Mendeleev Commun., 2026, **36**, 50–52

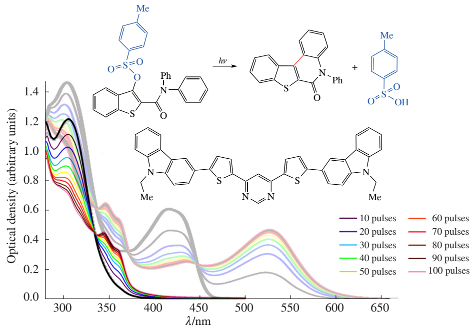
Photoacid generation from substituted benzo[*b*]thiophene-2-carboxanilides

Lubov G. Samsonova,[a] Natalya V. Izmailova,[a] Ruslan M. Gadirov,*[a] Roman A. Irgashev,[b] Nikita A. Kazin,[b] Yuriy A. Kvashnin,[b] Alexander S. Steparuk,[b] Gennady L. Rusinov[b] and Egor V. Verbitskiy[b,c]

[a] *Tomsk State University of Control Systems and Radioelectronics, 634021 Tomsk, Russian Federation. E-mail: grm882@yandex.ru*
[b] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 620137 Ekaterinburg, Russian Federation*
[c] *Ural Federal University, 620002 Ekaterinburg, Russian Federation*

DOI: 10.71267/mencom.7828

The photolysis of 3-chloro- and 3-sulfonato-substituted benzo[*b*]thiophene-2-carboxanilides was explored using 3rd harmonic Nd-YAG laser radiation (355 nm) in toluene. The acid production was monitored by the formation of the protonated form of 4,6-bis[5-(9-ethyl-9*H*-carbazol-3-yl)-thiophen-2-yl]pyrimidine serving as an indicator. The quantum yield of the acid produced had the order of 10^{-2} and depended on the structural characteristics of the molecules involved.



Keywords: photochemical acid generator, 6π-electron photocyclization, benzo[*b*]thiophene-2-carboxanilides, phototransformation, acid–base indicator.

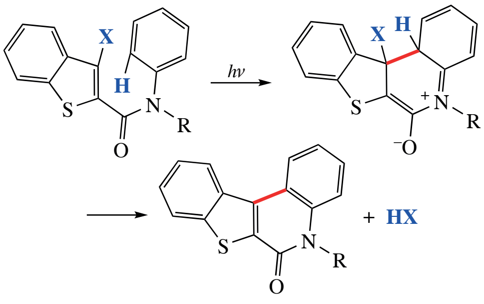
Photochemical acid generators (PAGs) are compounds that change upon light exposure to produce acids. They are essential materials in microlithography and cationic photopolymerization[1] and become popular in the field of biology, particularly in the synthesis of oligonucleotides.[2–5] As laser light sources become more widely available, it is essential to find PAGs that produce acid when exposed to a wavelength of 355 nm. This is important because Nd-YAG lasers equipped with a third-harmonic converter, which can generate this specific radiation, are becoming more affordable and widely adopted in optical systems for mask-free laser lithography and labeling. To date, numerous compounds have been studied for their ability to generate acids through photolysis.[6,7] Generally, PAGs can be classified into ionic and nonionic categories.

Ionic systems consisting of cationic and anionic components[8–12] typically include organic salts where groups such as BF_4^-, SbF_6^-, AsF_6^-, PF_6^-, and RSO_3^- serve as counter-anions. The photodissociation of these compounds occurs *via* a radical pathway, often requiring the extraction of a proton from the solvent to produce Brønsted or Lewis acid. These PAGs are known for over 100 years and have a wide range of stability and solubility. However, their application remains limited due to the narrow wavelength range in which they can be effectively used. Current developments in ionic PAGs focus on adjusting structural parameters to enable their use in the near-infrared region or through two-photon absorption techniques.[13,14]

