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Structure and photochromism of 2-(*N*-acyl-*N*-arylaminomethylene)benzo[*b*]thiophen-3(2*H*)-ones

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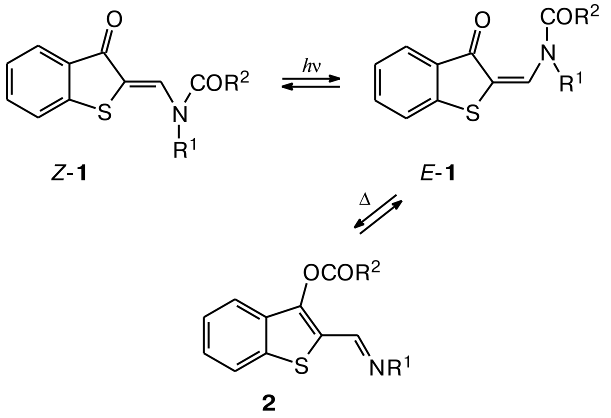
It was shown by electron absorption spectroscopy and X-ray diffraction analysis that steric strains in photochromic 2-(*N*-acyl-*N*-arylaminomethylene)benzo[*b*]thiophen-3(2*H*)-one molecules *ortho*-substituted in the *N*-phenyl ring increase the quantum yield of the N→O photoinduced rearrangement in accord with an increase in the steric constant of the *ortho*-substituent.

Key words: benzo[*b*]thiophene, ketoenamines, photochromic compounds, quantum yield, steric constant.

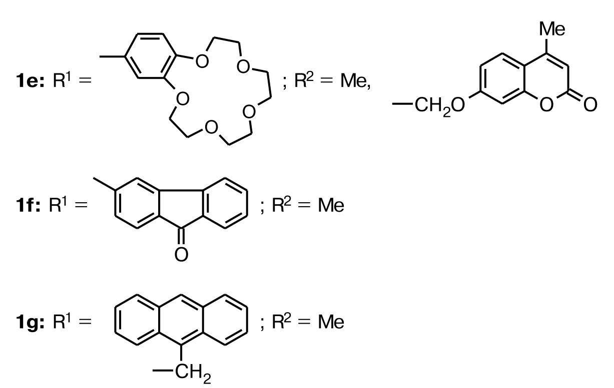
Photochromism of 2-(*N*-acyl-*N*-arylaminomethylene)benzo[*b*]thiophen-3(2*H*)-ones (**1**) is based on photoinitiated *Z*/*E*-isomerization relatively to the C=C bond followed by the thermal N→O migration of the acyl group (Scheme 1).[1,2]

Compounds of this type (λ_{max} (**1**) > λ_{max} (**2**)) are of interest as systems with negative photochromism,[3,4] whose molecules can accumulate the light energy released during the catalytically controlled process **2** → **1**. A wide variability of their structures also predetermined a possibility of using ketoenamines **1** as chemosensors for metal cations[5,6] (**1e**), molecular switches of an optical signal[7] (**1f**), and fluorescent sensors for a change of the pH of a medium[8] (**1g**) acting according to principle of the PET effect.[9] Reasons for the appearance of chiral properties of ketoenamines **1** *ortho*-substituted in the *N*-phenyl ring were studied.[10] The examples presented show that the structure of a molecule of the type **1**, in particular, spatial interactions between the *N*-aryl and *N*-acyl substituents and the heterocyclic moiety, can exert a determining effect on the spectral luminescence properties and photochromism of these compounds. Nevertheless, a relationship between steric interactions in the ground state in molecules of this type and their spectral and photochemical properties (λ_{max}, ε_{max}, λ_b,* $\varphi_{1\to2}$) has not been studied up to date. It can be useful to establish such a relationship for design of chiral chemosensors or switches of an optical signal. According to this, the following tasks of the present

Scheme 1



1a—d: R^1 = 2-R^3-C$_6$H$_4$, R^2 = Me, R^3 = F (**a**), Cl (**b**), Br (**c**), I (**d**)



1e: R^1 = ; R^2 = Me,

1f: R^1 = ; R^2 = Me

1g: R^1 = ; R^2 = Me

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* Long-wave absorption boundary λ_b with $\varepsilon \approx 1.0$ L mol^{-1} cm^{-1}.

