Pergamon

Tetrahedron Letters, Vol. 35, No. 33, pp. 6113-6116, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01275-X

Synthesis and Computational Studies of Hyperpolarizable Zig-Zag Chromophores

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Abstract: The highly hyperpolarizable zig-zag chromophores were synthesized using palladium coupling reactions and their nonlinear optical properties were studied by AM1 semi-empirical methods showing the possession of large off-diagonal hyperpolarizable, β, tensor components.

Design of molecular and polymeric materials possessing large second order non-linear response has recently aroused much attention because of their potential applications in electrooptic modulation and second harmonic generation (SHG).[1] The classical donor-acceptor π-conjugated chromophores such as 1,4-disubstituted benzenes, 4,4'-disubstituted stilbenes and 4,4'-disubstituted tolanes have been experimentally and theoretically studied;[2,3] however, there has been little attention to 1,2-disubstituted π-conjugated systems. We report here a new class of highly hyperpolarizable 1,2-disubstituted π-conjugated system, zig-zag chromophores **2** and **3** (Fig. 1) to obtain off-diagonal β tensor components which are useful in electric field poled polymers[4] and to deal with the solubility problems on the highly π-conjugated system containing more than 2 aromatic rings which is an attractive candidate for electrooptic applications.[5]

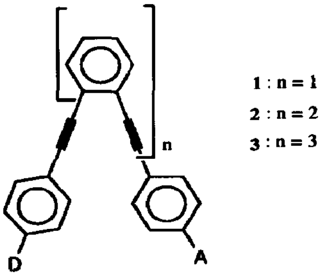
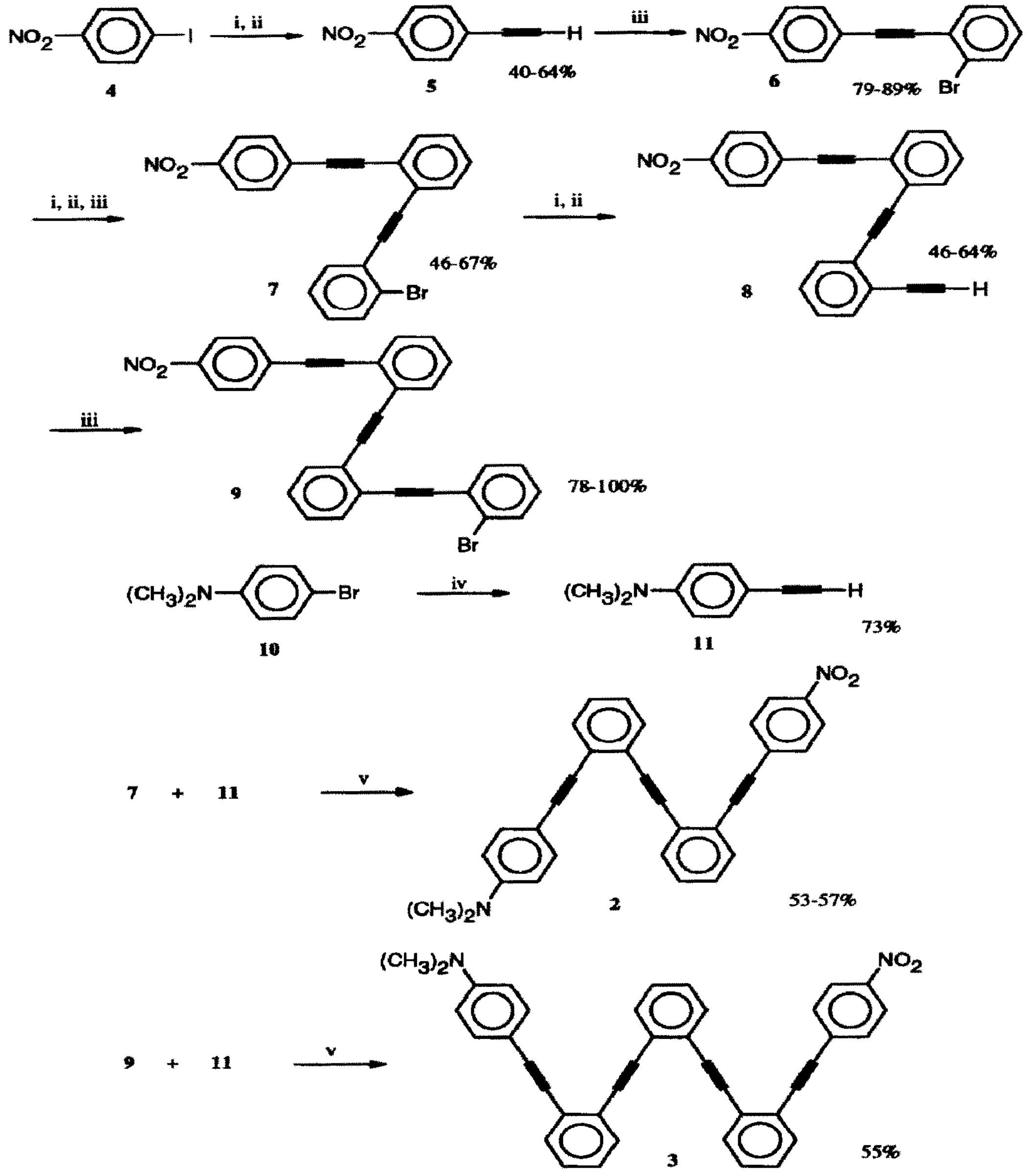


