Detritylation by Self-Contained Photoacid Generators on the Base of Substituted Benzo[b]thiophene-2-Carboxanilides under UV-Laser and Lamp Irradiation

Natalia V. Izmailova*, Lubov G. Samsonova, and Ruslan M. Gadirov
Tomsk State University of Control Systems and Radioelectronics, 40 Lenina av., Tomsk 634050, Russian Federation
*e-mail: nataliagoleinova@mail.ru

Abstract. New self-contained acid photogenerators based on substituted benzo[b]thiophene-2-carboxanilides were studied under irradiation with the 3rd harmonic of an Nd-YAG laser (355 nm) and an excimer XeCl lamp (308 nm) in toluene and methylene chloride solutions. The quantum yield of phototransformations of compounds during lamp and laser photolysis was estimated for both solvents. A model experiment was carried out using photogenerated acids to remove the dimethoxytrityl group from 5′-O-(4,4′-dimethoxytrityl)-2-deoxythymidine-3′-O-[O-(2-cyanoethyl)-N,N′-diisopropylphosphoramidite].

Keywords: acid photogenerators; 6π-electrocyclization; benzo[b]thiophene-2-carboxanilides; laser photolysis; detritylation.

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1 Introduction

Many technological processes such as polymerization initiation, deprotection during oligonucleotide synthesis, production of polymer coatings, resins, adhesives, inks and others require the participation of acid at a certain stage. Photogenerated acids have been used for these purposes for decades. Compounds – Photoacid generators (PAGs) – undergo photochemical transformations when exposed to light, one of the products of which is acid. PAGs are divided into two broad classes: ionic and nonionic. Among the ionic PAGs, the most popular are the onium salts of diaryliodonium and triarylsulfonium, which contain strong acid anions as counterions. These complexes have been known for over a century and can vary significantly in stability and solubility [1]. They are widely used in photoinitiation of cationic polymerization of epoxy monomers and other cationically polymerizable monomers such as vinyl esters, as well as in the manufacture of photoresists, photocurable coatings, printing inks, and adhesives. However, the narrow spectral range for excitation and the limited range of organic solvents, especially non-polar ones, limit their application in other areas.

Non-ionic PAGs have also been known for decades. Nonionic PAGs are mostly esters, and the most popular among them are iminosulfonates, imidosulfonates and benzylsulfonates. When irradiated with light, they generate carboxylic, sulfonic, phosphoric, and hydrohalic acids. A review of both types of PAG can be found in Refs. [1–3].

To form a Brønsted acid, both ionic and nonionic PAGs extract a proton from a proton-donating environment. When working with aprotic solvents, such PAGs are ineffective.

In the last decade, scientists have turned their interest to so-called “self-contained” compounds that generate both acid ions when irradiated. Such compounds are characterized by 6π-electrocyclization initiated by light. The mechanism of photoacid formation is shown in Fig. 1. One of the first works on photogeneration of acid through photo-electrocyclic ring closure was carried out on benzothiophene carboxanilides [4] Compounds of the terarylene series are also promising [5–8]. In our previous work [9], we investigated a number of new compounds from the class of benzothiophene carboxanilides with various substituents in the benzothiophene moiety with the formation of hydrochloric, methanesulfonic, and toluenesulfonic acids in toluene solutions. 4,6-Bis[5-(9-ethyl-9H-carbazol-3-yl)thiophen-2-yl]pyrimidine (IND) was used as an acid indicator, which readily forms a protonated form, giving the solution a crimson color. The compounds were irradiated with the 3rd harmonic of an Nd-YAG laser with a wavelength of 355 nm.

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In the present work, we expanded the set of PAGs and investigated them for deprotection of the dimethoxytrityl (DMT) group from 5′-O-(4,4′-dimethoxytrityl)-2′-deoxythymidine-3′-O-[O-(2-cyanoethyl)-N,N′-diisopropylphosphoramidite] (DMT-dT) which is commonly used in the phosphoramidite approach for oligonucleotide synthesis [10]. Two sources were used for irradiation: the 3rd harmonic of an Nd-YAG laser (355 nm) and an excimer XeCl lamp (308 nm). It should be noted that the excitation at 355 nm occurs in the red wing of the main absorption band far from the maximum, where the extinction coefficient is at best ~1000 $dm^3mol^{-1}cm^{-1}$, while the emission at 308 nm is close to the maximum of the absorption bands.