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work were stated: (1) synthesis of a series of ketoenamines **1a—c** *ortho*-substituted in the *N*-phenyl ring; (2) establishment of their structure and specific features of photoinitiated reactions (see Scheme 1) depending on a steric constant υ of the *ortho*-substituent.

Results and Discussion

Compounds **1a—c** were synthesized by the condensation of 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde with the corresponding amines in acetonitrile followed by the acylation of ketoenamines **3a—c** that formed with acetyl chloride in the presence of triethylamine. According to the data of IR and ^{1}H NMR spectroscopies, they have a structure of *N*-acylated ketoenamines and exist in the *Z* form. Their IR spectra contain absorption bands of the amidic (1710—1715 cm^{-1}) and exocyclic (1675—1680 cm^{-1}) carbonyl groups. In the ^{1}H NMR spectra in CDCl$_3$, the signal of the methinic proton lies in the region characteristic of *Z* structures (δ 8.9).[10] The electronic absorption spectra (EAS) exhibit bands in a region of 423—429 nm typical of *Z*-ketoenamine isomers of the type **1**. In toluene, which is characterized by a low solvent polarity E_T,[11] the position of λ_{max} and the intensity ε_{max} of the long-wave absorption maximum depend weakly on the steric constant of the *ortho*-substituent υ.[12] However, in DMSO, which is a solvent with high E_T, the following regularity is observed: λ_{max} and especially ε_{max} increase in parallel with υ (Table 1). The quantum yields of photoinitiated transformations increase in the same direction (see Scheme 1). The highest quantum yield φ = 0.41 is observed for ketoenamine **1d** with the bulkiest *ortho*-substituent, *viz.*, iodine atom. Evidently, maximum steric interactions affect the simple and double bond lengths and interatomic distances in molecule **1d**. These interactions also determine the shape and intensity of the absorption band of the *O*-acetyl isomers of ketoenamines **2a—d**, which are formed in the photoinitiated process (see Scheme 1). For the least bulky substituent in the *ortho*-position of the phenyl ring R = F, the absorption maximum of isomer **2a** is typical of bands of this type[2] and comparable in intensity with a shorter-wave maximum of 313 nm (Fig. 1), whereas in the case of R = I, steric interactions result in the situation when this band experiences a hypsochromic effect and appears as an additional inflection of the shorter-wave band at 317 nm (Fig. 2). All these data indicate strong steric interactions and the acoplanarization of structures **1d** and **2d**.

Table 1. Spectral and photochemical characteristics of ketoenamines **1** ($R^1 = 2\text{-}R^3C_6H_4$, R^2 = Me)

Compound	R^3	υ	Solvent	EAS, λ_{max}/nm ($\varepsilon_{max}\cdot10^{-4}$/L mol^{-1} cm^{-1})	$\varphi_{1\to2}$
1a	F	0.27	Toluene	307 (2.44), 423 (1.24)	0.14
			DMSO	310 (1.31), 428 (0.62)	
1b	Cl	0.55	Toluene	307 (2.22), 425 (1.10)	0.29
			DMSO	311 (1.68), 429 (0.80)	
1c	Br	0.65	Toluene	308 (2.40), 423 (1.21)	0.35
			DMSO	311 (1.86), 429 (0.94)	
1d	I	0.78	Toluene	309 (2.52), 427 (1.28)	0.41
			DMSO	312 (2.08), 431 (1.10)	

Note: υ is the steric constant, and $\varphi_{1\to2}$ is the quantum yield.