Nonionic photochemical acid generators are commonly used to initiate polymerization processes because of their solubility in many solvents and their effectiveness within a polymer matrix. These compounds can be classified into three categories based on the type of dissociative bond they possess. Upon irradiation, they generate acidic compounds by forming stable photo-dissociated radicals from C–O, S–O, or N–O bonds. This process is followed by the release of proton from protonic solvent. Typically, nonionic PAGs belong to benzylic, sulfonic, and imino ester families.[15,16]

As mentioned above, the types of considered PAGs require a proton-donating environment, which is most often a solvent. However, many tasks exclude the use of such solvents, therefore, a new type of compound has been proposed that forms an acid molecule as a whole due to the 6π-electron photocyclization of the ring of the molecule during irradiation. During direct photolysis of such molecules, a proton and an acid residue are split off from the initial molecule and an acid molecule is formed without the participation of a solvent (Scheme 1).[17]

In this study, we examined benzo[*b*]thiophene derivatives that feature either a sulfonato group or chlorine atom at the



Scheme 1

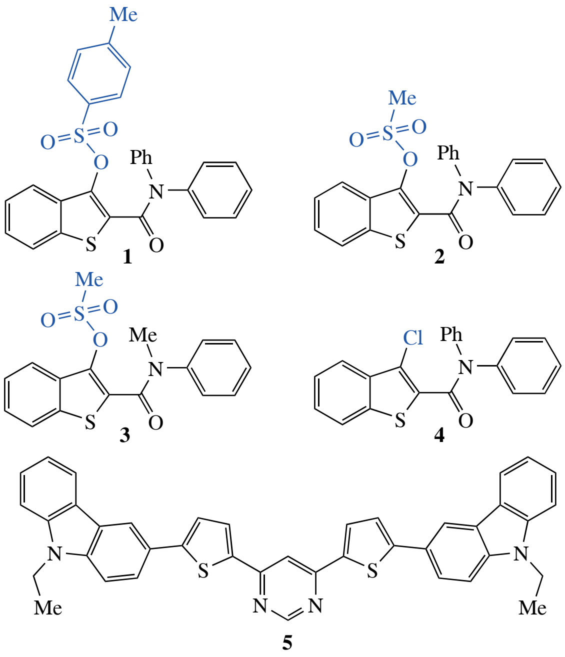


Figure 1 Structures of the studied compounds.

position 3 (Figure 1). Their synthesis and experimental details are given in Online Supplementary Materials.

According to the mechanism of electrophotocyclization, in the excited state there should be a cleavage of the 3-positioned C–O or C–Cl bond in the benzo[*b*]thiophene fragment with the formation of acidic anions RSO$_3^-$ or Cl$^-$, the abstraction of a proton from the phenyl group of the amide fragment with subsequent ring closure accompanied by the formation of sulfonic or hydrochloric acid, respectively. A pyrimidine derivative **5** (see Figure 1) was used to indicate the formation of the acid since it easily undergoes protonation thus colouring the solution crimson.[18]

Compounds that change their structure under acidic conditions are frequently employed in various applications. Examples include rhodamine B,[19] tetrabromophenol blue,[20,21] and phenolphthalein.[22] The use of compound **5** has proven to be an advantageous because it dissolves easily in organic solvents, and spectral properties of its protolytic forms (both neutral and protonated) fall within a spectral region that does not overlap with the absorption characteristics of the compounds being studied. Absorption and fluorescence spectra of compound **5** in the presence of dichloroacetic acid are given in Online Supplementary Materials, Figure S1.