Fig. 1: Zig-Zag Chromophores. D, electron donor and A, electron acceptor.

These zig-zag chromophores are basically composed of an oligomeric 1,2-phenylene(2,1-ethynediyl) unit as a conjugation core, an electron-donating group at one end and an electron-withdrawing group at the other end. When there is an even number of the repeating 1,2-phenylene(2,1-ethynediyl) unit, n, the donor and acceptor groups are on the opposite side of the zig-zag skeleton as in the example of chromophore **2**, where n = 2. On the other hand, when n is an odd number, both the donor and acceptor groups are on the same side such as chromophore **3**, where n = 3. The synthetic pathway for **2** and **3** are outlined in Scheme 1. 4-nitrophenylacetylene, **5** was prepared by cross-coupling of 4-iodonitrobenzene, **4** and trimethylsilylacetylene in the presence of 2 mole% of $PdCl_2$, 2 mole% of PPh_3 and 1 mole% of CuI as catalysts in Et_3N at 70-75 °C under inert atmosphere[6] and then followed by the desilylation using tetra-n-butylammonium fluoride in aqueous THF. Subsequent catalytic palladium-copper cross-coupling reaction of **5** and 2-bromoiodobenzene under the same reaction conditions afforded **6** in good yield. By repeating these sequential steps, the phenylethynyl skeleton was stepwisely built up, giving compounds **7**, **8** and **9**. Initial attempt to prepare **2** by cross-coupling of **9** and 4-bromo-N,N-dimethylaniline, **10** under standard coupling conditions was in vain. The next logical step was to cross couple **7** and **11**. Compound **11** was prepared in similar coupling conditions except that piperidine was used as a solvent which allowed to be heated at a higher temperature resulting in a better yield. Zig-zag chromophore **2** was obtained in moderate yield by cross-coupling between **7** and **11**. It is important to note that the cross-coupling reaction does not occur if the electron donating and withdrawing properties of the reactants interchange. Using the same strategy, chromophore **3** was also synthesized by cross-coupling of **9** and **11**. Unlike chromophore **2**, chromophore **3** was purified by alumina column chromatography because it decomposed in silica. All compounds were well characterizated by NMR spectroscopy[7] with satisfactory elemental analysis but the reported yields were not optimized.

A vectorial projection of β tensor along the molecular dipole moment, $\beta_\mu(2\omega)$, is usually derived from the Electric Field Induced Second Harmonic Generation (EFISH) measurement.[8] However, the measured $\beta_\mu(2\omega)$ does not thoroughly reflect the intrinsic NLO properties of these non-classical zig-zag chromophores. Furthermore, the contributions from the off-diagonal β tensor components were expected to play an important role in macroscopic susceptibility.[9] As a result, the computational approach, instead of EFISH was employed to probe their NLO properties. The AM1 semi-empirical calculation[10] was used to optimize the molecular geometry and calculate physical properties such as dipole moment. Although the unsubstituted analog of **3** conforms in a helical structure in crystalline state,[11] both the optimized geometries of **2** and **3** show zig-zag conformations in gas phase. As pointed out in our early study,[12] the rotation barrier around the acetylenic linkage is rather small. In the case of **3**, the energy difference between helical and zig-zag conformations is about 1 kcal/mole.

The vectorial projection of static β along permanent dipole moment, $\beta_\mu(0)$, and β tensor components were calculated by Finite Field method using AM1 parameters.[13] The computational results and UV-VIS spectroscopic measurement were summarized in Table 1. For linear chromophores such as *p*-nitroaniline (PNA), there is only one dominant diagonal β tensor component, β_{xxx}, contributing to the overall molecular hyperpolarizability. Besides β_{xxx}, the zig-zag chromophores possess relatively large off-diagonal β tensor components such as β_{yxx} in **2** and β_{xyy} in **3** which provide significant contributions to the macroscopic susceptibility of materials. Furthermore, these off-diagonal β tensor components are not critically affected by the dipolar relaxation; therefore, they are good candidates for poled polymers.[4] The UV-VIS spectra of **2** and **3** show broad absorption bands which are attributed to the overlapping of several electronic transitions arising from different conformers in solution. The ease of rotation around acetylenic framework and vibration of the extended phenyl-ethynyl skeleton also lead to a small extinction coefficient of the long-wavelength absorption, λ_{max}. However, λ_{max} shifts to a longer wavelength with the incorporation of a donor, dimethylamino group and an acceptor, nitro group into the phenyl-ethynyl backbone



