

# Synthesis of Novel Triazine Derivatives and Their Properties as Photoacid Generator<sup>a</sup>

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## Abstract

Photoacid generators, which undergo photochemically bond cleavage reactions to produce acid, can be used in imaging systems based on acid induced or catalyzed reactions, such as epoxide polymerization, photoresist, computer-to-plate, protonic conduction and the control of vesicle formation.

A series of novel triazine derivatives from calix[4]arenes were synthesized, their properties as photoacid generator sensitive in violet spectral regions, especially in wavelength at 366 and 405 nm, were systematically investigated. All the newly synthesized compounds were characterized with IR, <sup>1</sup>HNMR, <sup>13</sup>CNMR, DSC and MS, and these data were found in good agreement with expected structures. Their quantum yields of acid formation in acetonitrile were measured.

## Introduction

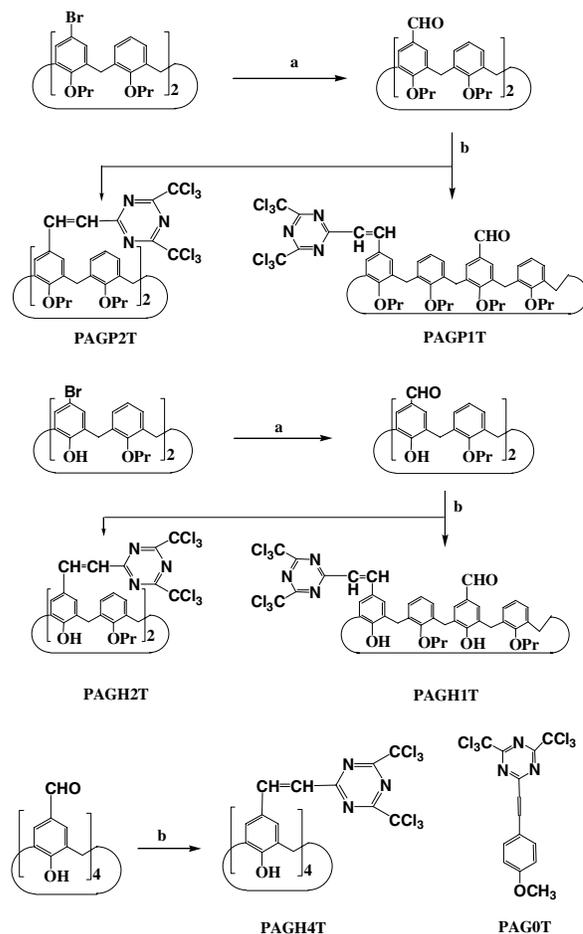
Calix[4]arenes are very well known for their unique molecular architecture and can provide a  $\pi$ -basic bowl-shaped hemisphere. Thus they are useful for construction of a globular multi-functional  $\pi$ -basic molecule by connecting the upper rim with some functional groups<sup>[1]</sup>. Photoacid generators, such as onium salts<sup>[2]</sup>, triazine derivatives, which can undergo photochemically bond cleavage reactions to produce acid, such as Trifluoromethylsulfonic acid<sup>[3]</sup> and hydrogen chloride have been deeply studied due to their considerable scientific and technological value<sup>[3]</sup>. The technological relevance is related to the photoproduction of a strong or middle-strong acid that can be used in photo-acid-generation reaction<sup>[4]</sup>, photoresists<sup>[5]</sup>, computer-to-plate, protonic conduction and the control of vesicle formation. Data on quantum yield of acid formation ( $\Phi_{H^+}$ ) and its measurement are of scientific interest and crucial for the design of more efficient photoacid systems<sup>[6]</sup>.

We especially focused our interest on such kinds of PAGs that can produce strong acid under exposure at 366, 410 and 488 nm. Here, we designed a novel kind of PAGs which was constructed on the basis of calix[4]arenes and possessed multi-functional units in one molecule. Different calix[4]arene based triazine derivatives were synthesized and their properties as photoacid generator were systematically examined. We expected they would find use in 365 or 410 nm imaging applications as a kind of efficient PAGs.