2 Experimental Part

The studied compounds were synthesized at the I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences and described in Ref. [9].

The structures of the molecules are shown in Fig. 1. Solutions of the compounds with a volume of 2 ml were irradiated in a standard quartz cuvette with a Nd^{3+}:YAG laser (type LQ529B, Solar Laser Systems, Republic of Belarus) with characteristics – 355 nm, 33 mJ/pulse, 0.17 J/cm^2, σ_{imp}=10 ns or an excimer XeCl lamp – 308 nm, type BD P (barrier discharge, portable). The excilamp has a cylindrical shape and is enclosed in a metal housing with an output UV window of 60 cm^2. The excilamp is developed at the Institute of High Current Electronics SB RAS [11–13]. The distance from the excilamp to the irradiated solution was 13 cm. The intensity of the incident radiation on the cuvette was 3 mW/cm^2. To record the absorption spectra, an AvaLight-DH light source and an AvaSpec 2048-2 spectrometer (Avantes V.B., Netherlands) were used, located perpendicular to the radiation source.

To confirm acid formation during photolysis, the pyrimidine derivative 4,6-Bis[5-(9-ethyl-9H-carbazol-3-yl)thiophen-2-yl]pyrimidine (further in the text IND) was used. The absorption bands of its neutral (420 nm) and protonated (530 nm) forms are spectrally well separated and do not overlap with the absorption of the photolysis products of the starting compounds.

Detritylation was performed in dichloromethane (DCM) solutions at PAGs concentrations of 10^{-3} mol/L and DMT-dT– 5×10^{-5} mol/L.

The quantum yield of the compound phototransformation in DCM is determined in the same way as in Ref. [9] using the following Eq.:

$$\gamma = \frac{N_{ph}}{N_{abs}}, \quad (1)$$

where *Nph* is the number of molecules that have undergone phototransformation while *Nabs* is the number of absorbed photons. *Nph* was determined by the decrease in the intensity of the main absorption band at the initial stage of photolysis when the absorption of photoproducts in this region is negligible:

$$N_{ph} = \frac{(D_0 - D)\times C_0 NV}{D_0 \times 10^3}, \quad (2)$$

where D_0 and D are the optical density of the solution before and after irradiation, C_0 is the initial concentration of the compounds (in our case, C_0=10^{-4} mol L^{-1}), N is the Avogadro constant, V is the irradiated volume (2 ml). Since the excitation in both cases was carried out by monochromatic radiation, the energy absorbed by the volume of the solution (in J) can be converted easily into the number of photons, taking into account the transmittance of the solution at the excitation wavelength (T) and the photon energy E_{355}=5.6×10^{-19} J, E_{308}=6.44×10^{-19} J.

$$N_{abs}^{308} = \frac{W\cdot t\cdot S\cdot(1-T_{308})}{h\nu_{308}}$$
$$\text{or } N_{abs}^{355} = \frac{E_{imp}\cdot n\cdot(1-T_{355})}{h\nu_{355}}, \quad (3)$$

where W – the lamp power density (W·cm^{-2}), t – time of irradiation (s), S – the irradiated solution area (cm^2), E_{imp} – impulse energy (J), n– the number of laser pulses and T – transmission at excitation wavelength.

3 Results and Discussion

As mentioned above, self-contained acid photogenerators are interesting in that they generate both acid counterions when irradiated. The mechanism of light-induced 6π--electrocyclization is shown in Fig. 1.

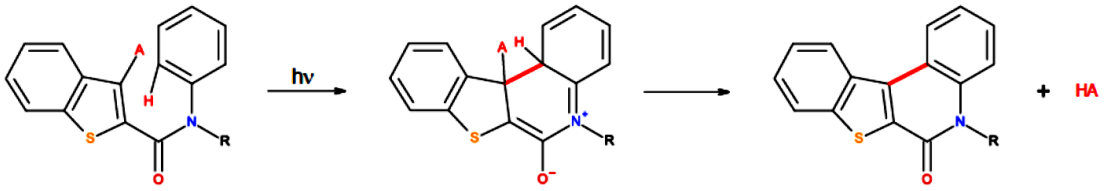


Fig. 1 The mechanism of photogeneration of acid by 6π electrocyclization.