Scheme 1.: Reagents and Conditions. (i) trimethylsilylacetylene, $PdCl_2$, CuI, PPh_3, NEt_3, 70°C, (ii) n-Bu_4F, aqueous THF, room temp., (iii) 2-bromoiodobenzene, $PdCl_2$, CuI, PPh_3, NEt_3, 70°C, (iv) trimethylsilylacetylene, $PdCl_2$, CuI, PPh_3, piperidine, 85°C, (v) $PdCl_2$, CuI, PPh_3, NEt_3, 70°C.

Table 1. Results of AM1 semi-empirical calculations and physical measurements.

Compds.	Calc μ (D)	Calc $\beta_\mu(0)$ $\times 10^{-30}$ (esu)	Selected β Tensors $\times 10^{-30}$ (esu)	λ_{max} (nm)
PNA	7.3	5.4	$\beta_{xxx} = 11.0$	348
2	7.4	25.6	$\beta_{xxx} = 36.7, \beta_{vxx} = 12.5$	353
3	6.1	12.4	$\beta_{xxx} = 12.4$, $\beta_{xyy} = 20.8$	371

Calc μ obtained from AM1 semi-empirical calculations, Calc $\beta_\mu(0)$ and selected β tensor components calculated by Finite Field method using AM1 parameters, λ_{max} measured in chloroform

(**2**: λ_{max}= 353 nm in $CHCl_3$ vs corresponding unsubstituted phenyl-ethynyl compound λ_{max} = 316 nm in EtOH[11] and **3**: λ_{max} = 371 nm in $CHCl_3$ vs corresponding unsubstituted phenyl-ethynyl compound λ_{max} = 303 nm in EtOH[11]). In addition, the solid samples of these chromophores exhibit red shift in colour (orange-red in **2** and deep red in **3**) as compared to the solution samples. This is due to the restricted rotation and vibration of the molecular framework in solid phase resulting in a better overlapping of p-orbitals and thus enhancing electrons delocalization. The improvement in NLO responses will also be anticipated in condensed phase. The NLO properties of these zig-zag chromophores and the extended analogies in polymer matrix are under investigation.

Acknowledgement: M.S.W. thanks CNRS for the financial support.

References and Notes:

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1. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Chemla, D. S.; Zyss, J. Eds.; Academic Press, Orlando, FL, vols. 1 and 2, 1987.
2. (a) Cheng, L. T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631-10643. (b) Cheng, L. T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643-10651.
3. Matsuzawa, N.; Dixon, D. A. *J. Phys. Chem.* **1992**, *96*, 6232-6241.
4. Watanabe, T.; Kagami, M.; Yamamoto, H.; Kidoguchi, A.; Haysahi, A.; Sato; H.; Miyata, S. *Polymer Preprints* **1991**, *33*, 88-89.
5. Jen, A. K. Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90-92.
6. Takahaski, S.; Kuoryama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627-630.
7. Selected spectroscopic data for **2**:^{1}H NMR (200 MHz $CDCl_3$) δ 8.07 (J = 8.7 Hz, 2H, d), 7.62-7.55 (6H, m), 7.38-7.27 (6H, m), 7.52 (J = 8.7 Hz 2H, d), 2.95 (6H, s).
   3:^{1}H NMR (200 MHz $CDCl_3$) δ 8.09 (J = 8.7 Hz, 2H, d), 7.71-7.08 (16H, m), 6.62 (6H, m), 7.52 (J = 8.9 Hz 2H, d), 2.99 (6H, s).
8. Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446-457.
9. Brédas, J. L.; Meyers, F.; Pierce, B. M.; Zyss, J. *J. Am. Chem. Soc.* **1992**, *114*, 4928-4929.
10. Stewart, J. J. P. Mopac version 6.0, **1990**.
11. Grubbs, R.H.; Kratz, D. *Chem. Ber.* **1993**, *126*, 149-157.
12. Wong, M. S.; Nicoud, J. F. *J. Chem. Soc., Chem. Commun.* **1994**, 249-250.
13. Henry, A. K.; Stewart, J. J. P.; Dieter, K. M. *J. Comput. Chem.* **1990**, *11*, 82-87.

(*Received in France* 13 *June* 1994; *accepted* 29 *June* 1994)