The absorption of the compounds studied falls within the UV region with maxima at approximately 290–305 nm. The irradiation wavelength of 355 nm is near the edge of the absorption band, where the extinction coefficient at this wavelength (ε_{355}) is just under 1000 dm^3 mol^{-1} cm^{-1}. In contrast, for compound **3** this value is 10 times lower (Table 1). However, excited state transitions that occur away from the maximum of the absorption band result in significant phototransformation of the molecules being studied. Figure 2(*a*) illustrates the photolysis of compound **1**. Irradiation results in a decrease in the intensity of the main absorption band and an increase in optical density in the longer-wavelength region. The presence of an isosbestic point at 335 nm clearly indicates that we are detecting two substances, namely, the original compound **1** and the product of the photoreaction, which is most likely due to the photocyclization reaction. Figure 2(*b*) illustrates the photolysis of a mixture containing compounds **1** and **5**. The formation of a second product, an acid, is confirmed by the protonation of base **5** which is evidenced by a decrease in the intensity of its neutral form at 412 nm and an increase in the absorption of the protonated form at 530 nm. A similar pattern of photolysis is observed for compound **2**, as illustrated in Figures 3(*a*),(*b*).

Table 1 Spectral characteristics of the studied compounds in toluene.

Compound	λ_{abs}/nm	ε_{max}/ dm^3 mol^{-1} cm^{-1}	ε_{355}/ dm^3 mol^{-1} cm^{-1}	γ	φ
1	304	13 200	1100	0.072	0.02
2	305	12 300	920	0.06	0.008
3	288	12 330	90	0.018	0.009[a]
4	297	12 000	930	0.024	–

[a] Estimated after 520 irradiation pulses.

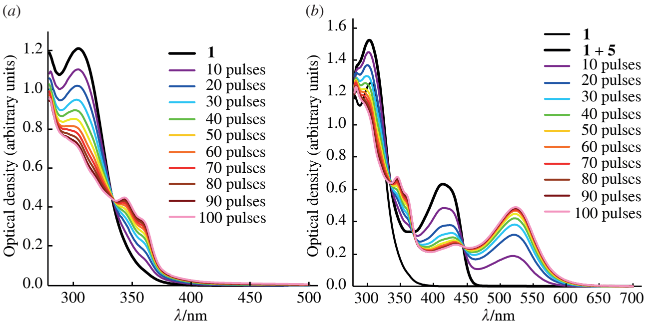


Figure 2 Photolysis of (*a*) compound **1** and (*b*) in a mixture with **5**.

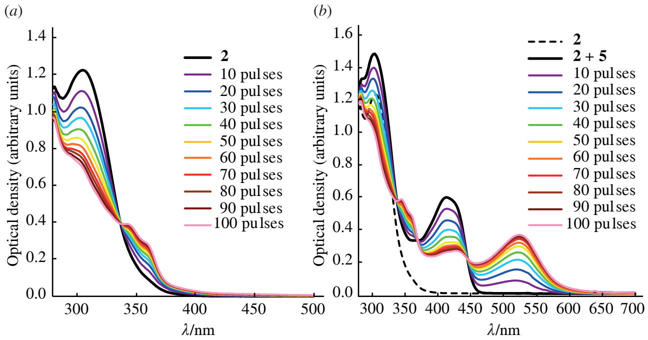


Figure 3 Photolysis of (*a*) compound **2** and (*b*) in a mixture with **5**.

The situation for compound **4** having a chlorine substituent is somewhat different (Figure 4). While the nature of the phototransformation and the formation of the photoproducts on the long-wavelength side are comparable to the previously discussed compounds, hydrochloric acid cannot be detected using indicator **5** whose absorption in the region of the protonated form (530 nm) is extremely small as shown in Figure 4(*b*). This may be due to both the lower efficiency of photogeneration of the acid of the compound with the Cl counterion and the lower strength of HCl in toluene against sulfonic acids HSO$_3$R.

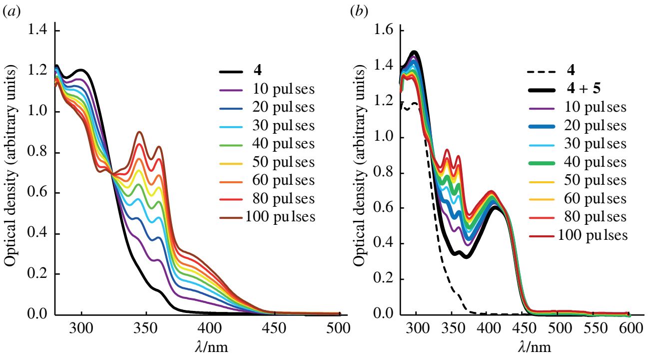


Figure 4 Photolysis of (*a*) compound **4** and (*b*) in a mixture with **5**.

