring, a doublet at δ_C 54.53 ppm from the N–CH carbon atom, and a triplet at δ_C 33.59 ppm from two magnetically equivalent methylene carbon atoms (CH_2S) in the thietane ring. Compound **VIII** displayed in the ^1H NMR spectrum two doublets of doublets from methylene protons in the *cis* (δ 3.31 ppm) and *trans* positions (δ 4.08 ppm) with respect to the triazolyl substituent in position *3* and a multiplet at δ 5.74 ppm from 3-H in the thietane ring. The coupling constants for protons in the thietane ring are as follows: $^2J = -7.8$, $^3J_{trans} = 8.3$, $^3J_{cis} = 7.9$ Hz.

Molecules **I**–**III** possess an ylidenehydrazino group on C^5 in the triazole ring, as well as thietane (**I**), 1-oxo-λ^4-thietane (**II**), or 1,1-dioxo-λ^6-thietane ring (**III**) on the triazole N^1 atom. The presence of two doublets at δ 8.31 and 8.10 ppm (^3J = 8.2 Hz) in the ^1H NMR spectra of **I**–**III** corresponds to *para*-substitution of the aromatic ring. Thietane fragments containing an sp^2-hybridized sulfur atom (sulfoxide S=O or sulfone O=S=O) are characterized by reduced vicinal ^1H–^1H coupling constants (^3J = 4.5–4.8 Hz) and appreciable downfield shift of methylene carbon signals (SCH_2).

Signals from carbon nuclei in the triazole ring of compounds **I**–**III** appear in a considerably weaker field relative to those typical of model compound **VI** (up to 8 ppm). Presumably, the observed downfield shift results from partial π-electron density transfer from the ring to the hydrazone fragment. The ^{13}C and ^1H NMR spectra of compound **III** also contained signals belonging to the other isomer, which was characterized by different chemical shifts of carbon nuclei in the hydrazine fragment. In keeping with the signal intensities, the ratio of the *cis* and *trans* isomers was estimated at 3 : 7.

Figures 1 and 2 show the photoluminescence and luminescence excitation spectra, respectively, of compounds **I**–**III**, the corresponding spectra of **IV**–**VII** are shown in Fig. 3, and the calculated luminescence parameters are given in Table 1. Bromination of 1,2,4-triazole **IV** at positions *3* and *5* (compound **V**) did not change the spectral pattern in the short-wave region, while a new long-wave absorption band appeared at λ 662 nm; the luminescence quantum yield of **V** was higher than that found for compound **IV** by a factor of 9 in the blue region and by a factor of 1.6 in the red region. Introduction of a thietanyl substituent into the 3,5-dibromo-1,2,4-triazole molecule changes the fluorescence pattern in the short-wave region. Unlike structured bands in the fluorescence spectra of **IV** and **V**, the fluorescence spectrum of **VI** is represented by a diffuse band with its maximum at λ 335 nm; the emission spectra of **IV**–**VI** in the red region are similar. Replacement of one bromine atom in molecule **VI** by hydrazine fragment is accompanied by variations in both short-wave (a new band appears at λ 412 nm) and long-wave regions (the band at λ 616 nm disappears). Simultaneously, the short- and long-wave fluorescence quantum yields increase (Φ = 0.014 and 0.006, respectively).

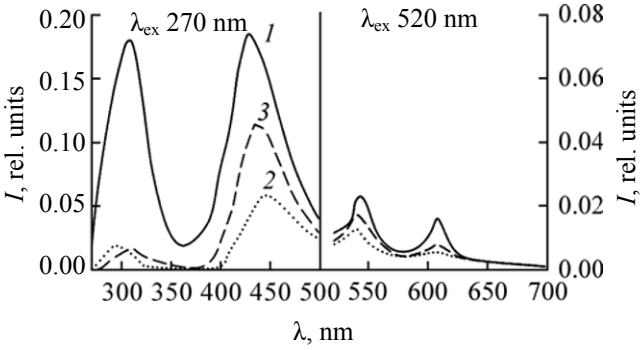


Fig. 1. Luminescence spectra of compounds (*1*) **I**, (*2*) **II**, and (*3*) **III**; $c = 10^{-4}$ M, slit width 15/15 nm, solvent DMSO, 20°C.

