

3-Nitrochromenes for Second Order Nonlinear Optical Applications

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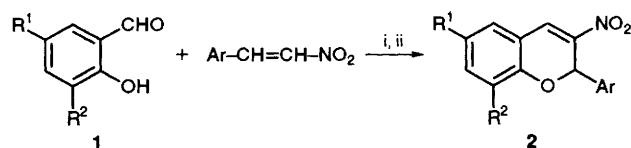
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3-Nitrochromenes bearing various substituents have been prepared by the reaction of substituted salicylaldehydes with nitrostyrenes; some of these compounds have been found to display efficient optical second harmonic generation.

Organic materials with second-order nonlinear optical properties have been the subject of intense investigation owing to their large nonlinearity and ultrafast response times.¹ These materials have many potential applications in a variety of laser-related technologies such as telecommunication, optical computing, optical storage, and optical information processing. The design of these molecules rests on the combination of an electron donor, a π -conjugated electronic system, and an electron acceptor. Donor-acceptor substituted aromatic compounds have been extensively studied for second-order nonlinear materials. In this paper we report a new system for second harmonic generation (SHG); 3-nitrochromenes with appropriate substituents are potential candidates for future nonlinear optical applications.

3-Nitrochromenes **2** were prepared in 70–80% yield by the reaction of substituted salicylaldehydes **1** with nitrostyrenes

under basic conditions.² Nitrostyrenes were prepared by the reaction of aromatic aldehydes with nitromethane. As this method affords **2** with a variety of substituents, the effect of the substituent on SHG efficiency can be investigated in a systematic way. 3-Nitrochromenes thus obtained are all yellow crystals with an absorption maximum at about 390 nm.



Reagents and conditions: i, Et_3N , CH_2Cl_2 , room temperature; ii, Al_2O_3

Table 1 Preparation of 3-nitrochromenes **2**, and SHG efficiency of **2**

| Entry | R ¹ | R ² | Ar | Yield (%) | $\lambda_{\max}/\text{nm}^a$ | SHG efficiency ^b |
|-------|----------------|----------------|--|-----------|------------------------------|-----------------------------|
| 1 | H | H | Ph | 84 | 392, 319 | 0 |
| 2 | H | H | <i>p</i> -MeOC ₆ H ₄ | 80 | 390, 318 | 0.013 |
| 3 | H | OMe | Ph | 70 | 345 | 0 |
| 4 | H | OMe | <i>p</i> -MeOC ₆ H ₄ | 84 | 346 | 0 |
| 5 | Cl | H | Ph | 68 | 399, 314 | 0.091 |
| 6 | Cl | H | <i>p</i> -MeOC ₆ H ₄ | 80 | 396, 312 | 62 |
| 7 | Cl | H | 2-Thienyl | 73 | 393, 312 | 43 |
| 8 | Cl | H | 3,4-(MeO) ₂ C ₆ H ₃ | 78 | 395, 312 | 0.013 |

^a In CH₂Cl₂. ^b Measured by the powder method using a YAG laser (1064 nm). Values are relative to urea.

We investigated the SHG efficiencies of **2** by means of the powder technique.³ This is a convenient method for screening a large number of powdered materials for non-linear optical activities by observing the light emitted from the powdered materials on laser irradiation. The SHG efficiency was determined relative to a reference compound (urea). The results are summarized in Table 1. Compounds in entries 2, 5, 6, 7 and 8 gave SHG effects, compounds in entries 6 and 7 displaying by far the most intense signals, much stronger than that of urea. They have an SHG efficiency 62 and 43 times that of urea, respectively. This value is remarkable among existing nonlinear optical materials based on nitroaromatic derivatives.¹ The lack of SHG for compounds in entries 1, 3 and 4

could be caused by bulk effects. The magnitude of the SHG signals obtained from the powder test is mainly governed by crystallographic factors. As shown in Table 1, a small change of substituents in **2** has a large effect on the SHG efficiency. The present results, albeit qualitative, indicate that fused heteroaromatic compounds such as **2** are good candidates for the design of new non-linear optical materials.⁴ More quantitative treatment is necessary to understand structural factors that govern intrinsic hyperpolarizability of **2**. Such work is now in progress.

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