Table 1 Spectral characteristics of the studied compounds in methylene chloride.

Compound	λ_{abs}, nm	ε_{max}, $dm^3mol^{-1}cm^{-1}$	ε_{308}, $dm^3mol^{-1}cm^{-1}$	ε_{355}, $dm^3mol^{-1}cm^{-1}$
PAG1	299 244	12740 20100	11770	830
PAG2	302 244	13900 19420	13310	950
PAG3	303 246	15650 21700	15250	1130
PAG4	290 238	11820 16950	7700	130
PAG5	291 240	10990 17630	7840	90

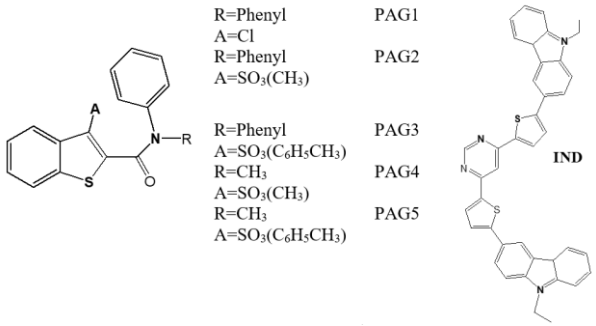


Fig. 2 Structure of the studied PAGs and indicator.

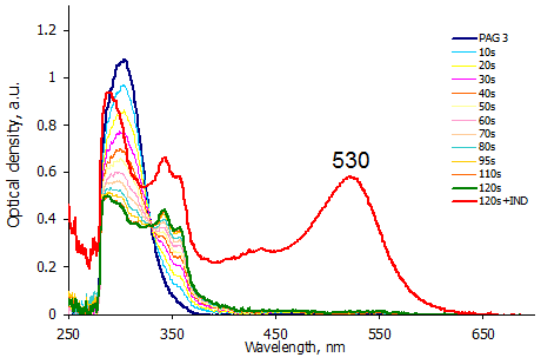


Fig. 3 Phototransformation of PAG3 in toluene (C=10^{-4} mol L^{-1}) upon irradiation with a XeCl-lamp. The indicator is added after irradiation for 120 s.

Figure 2 shows the structures of the studied compounds. PAGs (1–3) differ from each other only in their acidic substituents, which form hydrochloric, methylsulfonic, and toluenesulfonic acids upon photolysis. In PAGs (3–4), one phenyl ring on the right moiety is replaced by a methyl group, resulting in a slight (~10 nm) blue shift of the absorption band, but a noticeable decrease in extinction at the laser excitation wavelength (Table 1).

Figure 3 shows the dynamics of changes in the absorption spectrum for PAG3 in toluene when irradiated with a XeCl lamp. Since the fundamental structure of the molecules is similar, the photolysis pattern is similar for all PAGs, for both excitation sources. The spectrum contains isosbestic point, which indicates that two compounds are recorded: the original and the photoproduct. The formation of acid during photolysis is confirmed by an indicator added to the irradiated solution, which forms a protonated form (~530 nm). The protolytic properties of the indicator molecule were investigated in our previous work [9].

Using Eq. (1), the quantum yield of phototransformation of compounds was estimated upon irradiation with a XeCl lamp and Nd:YAG laser in solutions of toluene and DCM (Table 2). When irradiated with a laser, the quantum yield values are of the same order of magnitude – 10^{-2} in both solvents, with some difference depending on the substituent. When they irradiated with a lamp, the quantum yield values for toluene and DCM differ significantly. In toluene it is almost ten times higher than DCM. It should be noted that in DCM the decay quantum yield for both excitation sources is of the same order (~10^{-2}). Since photolysis for all cases of excitation and solvents occurs with the formation of isobestic points in the absorption spectra, it can be assumed that the obtained values of the quantum yield are also the same for the formation of acid, since non-proton-donating solvents were used.