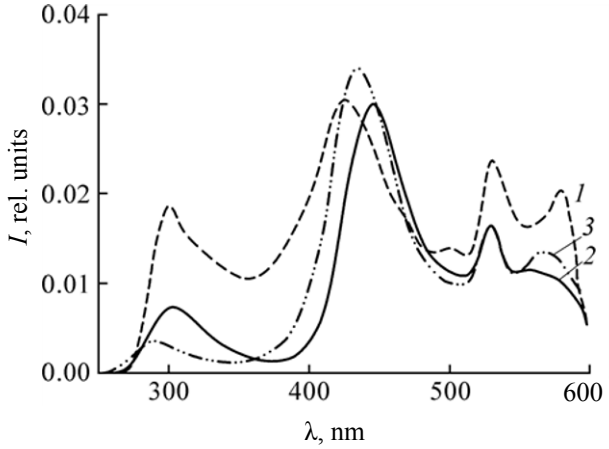


Fig. 2. Luminescence excitation spectra of compounds (*1*) **I**, (*2*) **II**, and (*3*) **III**; $c = 10^{-4}$ M, λ_{em} = 610 nm, slit width 10/10 nm, solvent DMSO, 20°C.

Among 1,2,4-triazole derivatives **I**–**III**, the highest photoluminescence quantum yield was observed for compound **I** ($\Phi = 1.5 \times 10^{-5}$, Table 1). Oxidation of the thietane ring to oxo-λ^4-thietane sharply reduces the fluorescence quantum yield down to 3×10^{-7}, i.e., by a factor of 40 as compared to 1,2,4-triazole. However, contrary to the expectations, subsequent oxidation of the sulfoxide group to sulfone (**III**) leads to increase of the fluorescence quantum yield to 10^{-6}. Presumably, sharp reduction of the fluorescence quantum yield is

