



*Dedicated to Professor Eugen Segal
on the occasion of his 80th anniversary*

SYNTHESIS AND PROPERTIES OF NEW 2-BENZOTHAZOLE AND 2-BENZOXAZOLE-NITROARYL-SULFIDES**

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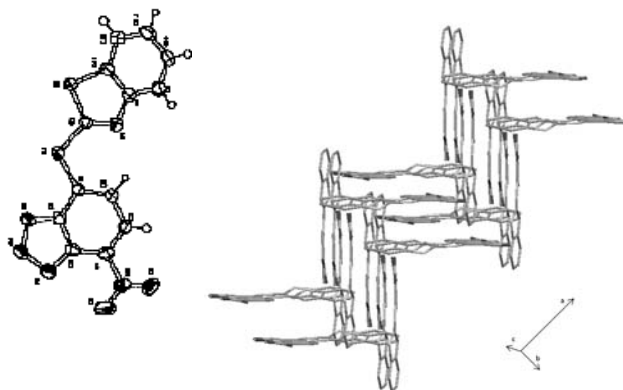
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2-Mercaptobenzothiazole (**1**) reacts with halo-nitro-aromatics (**2a–2g**) by nucleophilic substitution yielding crystalline sulfides (**3a–3g**). The following halo-nitro-aromatics were employed: **2a**, 4-chloro-7-nitrobenzofurazan or NBD-Cl; **2b**, picryl chloride; **2c**, 1-fluoro-2,4-dinitrobenzene; **2d**, 2-chloro-3,5-dinitropyridine; **2e**, 1,5-difluoro-2,4-dinitrobenzene; **2f**, 4-chloro-3,5-dinitro-trifluorotoluene, and **2g**, 2-chloro-3,5-dinitrotrifluorotoluene. Also 2-mercaptobenzoxazole (**4**) reacts with NBD-Cl (**2a**) yielding crystalline sulfide (**5**). Compounds **3a** and **5**, two benzofurazan derivatives, are fluorescent (**3a**, which has more intense fluorescence than **5**, was investigated by X-ray crystallography, differential scanning and thermal calorimetry, electronic absorption and emission spectrometry in solution and in solid state). All compounds were characterized by MS, ¹H-NMR, ¹³C-NMR, IR, electronic absorption spectrometry, and reverse-phase thin-layer chromatography which led to the determination of molecular hydrophobicities.



2-(4-Nitro-2,1,3-benzoxadiazole-7-yl)-thiobenzothiazole (brick-red crystals)

INTRODUCTION

Electronic push-pull effects in strongly dipolar molecules may lead to interesting theoretical and

practical applications¹⁻¹⁷ such as the record breaking dye-sensitized solar cells reaching over 12 % efficiencies using push-pull porphyrins.^{18,19} Recently, Türker, Bayar, and Balaban published a

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** Supplementary information on <http://web.icf.ro/rrch> or <http://revroum.getion.ro/>

DFT study of push-pull fulminenes and hexahelicenes.²⁰ Some benzothiazole derivatives have interesting biological activities.²¹⁻²⁴ 2-Mercaptobenzothiazole is used industrially for accelerating the vulcanization of synthetic rubber,^{21,23} and as a ligand in complexes with metallic cations.²⁵⁻²⁷ 2-Mercaptobenzoxazole and its derivatives have similar applications.²⁸⁻³³

The present communication describes eight push-pull molecules (**3a-3g** and **5**) containing one (poly)nitroaromatic electron-acceptor group and one or two electron-donor groups (2-thio-benzothiazole or 2-thio-benzoxazole). Compounds **3a-3g** were synthesized by reacting 2-mercaptobenzothiazole (2-sulfanylbenzothiazole **1**) with various halo-nitro-heteroaromatic (**2a**) and halo-nitro-aromatics (**2b-2g**). The compounds **3b,c** were known, but no data were provided on physico-chemical properties.^{34,35} Compound **5** was synthesized by reacting 2-mercaptobenzoxazole (2-sulfanylbenzoxazole **4**) with **2a**. The push-pull structural design of compounds **3a-3g** and **5** and their properties recommend these small organic molecules for possible nonlinear optical properties.