Figure 4 shows the intensity of the protonated form of the indicator (PF-IND) at λ=530 nm added to irradiated compounds with a XeCl lamp for 150 s in toluene and DCM. The intensity of PF-IND may depend on the quantum yield of photoacid formation, its activity in different solvents and its molecular nature. In our case, hydrochloric, methylsulfonic and toluenesulfonic acids are form. Based on the quantum yield, the PF-IND intensity in irradiated toluene should be much higher (since the quantum yield is significantly higher) than we observe in DCM in Fig. 4. The comparable PF-IND intensities in both solvents for all PAGs (except PAG1) are most likely due to the different activities of the formed acids in toluene and DCM. It is significantly higher in DCM, as can be seen from the figure. Interestingly, the indicator does not detect hydrochloric acid in toluene. Either its activity in toluene is so low, or the chlorine anion formed during photolysis chemically reacts with toluene.

Table 2 Quantum yield of the compound phototransformation upon irradiation with a XeCl lamp and the 3rd harmonic of a Nd:YAG laser in toluene and dichloromethane solutions.

PAGs	λ_{ex} = 355 nm		λ_{ex} = 308 nm	
	Toluene	DCM	Toluene	DCM
PAG1	0.024	0.025	0.15	0.042
PAG2	0.06	0.018	0.30	0.021
PAG3	0.072	0.03	0.36	0.038
PAG4	–	–	0.11	0.022
PAG5	–	–	0.11	0.022

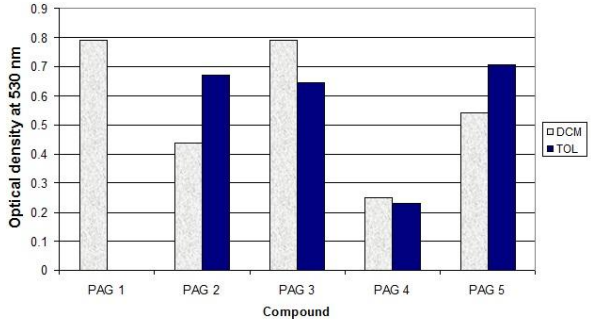


Fig. 4 Optical density of the IND protonated form when the PAGs ($C = 10^{-4}$ mol L^{-1}) were irradiated with XeCl-lamp for 150 s in toluene (TOL) and dichloromethane (DCM).

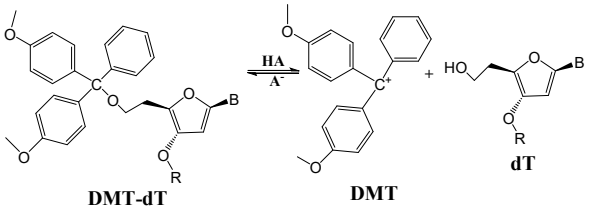


Fig. 5 Reaction of DMT cation formation in an acidic environment.

Deprotection, removal of the dimethoxytrityl group, during the synthesis of oligonucleotides is typically carried out with dichloro- or trichloroacetic acid of a certain concentration according to Fig. 5. The resulting cation (DMT) imparts a yellow-orange color to the solution and is easily detected by its strong absorption in the 506–511 nm region. Various PAGs have already been used in Refs. [10, 14–17] to remove the DMT group from both nucleoside monomers and synthesized nucleic acid chains during oligonucleotide synthesis [15–17]. In this study, detritylation was performed by irradiating PAGs ($C = 10^{-3}$ mol L^{-1}) with the addition of DMT-dT at a concentration of 5×10^{-5} mol L^{-1} in a dichloromethane solution. Both excitation sources were used.

Figure 6 shows the photolysis of PAG3 in DMC mixed with DMT-dT under irradiation with a XeCl excilamp (308 nm). For other PAGs, as well as with laser irradiation, the spectral changes are similar. Based on the DMT absorption intensity at 506 nm, it can be concluded that detritylation by photogenerated acids is efficient.

Figure 7 shows the dependence of the absorption of the DMT cation on the irradiation time for both light sources. When comparing PAGs (1–3), which differ only in that they generate different acids, at the beginning of irradiation, hydrochloric and toluenesulfonic acids begin to work simultaneously (curves 1, 3), while methanesulfonic acid lags behind (curve 2). With longer irradiation, the process of detritylation in a medium with hydrochloric acid is noticeably inhibited (curves 1, Fig. 7(a, b)), whereas with methanesulfonic and toluenesulfonic acids it continues. It should be noted that this behavior of PAGs is typical both when irradiated by a lamp and a laser.