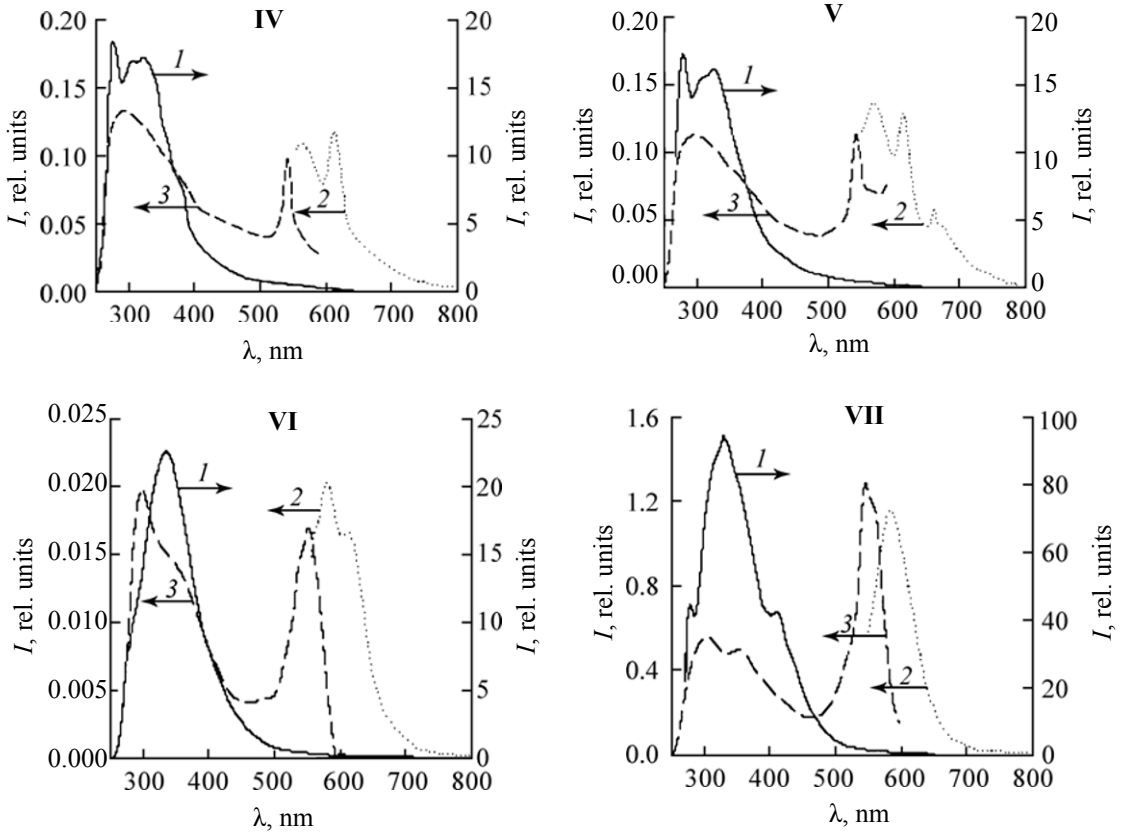


Fig. 3. Luminescence excitation spectra of compounds **IV**–**VII** upon excitation at (*1*) λ 270 nm and (*2*) λ 520 nm ($c = 10^{-3}$ M, slit width 15/15 nm) and (*3*) luminescence excitation spectra (λ_{em} = 650 nm, slit width 10/10 nm), solvent DMSO, 20°C.