RESULTS AND DISCUSSION

Synthesis of new compounds 3a-3g and 5

Nucleophilic aromatic substitution proceeds readily in haloaromatics that contain electron-withdrawing groups, such as **2a-2g** indicated in the Abstract. The benzofurazan group has an electron-withdrawing power that is comparable to that of a picryl (2,4,6-trinitrophenyl) group.³⁶⁻³⁹ When the nucleophile 2-mercaptobenzothiazole (**1**) was reacted with the electrophiles **2a-2g**, the reaction products **3a-3g** were obtained in yields that varied between 60 and 95%. A similar procedure was applied for the synthesis of compound **5** by reaction of 2-mercaptobenzoxazole **4** with **2a**; in this case the yield was 88% (Supplementary information, Experimental part). Structures of **3a-3g** and **5** may be seen in Fig. 1.

Thermal properties of compounds 3a-3g and 5

Among compounds **3a-3g**, the first one presents differences from the other ones: **3a** is fluorescent, and appears in two crystalline forms, yellow and brick-red crystals, formed spontaneously on evaporating the organic solvent. These two types

of crystals (with the same ESI-MS, after dissolution) can be separated manually. Both types of crystals produce yellow solutions with the same NMR and electronic absorption spectra; the thin-layer chromatography (TLC, on silica gel TLC-F₂₅₄ plates with toluene as eluent) yields a single spot for solutions of both types of crystals. However, crystals of **3a** behave differently in solid state by differential scanning calorimetry (DSC) and differential thermal gravimetry (DTG): (i) for the yellow crystals, DSC and DTG indicate a melting point at 147.8°C (148-149°C in open capillary), and three thermal effects at 128.5°C (endothermal), 133.6°C (exothermal), and 150.7°C (endothermal) with three onset temperatures (117.6°C, 130.8°C, and 147°C, respectively); (ii) for the brick-red crystals, the melting point is 151.6°C (154-156 °C in open capillary), and DSC shows only two thermal effects at 143.7°C (endothermal) and 155°C (endothermal), with two onset temperatures (140.7°C and 151.6°C, respectively); when several melting-cooling cycles were run, gradual interconversions were observed, affording mixtures of compounds.

The compound **5** by DSC analysis presents one thermal effect with onset at 167.3°C (endothermal); this value is similar to the melting point in open capillary (163.5-164.5°C). When several melting-cooling cycles were run, the compound decomposed.

Electronic absorption and fluorescence spectra of the synthesized compounds in solution

The results presented in Table S1 (Supplementary information, Electronic absorption and fluorescence spectra of the synthesized compounds) lead to the following observations: (i) for all compounds **3a-3g** and **5**, there is no correlation between λ_{\max} and $E_T(30)$ values; (ii) for compounds **3a-3g** a remarkable finding is that whereas most of the compounds have higher values for the longest wavelength absorption band in methylene chloride than in dimethylsulfoxide, for two compounds (**3d** and **3e**) the reverse is true (for **3a**, the maximum for the visible absorption band is practically the same); (iii) for compound **5**, the value for λ_{\max} is not affected by the solvent.

For compounds **3b-3g** and **5** if one compares their visible absorption bands in one and the same solvent with the same band of **3a**, the difference between the wavelength values ($\Delta\lambda_{\max}$, Table 1) indicates the bathochromic effect induced by the NBD moiety present in **3a**.