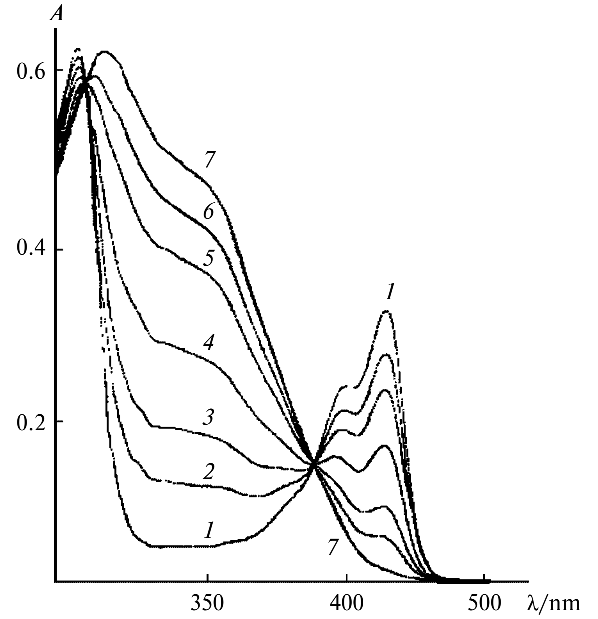

Fig. 1. Electronic absorption spectra of 2-[*N*-acetyl-*N*-(2-fluorophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (**1a**) in toluene before (*1*) and after irradiation for 5 (*2*), 10 (*3*), 20 (*4*), and 40 s (*5*) and 1 (*6*) and 2 min (*7*), λ_{rad} = 436 nm, $c = 2.5\cdot10^{-5}$ mol L^{-1}.

To verify this assumption, we carried out the X-ray diffraction study of 2-[*N*-acetyl-*N*-(2-iodophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (**1d**) containing an *ortho*-substituent with the highest steric constant υ = 0.78.[12]

The general view of a molecule of ketoenamine **1d** is shown in Fig. 3. The main distances and angles in the molecule are presented in Table 2. In crystal, the acetyl group at the nitrogen atom exists in the s-*trans*-position relatively to the C(1)—C(9) bond. The aryl group occupies the s-*cis*-position relatively to this bond, and steric interactions appeared between the sulfur atom and the C(13) and C(17) atoms of the *ortho*-iodophenyl moiety result in the mutually perpendicular arrangement of the benzothiophene and aryl rings, which decreases steric hindrances as much as possible. The dihedral angle between planes of these rings is 92.7°. Note that this is the maximum value of a dihedral angle of all values earlier determined by X-ray diffraction analysis for this type of compounds. For instance, this angle is 71° in

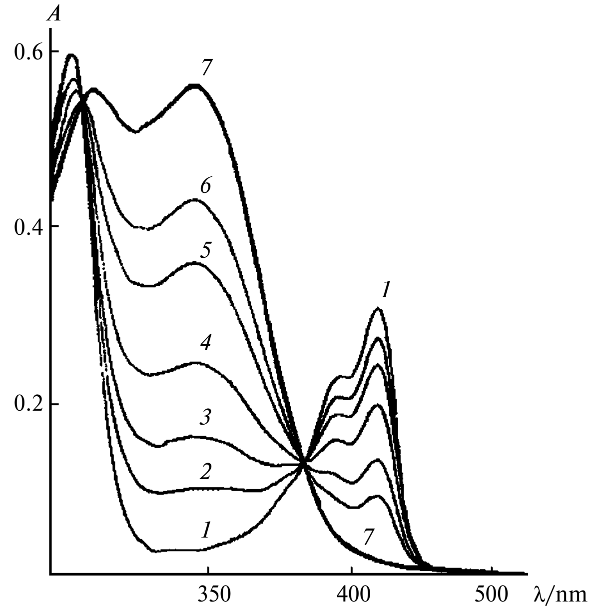

Fig. 2. Electronic absorption spectra of 2-[*N*-acetyl-*N*-(2-iodophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (**1d**) in toluene before (*1*) and after irradiation for 5 (*2*), 10 (*3*), 20 (*4*), and 40 s (*5*) and 1 (*6*) and 2 min (*7*), $\lambda_{\mathrm{rad}} = 436$ nm, $c = 2.5 \cdot 10^{-5}$ mol L^{-1}.

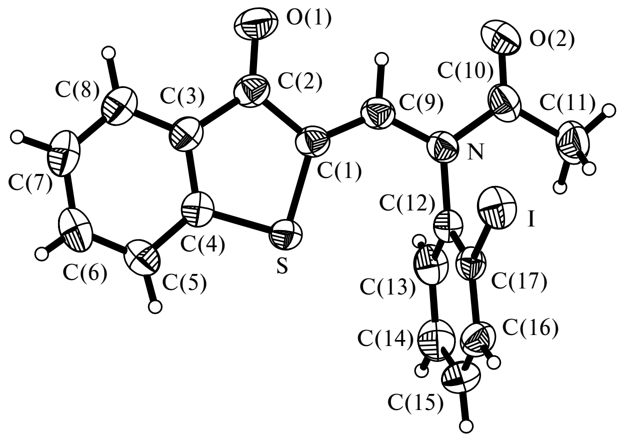

Fig. 3. Molecular structure of 2-[*N*-acetyl-*N*-(2-iodophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (**1d**).