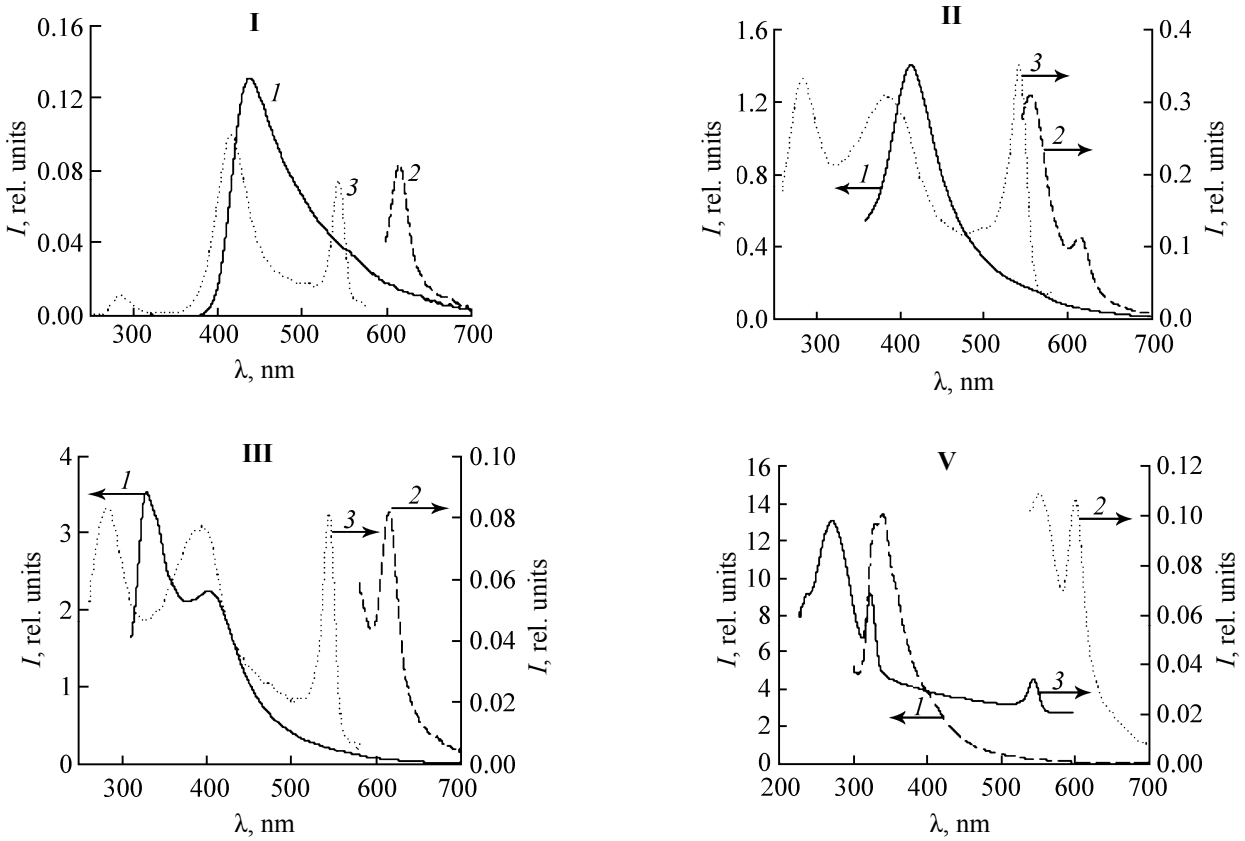


Fig. 4. Luminescence excitation spectra of compounds **I–III** upon excitation at (*1*) λ 270 nm and (*2*) λ 520 nm ($c = 10^{-4}$ M, slit width 15/15 nm) and (*3*) luminescence excitation spectra (λ_{em} = 650 nm, slit width 10/10 nm), solvent propan-2-ol, 20°C.

related to increased non-radiative loss of excitation energy for vibrations of bonds in the substituent in position *5* of the triazole ring.

There are no essential differences in the parameters of fluorescence excitation spectra of compounds **IV–VII**; the only difference is appearance of a new band at λ 356 nm in the spectrum of **VII**. Fluorescence excitation spectra of 1,2,4-triazole derivatives **I–III** revealed new luminescence bands in both short-wave and long-wave regions. Analogous patterns were observed for solutions of the same 1,2,4-triazole deriva-

Table 1. Fluorescence parameters of compounds **I–III** ($c = 10^{-4}$ M, λ_{excit} = 270 nm, slit width 15/15 nm) and **IV–VII** ($c = 10^{-3}$ M, λ_{excit} = 270, 520 nm, slit width 15/15 nm), DMSO, 20°C[a]

Comp. no.	λ_{ex}, nm	S_{ex}	D (λ_{excit} = 270 nm, l = 1 cm)	S_{ex}/D	$\Phi \times 10^5$
I	270	12	2	6	1.5
II	270	0.6	5.3	0.1	0.03
III	270	1	2	0.5	0.1
IV	270	990	0.5	2000	50
	520	11.1	0.004	2800	150
V	270	930	0.05	18600	460
	520	13.6	0.003	4500	240
VI	270	280	0.13	2200	50
	520	0.4	0.001	400	120
VII	270	5500	0.21	26200	1360
	520	0.4	0.0001	4000	590

[a] Hereinafter: S_{ex} stands for the light sum, D is the optical density, and Φ is the fluorescence quantum yield.

tives in propan-2-ol with a concentration of 10^{-4} M. A few differences included the lack of some bands in the luminescence and fluorescence excitation spectra, as well as displacement of some luminescence maxima, which may be attributed to the solvent effect (Fig. 4).