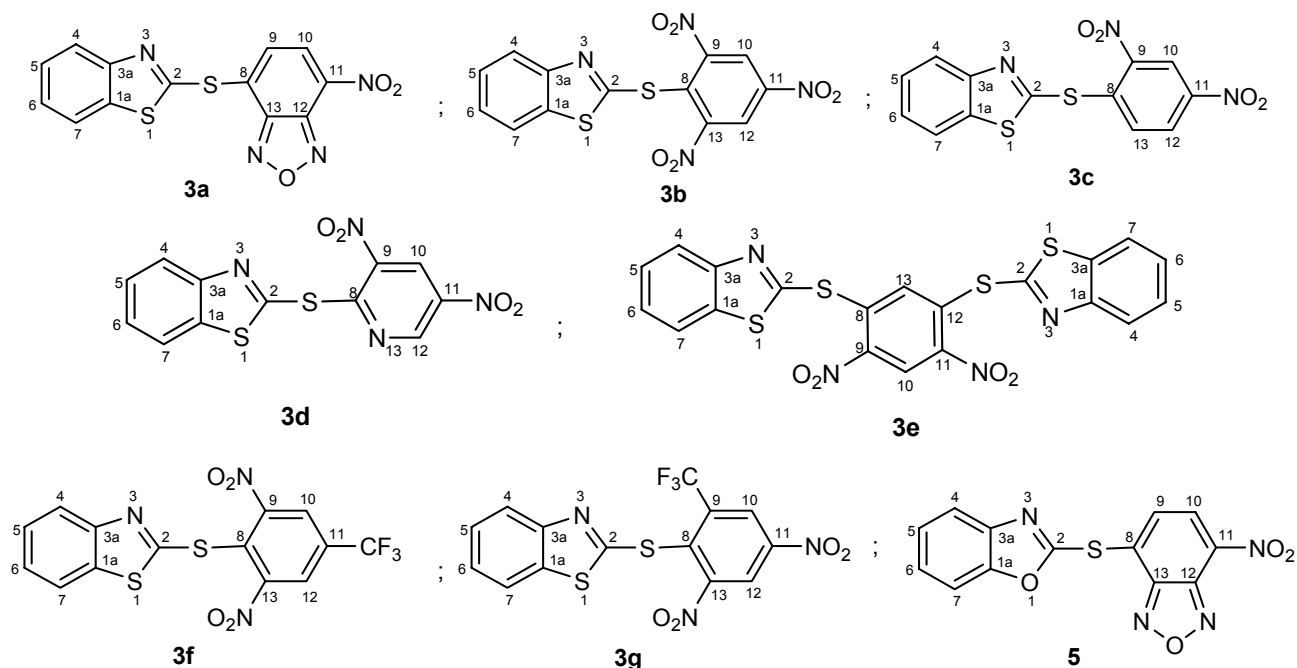
Fig. 1 – Structures of compounds **3a–3g** and **5**.

Table 1

Difference for the wavelength ($\Delta\lambda_{\max}$)^{a)}

Difference ($\Delta\lambda_{\max}$)	Value of $\Delta\lambda_{\max}$ (nm)	
	Dichloromethane	DMSO
λ_{\max} 3a - λ_{\max} 3b	7	28
λ_{\max} 3a - λ_{\max} 3c	69	66
λ_{\max} 3a - λ_{\max} 3d	92	82
λ_{\max} 3a - λ_{\max} 3e	92	63
λ_{\max} 3a - λ_{\max} 3f	34	77
λ_{\max} 3a - λ_{\max} 3g	30	77
λ_{\max} 3a - λ_{\max} 5	5	8

^{a)} for λ_{\max} see Table S1 (Supplementary information)

Table 2

The λ_{\max} (nm) and ϵ values ($L \times \text{mole}^{-1} \times \text{cm}^{-1}$) for two crystalline forms, yellow and brick-red of compound **3a**

Solvent	$E_T(30)$	λ_{\max} (ϵ)	
		Yellow	Brick-red
Dichloromethane	41.1	405 (11100)	405 (11600)
		279 (13400)	279 (13700)
Toluene	33.9	403 (9800)	403 (10100)
		283 (11900)	283 (12000)