## Experimental

n-BuLi was prepared by n-BuBr and Li, THF was dried over refluxing with Na, DMF was freshly distilled under nitrogen and stored over molecular sieves (4A), 2-methyl-4,6-bis(trichloromethyl)-s-triazine was prepared according to the literature<sup>[7]</sup>. Other reagents and solvents were used directly without

further purification. The reaction was carried out according to Scheme 1, Mono- and dibromo calix[4]arene derivatives were synthesized according to published literature<sup>[8]</sup>. Mono- and diformyl calix[4]arene derivatives were acquired by bromo derivatives with sequentially n-BuLi, DMF and hydrolyzation. The reaction of mono formyl calix[4]arene with 2-methyl-4,6-bis(trichloromethyl)-s-triazine always yielded two kinds of PAGS (PAGH2T and PAGH1T). The same reaction of diformyl calix[4]arene carried out at same condition also yielded two kinds of PAGs (PAGP2T, PAGP1T). The reaction of tetraformyl calix[4]arene with 2-methyl-4,6-bis(trichloromethyl)-s-triazine



Scheme 1 Preparation of PAGH2T, PAGH1T, PAGP2T, PAGP1T and PAGH4T, Reagents and conditions: a. n-BuLi, THF, -78°C / DMF / H<sub>2</sub>O. b. 2-methyl-4,6-bis(trichloromethyl)-s-triazine, pyridine, acetic acid

always gave a complex mixture called PAGH4T, which was directly used as PAG without further purification. The standard PAG PAG0T as a reference material was acquired by the reaction of 4-methoxybenzadehyde with 2-methyl-4,6-bis-(trichloromethyl)-s-triazine in the same reaction condition mentioned above.

The quantum yield of photoacid formation was determined by using a common method based on Rhodamine B<sup>[9]</sup>. The general procedure involved taking a PAG's acetonitrile solution (about 2 ml) and irradiating the solution for different minutes with monochromatic light at 366 or 405 nm. Absorption change ( $\Delta$  ABS) at 555 nm was recorded and fitted to a previously determined standard curve, a relationship between  $\Delta$  ABS and acid concentration, to read the number of acid molecules formed<sup>[8]</sup>. Quantum yield was calculated by dividing the number of acid molecules induced by monochromatic light with the number of photons absorbed.

## Results and Discussion

Mono- and dibromo calix[4]arene, momo- and diformyl calix[4]arene were synthesized in moderate yields according to literature<sup>[10]</sup>, PAGH2T, PAGH1T, PAGP2T, PAGP1T and PAGH4T were synthesized in low yields because of the steric crowding of the calix[4]arene. Their standard compound PAG0T was synthesized in high yield. All five PAGs were yellow and easy to be soluble in strong-polar, non-polar or weak-polar solvents such as acetonitrile, dimethylsulfone, 2-methoxyethanol and CH<sub>2</sub>H<sub>2</sub>, CHCl<sub>3</sub>, acetone, tetrahydrofuran, toluene except of PAGH4T which were highly soluble in acetonitrile, dimethylsulfone.

Their maximum absorption peak for compounds PAGH2T, PAGH1T, PAGP2T, PAGP1T and PAGH4T are all near 405 nm. These compounds (0.063 mN in acetonitrile) dissolved in acetonitrile were exposed under 365 nm or 405 nm, respectively, producing strong hydrogen chloride acid. Rhodamine B (0.05 mN in acetonitrile) in equal volume was added as an acid-sensitive indicator in measuring the photogenerated acid according to the literature<sup>[6]</sup>. Table 1 showed quantum yields for these compounds.

**Table 1 Quantum Yields for HCl Photogeneration of the Triazines at Room Temperature**

compound	Acid quantum yield(*10 <sup>2</sup> )	
	at 405 nm	at 365 nm
PAGH1T	1.14	0.056
PAGH2T	0.33	0
PAGP1T	0.39	0.17
PAGP2T	0.54	1.30
PagH4T	46.4	0
Pag0T	1.7	0

Radiation Intensity: 2.3\*10<sup>-3</sup> W/cm<sup>2</sup> at 366 nm and 1.55\*10<sup>-4</sup> W/cm<sup>2</sup> at 405 nm.

The data indicated that the photoacid generators were more sensitive at 405 nm than at 365 nm. PagH4T was of the highest quantum yield and could be used as excellent photoacid generator at 405 nm. And the rest calix[4]arene derivatives were much less sensitive at 365 nm and 405 nm and even worse than standard compound PAG0T. Though PAGH2T and PAGP2T were of two functional groups to afford acid under exposure, they had lower quantum yields than PAGH1T and PAGP1T. The study on properties of acid formation would be further carried out.

## Conclusions

A series of novel triazine derivatives based on calix[4]arenes were synthesized and their properties as photoacid generator in violet spectral regions, especially at 366 and 405 nm, were systematically investigated. Quantum yields of acid formation in acetonitrile were measured and PAGH4T was found most sensitive among all other investigated compounds at 405nm. Its quantum yield of photoacid generation at 405 nm was as high as 46.4%, indicating that PAGH4T would be possibly used in 405 nm imaging applications.

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