Two regions can be clearly distinguished in the luminescence excitation spectra of all the examined compounds. One of these is located in the visible and ultraviolet areas (excitation with UV light), and the other, in the red area (excitation with green light). The red luminescence, regardless of its character and nature, is unlikely to correspond to the *p*-nitrophenyl fragment, for it is also intrinsic to derivatives having no such fragment. Moreover, the red component is much more intense for bromo-substituted triazoles. Therefore, we believe that luminescence in the red region corresponds to emission from triplet excited triazole fragments. Increase in its intensity upon replacement of hydrogen by bromine is the result of heavy atom effect which favors triplet–singlet transitions. We can conclude that fluorescence is observed in the blue region and that phosphorescence is observed in the red region. This conclusion somewhat contradicts the luminescence spectra of deoxygenated solutions (by purging with argon), which were characterized by reduced emission intensity from the expected triplet level. A reasonable explanation implies that the lifetime of triazole molecule in the triplet excited state is very short. Analogous pattern is observed, e.g., for triplet excited molecules of some ketones which are not deactivated by dissolved oxygen as well [19].

Solutions of **I**–**III** in DMSO change their color with time. Immediately after dissolution, these solutions are greenish; they turn green in a few minutes and then become blue or violet. Change of the color is accompanied by variation of the absorption spectra in the visible region, whereas the spectral pattern in the short-wave region remains almost unchanged. The absorption maxima shift by 2–5 nm (Fig. 5). It was surprising that variations of the color of solutions and correspondingly of visible absorption spectra are not reflected in the luminescence excitation spectra of compounds **I**–**III**. The positions of maxima (λ_{max} 270, 430–432, 512 nm) in the excitation spectra of bright green and violet solutions of **I**–**III** do not change, while their intensities change insignificantly. This suggests that the color changes as a result of chemical processes involving those chromophores which are not responsible for fluorescence. In fact, differently colored

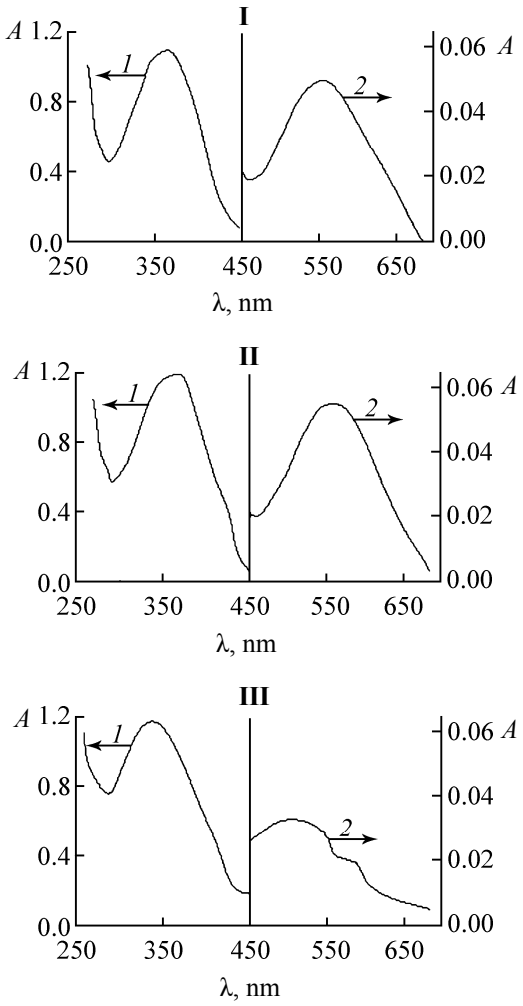


Fig. 5. Electronic absorption spectra of compounds **I**–**III** in the (*1*) ultraviolet and (*2*) visible regions ($c = 10^{-4}$ M, $l = 2$ mm, solvent DMSO, 20°C).

solutions of **III** are characterized by similar fluorescence spectra (λ_{max} 337, 454–460, 550, 600 nm). The color is also strongly affected by temperature and irradiation. Photolysis of solutions of **I**–**III** under irradiation with an SVD-120 mercury lamp leads to appearance of yellow color whose intensity increases upon prolonged irradiation, whereas the fluorescence intensity simultaneously decreases. After irradiation over a period of 2, the solutions become rich bright yellow, and their fluorescence intensity becomes vanishingly small (at a noise level). Presumably, irreversible change of color upon photolysis is related to oxidation processes. Taking into account that the sulfur atom in the thietane ring of compound **III** occurs in the maximal oxidation state, oxidation of other fragments, e.g., hydrazino group, may be presumed.