In solution, the exceptional bathochromic effect and fluorescence of compound **3a** must be due to the benzofurazan moiety, which has a comparable electron-withdrawing effect to that of the picryl group.^{31,36-39} For methylene chloride solutions of

3a (yellow crystals and brick-red crystals at the same $\lambda_{\text{ex}} = 480$ nm and $\lambda_{\text{em}} = 526$ nm) the fluorescence for the former solutions afforded a higher quantum yield value ($\Phi = 3.014 \times 10^{-4}$), whereas the latter solution had a lower value

($\Phi = 2.029 \times 10^{-4}$), relatively to quinine bisulfate;^{40, 41} this behavior may be explained by the ϵ value (which is included in calculating the Φ value) which is higher for brick-red crystals than for yellow crystals using two solvents (Table 2).

For compound **5** the fluorescence in solution was very low.

Electronic absorption and fluorescence spectra of the synthesized compounds in solid state

Absorption and fluorescence measurements of the two kinds of **3a** crystals in solid state revealed differences which vanish in solution: the yellow and brick-red crystals have the same absorption maximum at 403 nm, but the brick-red crystals have in addition a marked shoulder at 466 nm. Compound **5** in solid state has two different absorption maxima at 383 nm and 440 nm.

For compounds **3a** and **5**, Fig. S1 (Supplementary information, Electronic absorption and fluorescence spectra of the synthesized compounds) presents the fluorescence in solid state: (i) for $\lambda_{\text{ex}} = 480$ nm, the yellow crystals of compound **3a** present a sharp fluorescence maximum at 522 nm, whereas the brick-red crystals have a blunt maximum at 551 nm; (ii) for $\lambda_{\text{ex}} = 373$ nm, compound **5** presents a lower fluorescence maximum at 501 nm.

EPR spectra

Interestingly, the brick-red crystals are the only ones to evidence in solid state a weak EPR signal

(Fig. S2, Supplementary information, EPR spectra), probably due the intermolecular donor-acceptor process, due to crystal packing (by electronic spectra, bathochromic shift at 466 nm).

Hydrophobic-hydrophilic balance

Reverse-phase TLC (RP-TLC) allows the determination of the molecular hydrophobicity (R_{M0}) (Table S2 and Fig. S3, Supplementary information, Hydrophobic-hydrophilic balance). The molecular hydrophobicity R_{M0} decreases in the following order of compounds **3g** > **3e** > **3f** > **3c** > **3b** > **3a** > **3d** > **5**. For the first three compounds, this is understandable because of the fluorine-containing groups⁴² or the extra benzothiazole group. For the last compound in this sequence, the presence of a pyridine ring able to be a hydrogen-bond acceptor also explains the enhanced hydrophilicity.

X-Ray crystallography

The behavior of compound **3a** affording two differently colored crystals prompted us to study it by X-ray crystallography. Only the structure of the compound with the brick-red crystals of **3a** could be solved by X-ray analysis. Fig. 2 presents the single crystal X-ray diffraction structure of compound **3a** as an ORTEP view. The molecule is nonplanar, with two planar conjugated moieties of the nitrobenzofurazan electron-acceptor group, and the electron-donor sulfide bridge with the benzothiazole moiety. Data are presented in Table 3.