PAGs (4, 5), in which one phenyl ring on the right moiety of the molecules is replaced by a methyl group, resulting in a slight blue shift of the bands but a dramatic decrease in extinction at 355 nm, are not suitable for laser excitation. When irradiated with a lamp, their efficiency is only slightly weaker than PAGs (1–3) (curves 4, 5, Fig. 7(a)). In general, the detritylation process is more efficient with toluene sulfonic acid.

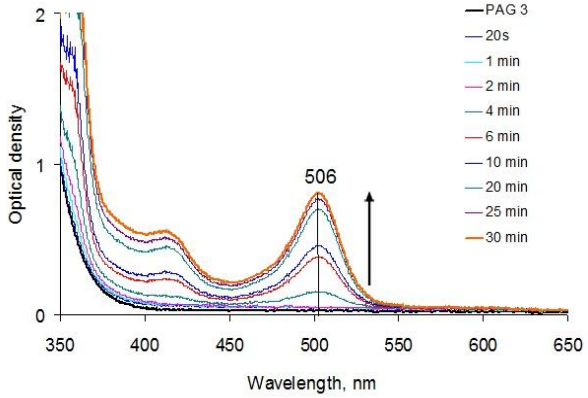
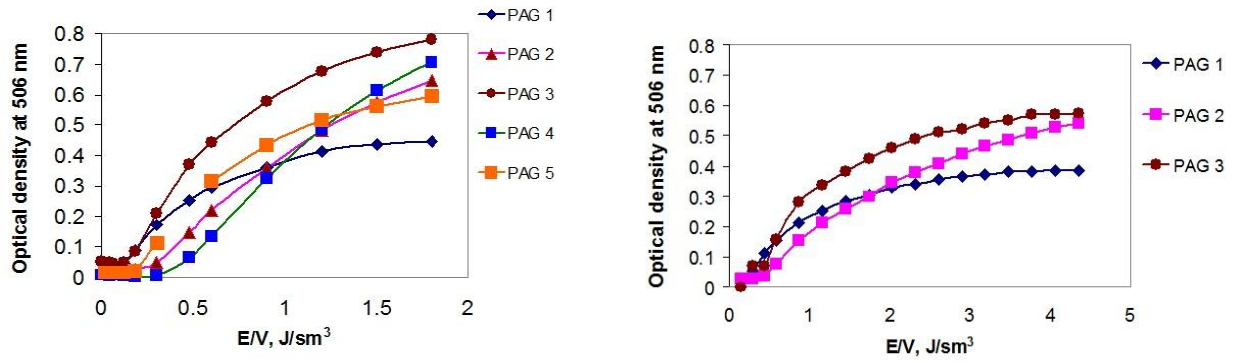


Fig. 6 Photochemical accumulation of DMT- cation at 506 nm during irradiation of a mixture PAG3 ($C = 10^{-3}$ mol L^{-1}) and DMT-dT ($C = 5\times10^{-5}$mol L^{-1}) in DCM under excitation 308 nm.



(a) (b)

Fig. 7 Formation of DMT-cations in DCM during irradiation of PAGs with (a) a XeCl-lamp and (b) Nd:YAG-laser (b). Concentration of PAGs are 10^{-3} mol L^{-1}, DMT-dT – 5×10^{-5} mol L^{-1}. E/V is the energy (dose) of the absorbed radiation in the volume of the solution, taking into account the transmission.

4 Conclusion

Thus, all the studied compounds form acids, both when irradiated with a XeCl lamp (308 nm) and with the 3rd harmonic of an Nd:YAG laser (355 nm) in both toluene and dichloromethane. An indicator was used to confirm acid formation. The formation of the acid in an aprotic solvent confirms the mechanism of 6π--photo-electrocyclization.

Photogenerated acids were tested for the removal of the dimethoxytrityl group from 5′-O-(4,4′-dimethoxytrityl)-2′-deoxythymidine-3′-O-[O-(2-cyanoethyl)-N,N′-diisopropylphosphoramidite under both lamp and laser irradiation. It has been shown that the fastest and most complete effect is achieved with toluenesulfonic acid.

Disclosures

The authors declare no conflicts of interest in this paper.

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