Table 2. Fluorescence parameters of tryptophan ($c = 10^{-5}$ M) at different slit widths of monochromator (SM-2203, DMSO, 20°C)

Slit width, *d*, nm	S_{ex}	D (λ_{excit} = 260 nm, l = 1 cm)	S_{ex}/D	Φ
15/15	1240	0.0234	52992	0.13
10/10	586	0.0234	25043	0.13
10/5	185	0.0234	7906	0.13

Unlike compound **III**, the sulfoxide group in the thietane ring of **II** is capable of being oxidized to sulfone. Photolysis of **II** is accompanied by appreciable variations in the fluorescence excitation spectra. After UV irradiation over a period of 30 min, the absorption pattern typical of the initial solution (λ_{max} 310, 425, 465 nm) disappears, and a diffuse band with its maximum at λ 400 nm arises. These variations should inevitably be reflected in the fluorescence spectra. In fact, the fluorescence spectrum of **II** before irradiation displayed radiative transitions with their maxima at λ 315 and 445 nm; after irradiation over a period of 30 min, the corresponding maxima were observed at λ 364 and 408 nm. In addition, the emission intensity changed considerably. Unlike sulfoxide **II**, the fluorescence intensity of triazole **VI** did not decrease after irradiation; by contrast, it increased. The fluorescence quantum yields before and after irradiation were 3×10^{-7} and 37×10^{-7}, respectively. As noted above, the fluorescence quantum yield for compound **III** was thrice as high as that for **II**. We can conclude that both variations in the excitation and emission spectra and increase in the fluorescence quantum yield after photolysis result from oxidation of the sulfoxide sulfur atom to sulfone and that this process involves the chromophore responsible for fluorescence.

EXPERIMENTAL

HPLC analysis was performed on a Shimadzu LC-20 instrument equipped with a spectrophotometric diode matrix detector and a 250×4.6-mm column packed with Luna C18 (grain size 5 μm; Phenomenex, USA); isocratic elution, water–acetonitrile (50:50), flow rate 1 ml/min; detection at λ 254 and 350 nm. The ^{13}C and ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer at 75.5 and 300 MHz, respectively. The ^{13}C NMR spectra were measured with broad-band decoupling from protons and with *J* modulation (JMOD); DMSO-d_6 and acetone-d_6 were used as solvents, and tetramethylsilane was used as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT 95 XP mass spectrometer (ion source temperature 200°C; direct sample admission into the ion source on heating from 50°C to 270°C at a rate of 22 deg/min). The precise *m*/*z* values were determined in the range from 1 to 1000 a.m.u. at a resolution of 10000 at 10% of peak height of all significant ions formed in the ion source) using peak matching technique; perfluorokerosene was used as reference. The electronic structure of compounds was calculated at the RHF/3-21G* level of theory (PC Gamess 7.0) with preliminary optimization of geometric parameters.

The electronic absorption spectra were measured on a Specord M-400 spectrophotometer (Carl Zeiss Jena). The fluorescence emission and fluorescence excitation spectra were recorded on an SM-2203 spectrofluorimeter (*Solar*, Minsk, Belarus); spectral range 220–820 nm; maximal admissible error Δp_λ in setting monochromator excitation and emission wavelength ±0.1 nm. Spectrophotometric measurements were performed in the ultraviolet (λ 200–400 nm) and visible regions (λ 450–700 nm) using 2-mm cells against the corresponding solvent. The emission spectra were recorded in the range from λ 250 to 700 nm; luminescence excitation wavelengths 270 and 520 nm; slit width 15/15 nm; 1-cm cell. The excitation spectra were recorded in the range λ 250–600 nm, luminescence wavelength 610 nm, slit width 10/10 nm. The fluorescence quantum yields were determined relative to D-tryptophan as reference according to the procedure described in [20] (Table 2).