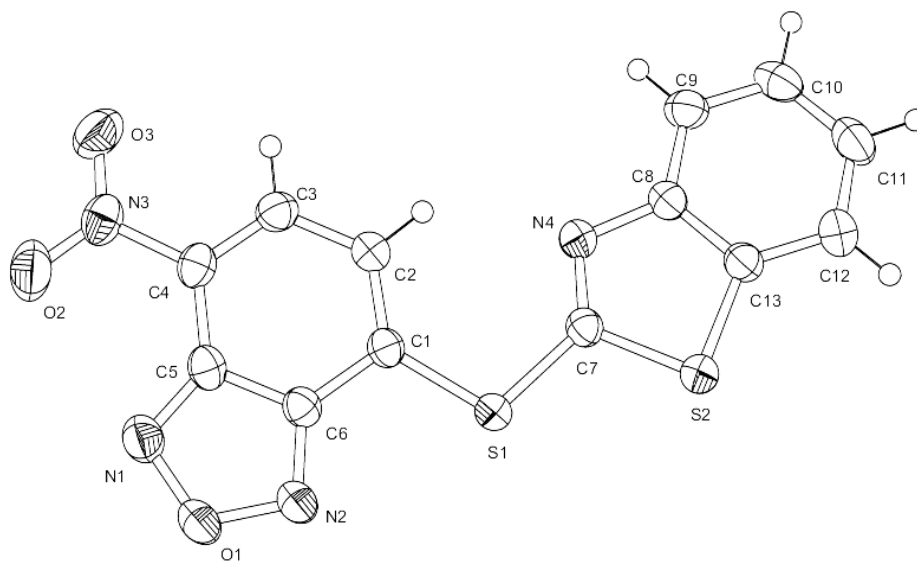


Fig. 2 – Ortep view of **3a** brick-red crystals. Thermal ellipsoids of non-H atoms are drawn at 50% probability level.

Table 3
X-Ray single-crystal data

Compound	3a
Formula	C ₁₃ H ₆ S ₂ O ₃ N ₄
M _w	330.34
Crystal system	monoclinic
Measurement temperature / K	293
Space group	P 2 ₁ /n
a/ Å	13.7650(2)
b/ Å	4.9564(1)
c/ Å	19.0550(4)
β/ °	91.674(1)
V/ Å ³	1299.47(4)
Z	4
Dc/g.cm ⁻³	1.689
Crystal colour	brick-red
Crystal size/mm ³	0.3*0.3*0.1
μ(Mo-Kα)/cm ⁻¹	4.29
N° of refl. Measured	14168
N° of unique refl.	3198
N° of observed refl. [F ² > 4σF ²]	2839
N° parameters refined	199
R ₁ [F ² > 4σF ²]	0.0316
wR ₁ [F ² > 4σF ²]	0.0804 ^a
R ₂ [all refl.]	0.0374
wR ₂ [all refl.]	0.0841
Goodness of fit [all refl.]	1.041
Residual Fourier/e. Å ⁻³	-0.283 ; +0.255

$$^a w=1/[\sigma^2(\text{Fo}^2)+(0.0365\text{P})^2+0.529\text{P}] \text{ where } \text{P}=(\text{Fo}^2+2\text{Fc}^2)/3$$