Table 2. Main bond lengths (*d*) and bond angles (ω) in ketoenamine **1d**

Bond	*d*/Å	Angle	ω/deg
I—C(17)	2.088(3)	C(4)—S—C(1)	91.0(1)
S—C(4)	1.754(3)	C(9)—N—C(10)	118.5(3)
S—C(1)	1.765(3)	C(9)—N—C(12)	120.5(2)
O(1)—C(2)	1.219(4)	C(10)—N—C(12)	120.9(2)
O(2)—C(10)	1.195(4)	C(9)—C(1)—C(2)	118.7(3)
N—C(9)	1.370(4)	C(2)—C(1)—S	112.2(2)
N—C(10)	1.413(4)	C(9)—C(1)—S	129.1(2)
N—C(12)	1.438(4)	O(1)—C(2)—C(1)	124.8(3)
C(1)—C(2)	1.482(4)	O(1)—C(2)—C(3)	126.1(3)
C(1)—C(9)	1.337(4)	C(3)—C(2)—C(1)	109.1(2)
C(2)—C(3)	1.476(4)	C(4)—C(3)—C(2)	113.2(2)
C(3)—C(4)	1.385(4)	C(8)—C(3)—C(2)	125.9(3)
C(3)—C(8)	1.380(4)	C(8)—C(3)—C(4)	120.8(3)
C(4)—C(5)	1.392(4)	C(3)—C(4)—C(5)	120.3(3)
C(5)—C(6)	1.369(5)	C(3)—C(4)—S	114.3(2)
C(6)—C(7)	1.406(6)	C(5)—C(4)—S	125.4(2)
C(7)—C(8)	1.375(5)	C(6)—C(5)—C(4)	118.8(3)
C(10)—C(11)	1.496(5)	C(5)—C(6)—C(7)	121.1(3)
C(12)—C(13)	1.385(4)	C(8)—C(7)—C(6)	119.7(3)
C(12)—C(17)	1.388(4)	C(7)—C(8)—C(3)	119.4(3)
C(13)—C(14)	1.376(5)	C(1)—C(9)—N	130.5(3)
C(14)—C(15)	1.385(6)	O(2)—C(10)—N	120.5(3)
C(15)—C(16)	1.369(5)	O(2)—C(10)—C(11)	123.2(3)
C(16)—C(17)	1.385(4)	N—C(10)—C(11)	116.4(3)
		C(13)—C(12)—C(17)	119.7(3)
		C(13)—C(12)—N	119.4(3)
		C(17)—C(12)—N	120.9(2)
		C(14)—C(13)—C(12)	120.2(3)
		C(13)—C(14)—C(15)	119.8(3)
		C(16)—C(15)—C(14)	120.4(3)
		C(15)—C(16)—C(17)	120.2(3)
		C(16)—C(17)—C(12)	119.7(3)
		C(16)—C(17)—I	119.0(2)
		C(12)—C(17)—I	121.3(2)

ortho-methylphenyl-substituted ketoenamine (υ = 0.52)[12] studied previously. However, even for this arrangement, the C(1)—C(9)—N bond angle is increased to 130.5(3)°, which allows the interatomic distances S...C(12) (3.05 Å), S...C(13) (3.30 Å), and S...C(17) (3.43 Å) to remain comparable with standard intramolecular contacts between valence-unbonded atoms. Other atoms in the molecule, including those of the acetyl group, are virtually coplanar to the plane of the benzothiophene ring and form a planar conjugated molecular system. This is also favored by a hydrogen bond between the methylene H(9) hydrogen atom and carbonyl O(2) oxygen atom (2.27 Å), and the H(9)...O(1) distance is equal to 2.47 Å in this case. When a plane is passed through the C(1)...C(11), N, and O(1) atoms, all atoms listed lie in a root-mean-square plane with an accuracy of 0.03 Å, and the S and O(2) atoms shift from this plane to opposite directions by 0.12 and 0.14 Å. The iodine atom and six carbon atoms of the phenyl ring lie in the same plane with an accuracy of 0.01 Å.

