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Rhodanine-methine as π-Electron Acceptor in Second-order Nonlinear Optical Chromophores

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Abstract: This study describes the synthesis, electronic absorption and second-order nonlinear optical properties of a series of new dialkylamino electron-donor and rhodanine-methine electron-acceptor substituted conjugated compounds. EFISH studies indicate that rhodanine-methine acceptor offers substantially enhanced molecular nonlinear properties ($\beta\mu$) compared to the well known and commonly used nitro acceptor.
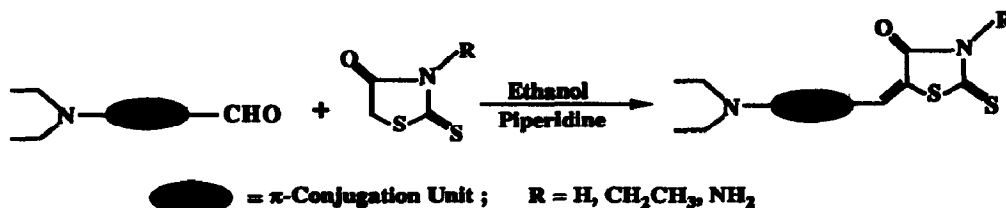
The use of donor-acceptor substituted conjugated compounds in the development of nonlinear optical materials for electro-optic devices[1] has drawn the attention of synthetic and physical organic chemists. Design and synthesis of such compounds with efficient second-order nonlinear optical properties ($\beta\mu$) are of current interest.[1,2] Structure-property relationships indicate that the molecular nonlinearity ($\beta\mu$) increases with increasing donor and acceptor strengths and with increasing conjugation length.[1,2] Since the nitro group is one of the strongest electron-withdrawing groups and correspondingly the dialkylamino group as an electron-releasing group, this pair is often found in well studied molecules (ex. N,N-dimethylamino-4-nitrobenzene, 1).[3] More recently, stronger electron-acceptors such as cyanovinyl groups have been exploited in the design of efficient nonlinear optical chromophores (ex. N,N-diethylamino-4-dicyanovinylbenzene, 2).[4] In this paper, we present a new class of efficient nonlinear optical chromophores containing rhodanine-methine group as the electron-acceptor.

In a previous study by Ikeda and co-workers,[5] a commercially available rhodanine-methine derivative 3 was examined for its second-order nonlinear optical activity in DMSO solution using 1.06 μm light. Because of the strong overlap between the charge-transfer absorption of 3 and the second harmonic generated from 1.06 μm light, the $\beta\mu$ value measured in their study was significantly resonance enhanced. Although attempts were made to eliminate the resonance contribution by separating the real component of $\beta\mu$ from its imaginary component, the role of the rhodanine-methine acceptor was not obvious from their study. Our objective in this study is to design and synthesize several push-pull compounds containing a rhodanine-methine acceptor, study their properties using 1.907 μm light and compare the strength of the rhodanine-methine acceptor with other conventional acceptors such as nitro and dicyanovinyl groups in influencing the molecular nonlinear optical properties.
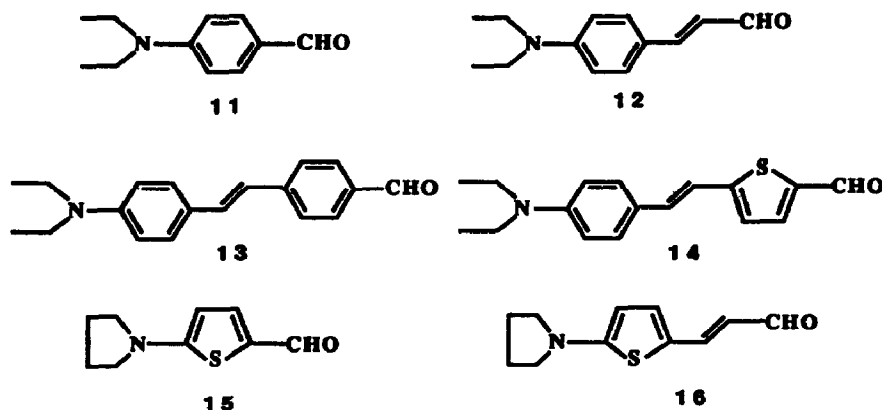
Donor-acceptor compounds studied in this work are shown in **Table 1**. Rhodanine-methine derivatives **4-10** were synthesized, while compound **3** was procured from Aldrich. In compounds **4-10**, rhodanine-methine group was introduced by the condensation reaction between the corresponding diethylamino substituted conjugated aldehyde and N-ethylrhodanine (N-aminorhodanine in the case of **4**) in ethanol. All the compounds were fully characterized by conventional spectroscopic and analytical methods.