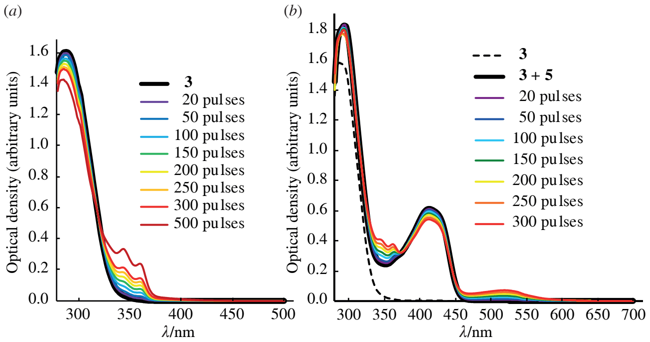


Figure 5 Photolysis of (*a*) compound **3** and (*b*) in a mixture with **5**.

The absorption of compound **3** occurs at the shortest wavelength as shown in Figures 5(*a*),(*b*). Consequently, the extinction at the irradiation wavelength is minimal, which means that a longer duration of irradiation is needed for the solution to begin changing colour in the presence of **5**.

During photolysis, the optical density at the irradiation wavelength (355 nm) increases significantly due to absorption by photoproducts. When calculating the value of quantum yield of phototransformations γ, the T value of the initial compounds was used. The γ was estimated after no more than ten excitation pulses when the effect of the products on the number of photons absorbed by the initial compounds is insignificant. The number of molecules that underwent the phototransformation was estimated by the drop in optical density at the maximum of the main absorption band also after ten irradiation pulses.

The γ of the initial compounds, determined from the equation S1 (see Online Supplementary Materials), is given in Table 1. Although it is of the same order (10^{-2}), its value depends on the nature of the acid residue as follows: 4-$MeC_6H_4SO_3$ > $MeSO_3$ > > Cl. It can be assumed that the strength of the C–O or C–Cl bond, which is broken during photolysis, is in the reverse order. Since the experiment shows that both acid and one spectrally registered product are formed during photolysis, it can be inferred that the calculated quantum yield γ represents the quantum yield of acid photogeneration.

During the combined irradiation of the photogenerators with compound **5** [see Figures 2(*b*)–5(*b*)], the processes of acid formation and protonation of **5** occur in parallel. The efficiency of formation of the protonated form of compound **5**, parameter φ, was estimated (see Table 1). For compound **4**, φ is not determined due to the large error in determining N_{Ph}. From the φ/γ ratio, one can roughly judge on the strength of the acid formed. For **1**, this ratio is 0.28, and for **2** it is 0.13, *i.e.*, $HSO_3C_6H_4Me$ is a stronger acid than HSO_3Me, and these acids are significantly stronger than HCl in toluene.

In summary, new photochemical acid generators based on sulfonic acids, which do not require a proton donor environment, have been synthesized and studied. The quantum yield for the photogeneration of the acid was estimated through direct photolysis of the compounds at a wavelength of 355 nm. It is on the order of 10^{-2}, with the values depending on the structure of the acid substituent, in the following order: 4-$MeC_6H_4SO_3$ > > $MeSO_3$ > Cl.

Compounds **1** and **2** allow for a soft acid effect when irradiated at 355 nm. Compound **3** also exhibits photochemical acid generation, but this substance is more effective when exposed to shorter wavelengths (shorter than 355 nm) because it has stronger absorption in this region. Despite the similarity of the molecular structure, compound **4** is a weaker photoacid generator.

This work was performed within the framework of the State Assignment of the Ministry of Science and Higher Education of the Russian Federation (project no. FEWM-2024-0001).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7828.

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Received: 16th May 2025; Com. 25/7828