The distribution of bond lengths in the planar part of molecule **1d** indicates that the electron density is delocalized in this part. The O(1)—C(2) bond length of 1.219 Å corresponds to a standard double bond in ketones of 1.23 Å, and the O(2)—C(10) bond (1.195 Å) is much shorter. The C(1)—C(9) bond of 1.337 Å is elongated and coincides with the lengths of similar C=C bonds in *trans*-diarylethylenes, and the N—C(9) bond (1.371 Å) is shortened, being medium between the ordinary N—C (1.472 Å) and double N=C (1.27 Å) bonds. The ordinary

C(1)—C(2) bond (1.481 Å) is also shortened. The configuration of bonds at the nitrogen atom is almost planar (the sum of angles at the nitrogen atom is equal to 359.9°), favoring the efficient conjugation of the free electron pair of the nitrogen atom with the rest π-system.

Thus, steric interactions of the *ortho*-substituent in the *N*-phenyl ring of 2-(*N*-acyl-*N*-arylaminomethylene)benzo[*b*]thiophen-3(2*H*)-ones with adjacent groups have been shown for the first time to change remarkably the spectral characteristics and increase the quantum yield of phototransformation of these compounds into the *O*-acetyl isomers in accord with an increase in the steric constant of the *ortho*-substituent.

Experimental

Electronic absorption spectra of compounds **1a—d** were recorded on a Specord M-40 spectrophotometer. Solutions were irradiated with a DRSh-250 mercury lamp using a set of changeable filters. Quantum yields for reactions in toluene were determined using potassium ferrioxalate.[13] IR spectra in Nujol were recorded on an Specord 75IR instrument, and ^{1}H NMR spectra were measured on a Varian Unity-300 instrument (300 MHz) in $CDCl_3$ using Me_4Si as the standard.

Synthesis of 2-[*N*-(2-halophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-ones (3a—d) (general procedure). A solution of the corresponding aniline (0.01 mol) in acetonitrile was added to a warm solution of 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde (0.01 mol) in acetonitrile. The mixture was heated in the presence of acetic acid (1 mL) for 30 min. A precipitate that formed on cooling was filtered off, washed with cold methanol, and crystallized from an appropriate solvent.

2-[*N*-(2-Fluorophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (3a). The yield was 83%, m.p. 178—179 °C. Found (%): C, 66.30; H, 3.61; N, 5.23. $C_{15}H_{10}FNOS$. Calculated (%): C, 66.41; H, 3.72; N, 5.16. IR, ν/cm^{-1}: 1650, 1620, 1450, 1410, 1375. ^{1}H NMR, δ: 7.00—7.60 (m, 7 H, Ar); 7.84 (d, 14 H, CH, *J* = 12.0 Hz); 8.00 (d, 1 H, Ar, *J* = 9.0 Hz); 12.44 (br.d, 1 H, NH, *J* = 12.0 Hz).

2-[*N*-(2-Chlorophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (3b). The yield was 76%, m.p. 165—166 °C. Found (%): C, 62.49; H, 3.89; N, 4.80. $C_{15}H_{10}ClNOS$. Calculated (%): C, 62.61; H, 3.50; N, 4.87. IR, ν/cm^{-1}: 1690, 1600, 1450, 1400, 1360. ^{1}H NMR, δ: 7.01—7.92 (m, 8 H, Ar); 8.6 (br.d, 1 H, CH, *J* = 8.0 Hz); 12.62 (br.d, 1 H, NH, *J* = 8.0 Hz).

2-[*N*-(2-Bromophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (3c). The yield was 79%, m.p. 176—177 °C. Found (%): C, 54.28; H, 3.12; N, 4.36. $C_{15}H_{10}BrNOS$. Calculated (%): C, 54.23; H, 3.03; N, 4.22. IR, ν/cm^{-1}: 1675, 1650, 1600, 1560, 1410, 1375. ^{1}H NMR, δ: 6.81—7.92 (m, 8 H, Ar); 8.58 (br.d, 1 H, CH, *J* = 12.0 Hz); 12.52 (br.d, 1 H, NH, *J* = 8.0 Hz).

2-[*N*-2-(Iodophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (3d). The yield was 69%, m.p. 198—199 °C. Found (%): C, 47.71; H, 2.58; N, 3.56. $C_{15}H_{10}NOS$. Calculated (%): C, 47.56; H, 2.68; N, 3.69. IR, ν/cm^{-1}: 1625, 1575, 1450, 1400, 1370. ^{1}H NMR, δ: 6.81—7.92 (m, 9 H, Ar); 12.36 (br.d, 1 H, NH, *J* = 8.0 Hz).