1*H*-1,2,4-Triazole (**IV**) and 3,5-dibromo-1*H*-1,2,4-triazole (**V**) were synthesized according to the procedures reported in [21] and [22], respectively. The spectral parameters of compounds **IV** and **V** were consistent with published data.

3,5-Dibromo-1-(thietan-3-yl)-1*H*-1,2,4-triazole (VI) was synthesized as described in [23]. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.77 d.d (2H, *cis*-CH_2S, J = 8.8, 9.4), 3.98 d.d (2H, *trans*-CH_2S, J = 8.8, 9.0), 6.10–6.18 m (6-H), ^{13}C NMR spectrum, δ_C, ppm: 33.59 t (C^7, C^8), 54.53 d (C^6), 140.81 (C^5), 127.84 (C^3).

3-Bromo-1-(thietan-3-yl)-1*H*-1,2,4-triazol-5-ylhydrazine (VII). Hydrazine hydrate, 1.30 g of a 56.8% solution, was added to 1.02 g of 3,5-dibromo-1-(thietan-3-yl)-1,2,4-triazole in 25 ml of butan-1-ol, and the mixture was heated for 1 h under reflux and evaporated to dryness under reduced pressure. The re-

sidue was treated with 20 ml of distilled water (2 × 10 ml), and the solvent was distilled off under reduced pressure to remove excess hydrazine hydrate. The precipitate was washed with water and dried. Yield 0.75 g (75%), mp 175–176°C (from water). IR spectrum, ν, cm^{-1}: 1654 (C=N); 3028, 3142, 3208 (N–H). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.24 d.d (2H, *cis*-CH_2S, *J* = 8.7, 9.0), 4.07 d.d (2H, *trans*-CH_2S, *J* = 9.0, 9.2), 5.34–5.70 m (6-H), 7.6 br.s (NH, NH_2). ^{13}C NMR spectrum, δ_C, ppm: 34.60 t (C^7, C^8), 55.65 d (C^6), 131.69 s (C^5), 139.41 s (C^3).

1-[3-Bromo-1-(thietan-3-yl)-1*H*-1,2,4-triazol-5-yl]-2-[1-(4-nitrophenyl)ethylidene]hydrazine (I). *p*-Nitro-acetophenone, 0.73 g, was added to a solution of 1.00 g of 3-bromo-1-(thietan-3-yl)-1*H*-1,2,4-triazol-5-ylhydrazine in 25 ml of ethanol. The mixture was heated for 2 h under reflux and cooled, and the precipitate was filtered off, washed with water, and dried. Yield 1.42 g (89%), mp 182–184°C (from butan-1-ol). IR spectrum, ν, cm^{-1}: 1378, 1504 (NO_2); 1612 (C=N); 3350 (N–H). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.55 s (3H, CH_3), 3.89 d.d (2H, *cis*-CH_2S, *J* = 8.8, 8.9), 4.03 d.d (2H, *trans*-CH_2S, *J* = 8.9, 9.1), 6.11–6.32 m (6-H), 8.05 d and 8.31 d (2H each, H_{arom}, *J* = 8.2), 9.62 br.s (NH). ^{13}C NMR spectrum, δ_C, ppm: 13.66 q (C^{13}), 33.59 t (C^7, C^8), 54.50 d (C^6), 124.53 d (C_{arom}), 127.81 d (C_{arom}), 137.83 (C^5), 145.18 (C_{arom}), 148.15 (C_{arom}), 148.61 (C^3), 153.32 (C^{12}). Mass spectrum, *m*/*z* (I_{rel}, %): 396 (29) $[M]^+$, 73 (100), 324 (93.8), 163 (12), 117 (39.3), 76 (21.2), 350 (10).