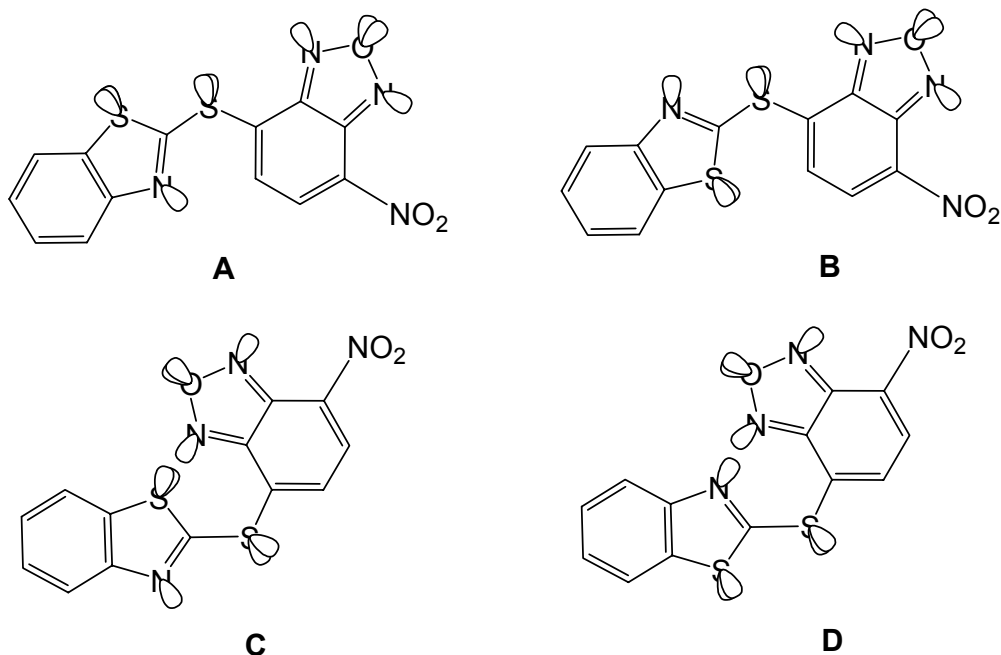


Fig. 3 – The hypothetical four possible planar rotamers of **3a** brick-red crystals.

If one considers the hypothetical four possible planar rotamers of **3a** shown in Fig. 3, it is evident that rotamers **C** and **D** have a more pronounced steric hindrance than **A** and **B**. In turn, among these latter rotamers, structure **A**, which is closer to

that observed experimentally, is the least encumbered by the unique lone electron pair of the thiazole nitrogen heteroatom than structure **B** with the two unshared electron pairs of the bulkier sulfur atom of the thiazole ring.

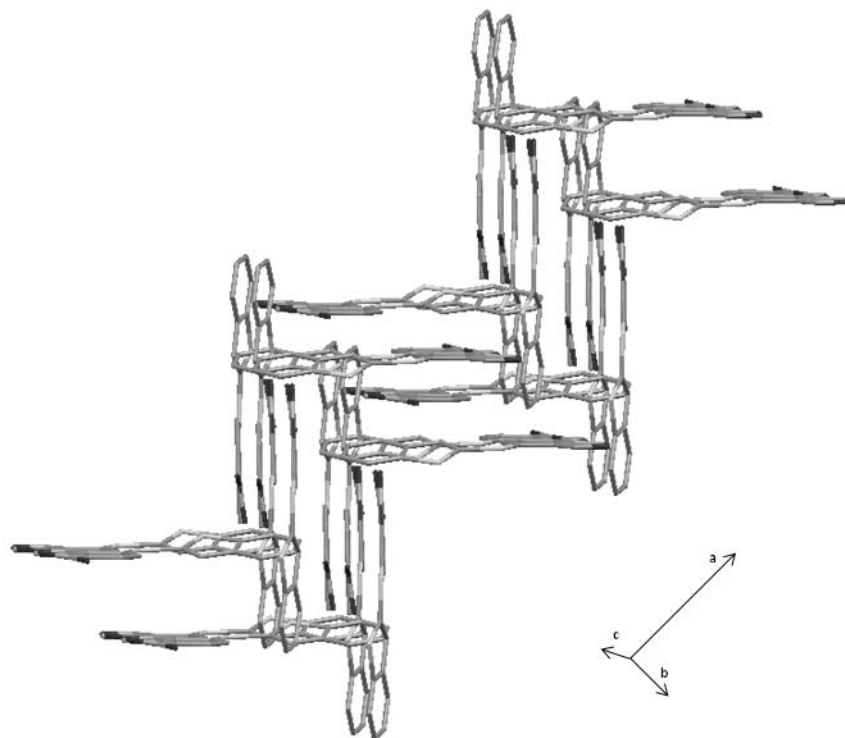
Fig. 4 – Crystal packing of **3a** brick-red crystals.