Table 1

| Compound	λ_{max}/nm in dioxane	$\beta\mu/10^{-48}$ esu at $\lambda = 1.907\ \mu m$
1	370	110
2	419	300
3	452	300
4	473	410
5	465	420
6	493	908
7	466	885
8	501	383
9	525	980
10	527	1165

The dialkylamino substituted conjugated aldehydes used in this study are shown below. N,N-Diethylamino-4-benzaldehyde **11** and N,N-diethylamino-4-cinnamaldehyde **12** are commercially available. Extended conjugated aldehydes **13** and **14** were prepared from **11** by following our previously reported synthetic sequence which involves Wittig-Horner condensation followed by formylation.[3] Compounds **15** and **16** were prepared from 2-pyrrolidinothiophene by lithiation and subsequent reaction with dimethylformamide and dimethylaminoacrolein, respectively.

Second-Order hyperpolarizabilities of all the compounds studied in this work were determined using an electric-field-induced second-harmonic generation (EFISH) technique described elsewhere.[6] In order to minimize possible resonance enhancement, measurements were made at a fundamental wavelength of 1.907 μm. The EFISH data obtained in 1,4-dioxane solvent for compounds 1-10 are presented in Table 1. As these molecules are likely candidates to be used as pendant side chains in poled polymer films, the $\beta\mu$ values reported here are a relevant figure of merit combining both the nonlinearity of the molecule and the ability of the molecule to couple with a macroscopic poling field.

Compounds 1-5 differ only by electron-acceptor substituents and, therefore, comparison of their $\beta\mu$ values reveals the dependence of molecular nonlinearity on the strength of the electron-acceptors. Compounds 1 and 2 possess nitro and dicyanovinyl substituents and the $\beta\mu$ values obtained for them are 110 x 10^{-48} esu and 300 x 10^{-48} esu, respectively. Compounds 3-5, all containing rhodanine-methine acceptor, differ only in the substitution on the nitrogen of the rhodanine-ring moiety. The ring-nitrogen in compounds 4 and 5 has amino and ethyl substituents respectively, whereas the ring-nitrogen in compound 3 does not have any substitution. The $\beta\mu$ values obtained for compounds 3, 4 and 5 are 300 x 10^{-48} esu and 410 x 10^{-48} esu and 420 x 10^{-48} esu respectively. Comparison of the $\beta\mu$ values of 1 and 2 with 3, 4 and 5 reveals that rhodanine-methine group is a

stronger electron-acceptor and produces significantly enhanced molecular nonlinearity compared to the commonly used nitro group. This data also suggests that dicyanovinyl and rhodanine-methine groups have comparable electron-accepting ability in influencing the molecular nonlinearity. Another salient feature of this data is that the ring-nitrogen substitution has an additive effect on the molecular nonlinearity. The stronger electron-accepting ability of the rhodanine-methine group and the sensitivity of molecular nonlinearity to the ring substitution may be accounted for the contribution of the gain of partial aromaticity of this acceptor in the resonance charge-separated state.
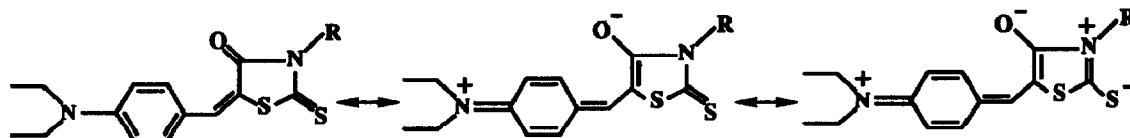
Using N-ethylrhodanine, several soluble extended conjugated donor-acceptor compounds were also synthesized. Comparison of the $\beta\mu$ values of compounds 5, 6 and 7 reveals that increase in conjugation by olefinic units causes more effective overlap between dialkylamino donor and rhodanine-methine acceptor than the benzenoid rings. Comparison of the $\beta\mu$ values of compounds 7 and 10 indicates that the replacement of the benzene ring with thiophene ring enhances the molecular nonlinearity in stilbene systems. This behavior is in accord with our earlier studies on push-pull thiophene stilbenes.[3,4b,4c]

In conclusion, we have demonstrated that the rhodanine-methine electron-acceptor can be easily introduced into a variety of donor substituted conjugated systems. These compounds possess enhanced (when compared to the corresponding nitro compounds) molecular second-order nonlinearities and inherent thermal stabilities on the order of 225-275°C. Considering the possibility that these compounds can be bifunctionalized through the nitrogen of the amino donor and the ring-nitrogen substitution of the rhodanine-methine acceptor, this class of compounds may play a significant role in the development of thermally stable crosslinked polymeric NLO materials[7] for electro-optic device applications.

Acknowledgements

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