1-[3-Bromo-1-(1-oxo-λ⁴-thietan-3-yl)-1*H*-1,2,4-triazol-5-yl]-2-[1-(4-nitrophenyl)ethylidene]hydrazine (II). *p*-Nitroacetophenone, 0.73 g, was added to a solution of 1.06 g of 3-bromo-1-(1-oxo-λ⁴-thietan-3-yl)-1*H*-1,2,4-triazol-5-ylhydrazine in 50 ml of ethanol. The mixture was heated for 1.5 h under reflux and cooled, and the precipitate was filtered off, washed with water, and dried. Yield 1.50 g (91%), mp 246–248°C (from 1,4-dioxane). IR spectrum, ν, cm^{-1}: 1340, 1504 (NO_2); 1598 (C=N); 3280–3600 (N–H). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.52 s (3H, CH_3), 3.77 d.d (2H, *cis*-CH_2SO, *J* = 8.3, 8.7), 3.97 d.d (2H, *trans*-CH_2SO, *J* = 5.6, 8.7), 6.19–6.23 m (1H, 6-H), 8.10 d and 8.32 d (2H each, H_{arom}, *J* = 7.9), 9.34 br.s (NH). ^{13}C NMR spectrum, δ_C, ppm: 13.69 q (C^{13}), 56.73 t (C^7, C^8), 56.80 d (C^6), 123.60 d (C_{arom}), 126.88 d (C_{arom}), 136.78 (C^5), 143.94 (C_{arom}), 146.88 (C^3), 147.07 (C_{arom}), 153.31 (C^{12}). Mass spectrum, *m*/*z* (I_{rel}, %): 412 (68.2) $[M]^+$, 89 (4.2), 324 (8.2), 163 (42.5), 117 (100), 76 (47.2), 366 (8.1), 349 (6.8).

1-[3-Bromo-1-(1,1-dioxo-λ⁶-thietan-3-yl)-1*H*-1,2,4-triazol-5-yl]-2-[1-(4-nitrophenyl)ethylidene]hydrazine (III). Hydrochloric acid, 0.6 ml, and *p*-nitro-acetophenone, 0.73 g (4.4 mmol), were added to a solution of 1.13 g of 3-bromo-1-(1,1-dioxo-λ⁶-thietan-3-yl)-1*H*-1,2,4-triazol-5-ylhydrazine in a mixture of 50 ml of ethanol and 10 ml of water. The mixture was heated for 1 h under reflux and cooled, and the precipitate was filtered off, washed with water, and dried. Yield 1.27 g (75%), mp 263–265°C (from 1,4-dioxane). IR spectrum, ν, cm^{-1}: 1138, 1318 (SO_2); 1142, 1588 (NO_2); 1612 (C=N); 3280, 3304 (N–H). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.25 s (CH_3, *cis*), 2.50 s (CH_3, *trans*), 3.38 d.d (2H, *cis*-CH_2SO_2, *J* = 4.4, 4.8), 4.70 d.d (2H, *trans*-CH_2SO_2, *J* = 4.0, 4.4), 5.71–5.82 m (6-H), 8.25 d (2H, H_{arom}, *J* = 7.8), 8.33 d (2H, H_{arom}, *J* = 7.8), 8.30 d (2H, H_{arom}, *J* = 7.9), 7.41 d (2H, H_{arom}, *J* = 7.9). ^{13}C NMR spectrum, δ_C, ppm: 13.70 q and 18.43 q (CH_3), 39.54 d (C^6), 70.71 t (C^7, C^8), 123.40 d (C_{arom}), 123.41 d (C_{arom}), 126.86 d (C_{arom}), 127.69 d (C_{arom}), 136.84 (C^5), 140.18 (C_{arom}), 143.93 (C_{arom}), 147.30 (C_{arom}), 148.05 (C^3), 154.18 and 155.92 (C^{12}). Mass spectrum, *m*/*z* (I_{rel}, %): 428 (60.6) $[M]^+$, 105 (13.1), 324 (15.1), 163 (33.7), 117 (100), 76 (57.7), 382 (3.1).

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