Acylated ketoenamines **1a—d** were synthesized according to a previously described procedure.[14]

2-[*N*-Acetyl-*N*-(2-fluorophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (1a). The yield was 94%, m.p. 178—179 °C. Found (%): C, 65.06; H, 3.92; N, 4.37. $C_{17}H_{12}FNO_2S$. Calculated (%): C, 65.16; H, 3.86; N, 4.47. IR, ν/cm^{-1}: 1710, 1680, 1600, 1560, 1255. ^{1}H NMR, δ: 2.60 (br.s, 3 H, Me); 7.20—7.90 (m, 8 H, Ar); 8.90 (br.s, 1 H, CH).

2-[*N*-Acetyl-*N*-(2-chlorophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (1b). The yield was 83%, m.p. 181—182 °C. Found (%): C, 61.79; H, 3.98; N, 4.12. $C_{17}H_{12}ClNO_2S$. Calculated (%): C, 61.91; H, 3.86; N, 4.25. IR, ν/cm^{-1}: 1715, 1680, 1600, 1570, 1250. ^{1}H NMR, δ: 2.20 (br.s, 3 H, Me); 7.15—7.84 (m, 8 H, Ar); 8.9 (br.s, 1 H, CH).

2-[*N*-Acetyl-*N*-(2-bromophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (1c). The yield was 94%, m.p. 170—171 °C. Found (%): C, 54.50; H, 3.97; N, 3.54. $C_{17}H_{12}BrNO_2S$. Calculated (%): C, 54.56; H, 3.23; N, 3.74. IR, ν/cm^{-1}: 1710, 1680, 1605, 1260. ^{1}H NMR, δ: 2.20 (br.s, 3 H, Me); 7.15—7.84 (m, 8 H, Ar); 8.90 (br.s, 1 H, CH).

2-[*N*-Acetyl-*N*-(2-iodophenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (1d). The yield was 82%, m.p. 183—184 °C. Found (%): C, 48.91; H, 2.70; N, 3.92. $C_{17}H_{12}INO_2S$. Calculated (%): C, 48.47; H, 2.87; N, 3.32. IR, ν/cm^{-1}: 1710, 1675, 1590, 1550, 1245. ^{1}H NMR, δ: 2.05 (br.s, 3 H, Me); 7.10—8.10 (m, 8 H, Ar); 8.94 (br.s, 1 H, CH).

X-ray diffraction study. Unit cell parameters of a crystal of **1d** and a three-dimensional array of intensities were obtained on a KM-4 four-circle automated diffractometer (Mo-Kα radiation, graphite monochromator). The yellow transparent crystals of **1d** were monoclinic, $C_{17}H_{12}INO_2S$, M = 421.24; a = 10.389(4), b = 8.405(2), c = 18.538(1) Å, β = 97.10(5)°, V = 1606.3(7) Å^3, Z = 4, ρ_{calc} = 1.742 g cm^{-3}, μ(Mo-Kα) = 2.13 mm^{-1}, space group $P2_1/n$.

Intensities of 3289 reflections were measured in an interval of angles $2\theta \le 52.2°$ using an ω/2θ scan mode from a single crystal 0.4×0.4×0.5 mm in size. After systematically extinguished reflections were excluded and intensities of equivalent reflections were averaged, the working array of measured $F^2(hkl)$ and $\sigma(F^2)$ was 3190 independent reflections of which 2814 reflections with $F^2 > 4\sigma(F^2)$ were used in subsequent calculations. The structure was solved by the direct method and refined by the full-matrix least-squares method against F^2 using the SHELXL-97 program for non-hydrogen atoms. The most part of H atoms were localized in the Fourier synthesis of difference electron density, and positions of several H atoms were calculated and further refined in the isotropic approximation. The final refinement parameters: R_1 = 0.031, wR_2 = 0.085 against 2814 observed reflections with $I \ge 2\sigma(I)$; R_1 = 0.0386, wR_2 = 0.087 against all 3190 measured reflections, GOOF = 1.096.

The full X-ray diffraction data, including coordinates of atoms and thermal parameters, were deposited at the Cambridge Structural Database.

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