Table 4

Selected interactions within the crystal packing of **3a** brick-red crystals

CH/ π interactions	Distance C---C (Å)	Angle C-H---C (°)
	C10 ⁱ ---C3 ⁱⁱ = 3.750(2)	C10-H10 ⁱ ---C3 ⁱⁱ = 150.5(1)
	C3 ⁱ ---C10 ⁱⁱⁱ = 3.641(2)	C3-H3 ⁱ ---C10 ⁱⁱⁱ = 127.0(1)
π -stacking interactions	Distance Cg(n)-Cg(m) (Å)	Dihedral between rings n & m (°)
	Cg(1) ⁱ ---Cg(2) ^{iv} = 3.766(1)	0.65(7)
	Cg(3) ⁱ ---Cg(4) ^v = 3.981(1)	0.16(8)

Symmetry codes: ⁱ: x, y, z; ⁱⁱ: 3/2-x, -3/2+y, 1/2-z; ⁱⁱⁱ: 3/2-x, 1/2+y, 1/2-z; ^{iv}: x, 1+y, z; ^v: x, -1+y, z. Cg(1) = centroid of ring S2C7N4C8C13; Cg(2) = centroid of ring C8C9C10C11C12C13; Cg(3) = centroid of ring C1C2C3C4C5C6; Cg(4) = centroid of ring O1N1C5C6N2.

The torsion angle between the two substituents of the sulfide bridge is equal to 15.38(6)°. Within the crystal the molecules are associated by pairs in the same plane, the sulfur atom of the benzothiazole and the oxygen atom of the benzofurazan facing respectively the oxygen atom of the benzofurazan and the sulfur atom of the benzothiazole of a symmetry related molecule (distance S2–O1 is equal to 3.227(1) Å). Thus these weak interactions organize compound **3a** as two infinite perpendicular sheets expanding along the crystallographic planes with Miller indices (22–8–6) and (22–8–6), respectively (Fig. 4, a color version of the packing may be seen in the Fig. 4S, Supplementary information, Crystal data and X-Ray crystallography). This packing involves two kinds of interactions in the crystal: π -stacking

contacts between planes belonging to the same sheet and CH/ π contacts between molecules belonging to different sheets (Table 4).

Calculations

The starting point of this investigation was the molecular design involving the synthesis of push-pull molecules with an electron-acceptor group (polynitroaryl or nitrobenzofurazan, NBD) and an electron-donor group (2-sulfanyl-benzothiazole or 2-sulfanyl-benzoxazole). Compounds containing a NBD moiety are expected to present nonlinear optical effects.^{43,44} Indeed, the electronic absorption spectra of the seven new compounds **3a–3g** seem to confirm such nonlinear optical effects for the NBD-containing compound **3a**.

A computational study involving molecular orbitals of compounds **3a–3g** and **5** is presented (Table S3, Supplementary information, Calculations), including: excitation energy, oscillator strength (f , defined as the strength of the transition, which is proportional to the square of the transition state's dipole moment), and orbital composition. Sixty excited singlet states were taken into consideration; doubly-excited states were not considered because their energies were too high. On comparing third excited states, the results indicate that the oscillator strength and the excitation energy are higher for compounds **3a** and **5** that contain an NBD moiety, with the f value of 0.9381 for **3a** and with the excitation energy for **5** being the highest among all eight new compounds. Fig. S5 presents the transition $76 \rightarrow 85$ for compound **3a**.

CONCLUSIONS

Eight sulfides (thioethers), **3a–3g** and **5**, with one or two benzothiazole or benzoxazole groups were synthesized from 2-mercaptobenzothiazole or 2-mercaptobenzoxazole and halo-nitro-aromatics by S_NAr substitutions of halogen. Together with two previously known sulfides, a comparative study of properties for eight sulfides **3a–3g** and **5** was undertaken. Interestingly, only **3a** is fluorescent (because of the benzofurazan moiety); this compound also had other remarkable properties, namely it had the highest value for the longest-wavelength absorption band, and it appeared in two crystalline forms, yellow or brick-red crystals. Push-pull design of compounds **3a–3g** and **5** recommend them as having nonlinear optical properties, especially the compound **3a** and then compound **5** as revealed also by theoretical calculations of molecular orbitals.

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