

Synthesis of Novel Non-centrosymmetric Crystalline Materials for Quadratic Non-linear Optics

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Racemic 6,6'-bis-(phenylethynyl)-1,1'-binaphthyls and five of the six 6,4'-disubstituted 2-naphthylphenylacetylenes designed and synthesized show non-linear optical (NLO) activity in the Kurtz and Perry second-harmonic generation (SHG) powder test.

There is an increasing need to develop organic molecules with large second order optical non-linearities. Molecules having a highly π -conjugated system with an electron donor at one end and an electron acceptor at the other end give rise to a large molecular hyperpolarizability, β ; however, the extended conjugation usually leads to a red shift of the transparency cut-off.¹ Furthermore, there are no accurate ways of predicting crystal packing, but there are several possible strategies for inducing an acentric arrangement of molecules.²

We report here the design and synthesis of two new classes of highly hyperpolarizable molecules, 6,4'-disubstituted 2-naphthylphenylacetylenes **1** and racemic 6,6'-bis-(phenylethynyl)-1,1'-binaphthyls **2** (Fig. 1). Type **1** includes a classical donor-acceptor dipolar chromophore and **2** a bis-dipolar system in which two hyperpolarizable chromophores are directly connected to form a V-shaped structure. Both kinds were prepared to explore solutions for the transparency-efficiency trade-off and reliable methods for the induction of the non-centrosymmetric dipolar arrangement in crystalline state. The general pathways for the syntheses of **1** and **2** are summarized in Scheme 1. Classical catalytic palladium coupling³ was employed to synthesize the diarylacetylene skeleton in which an acetylenic linkage and a phenyl group with an electron acceptor were sequentially built onto the naphthalene moiety equipped with an electron donor, either a hydroxy or a methoxy group in a conjugated position. The binaphthol framework **5** was readily obtained by phenolic oxidative coupling⁴ of 6-bromo-1-naphthol **3**. This bis-ether linkage of **6** was formed by the reaction of **5** and 1,3-dibromopropane in the presence of CsF as a base. Treatment of **5** and **6** as for **1** afforded a series of racemic 6,6'-bis-(phenylethynyl)-1,1'-binaphthyls **2**. All the new crystalline compounds were well characterized with UV-VIS ¹H NMR and ¹³C NMR spectroscopy and elemental analyses but the reported yields were not optimized.

The results of AM1 semi-empirical calculations,⁵ UV-VIS spectroscopic measurement and SHG powder test are given in Table 1. The solvatochromism and the intense low-energy transition are the characteristic of the intramolecular charge-transfer transition (ICT: **1d**, $\lambda_{ICT} = 365$ nm in THF and 372 nm in Me₂SO). There is a significant red shift of λ_{ICT} in this dipolar diarylacetylene series compared with the correspond-

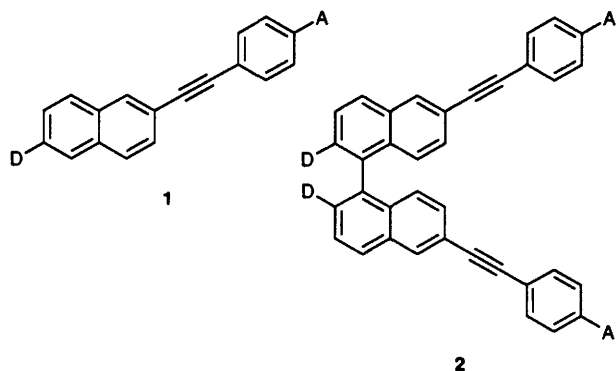


Fig. 1 6,4'-Disubstituted 2-naphthylphenylacetylenes (**1**) and racemic 6,6'-bis-(phenylethynyl)-1,1'-binaphthyls (**2**). D, electron donors; A, electron acceptors.

ing donor-acceptor 4,4'-disubstituted tolane (**1d**, $\lambda_{ICT} = 365$ nm vs. 4-methoxy-4'-nitrotolane, MONT, $\lambda_{ICT} = 352$ nm and **1e**, $\lambda_{ICT} = 343$ nm vs. 4-cyano-4'-methoxytolane, $\lambda_{ICT} = 322$ nm). This signifies a highly effective conjugation of the naphthalene moiety with the rest of the unsaturated system. An increase in the conjugation length increases β . The results from the finite-field calculation⁶ using AM1 parameters also showed that β for **1d** [β_{μ} (calc.) = 29×10^{-30} esu] is substantially greater than that of MONT [β_{μ} (calc.) = 15×10^{-30} esu].⁷

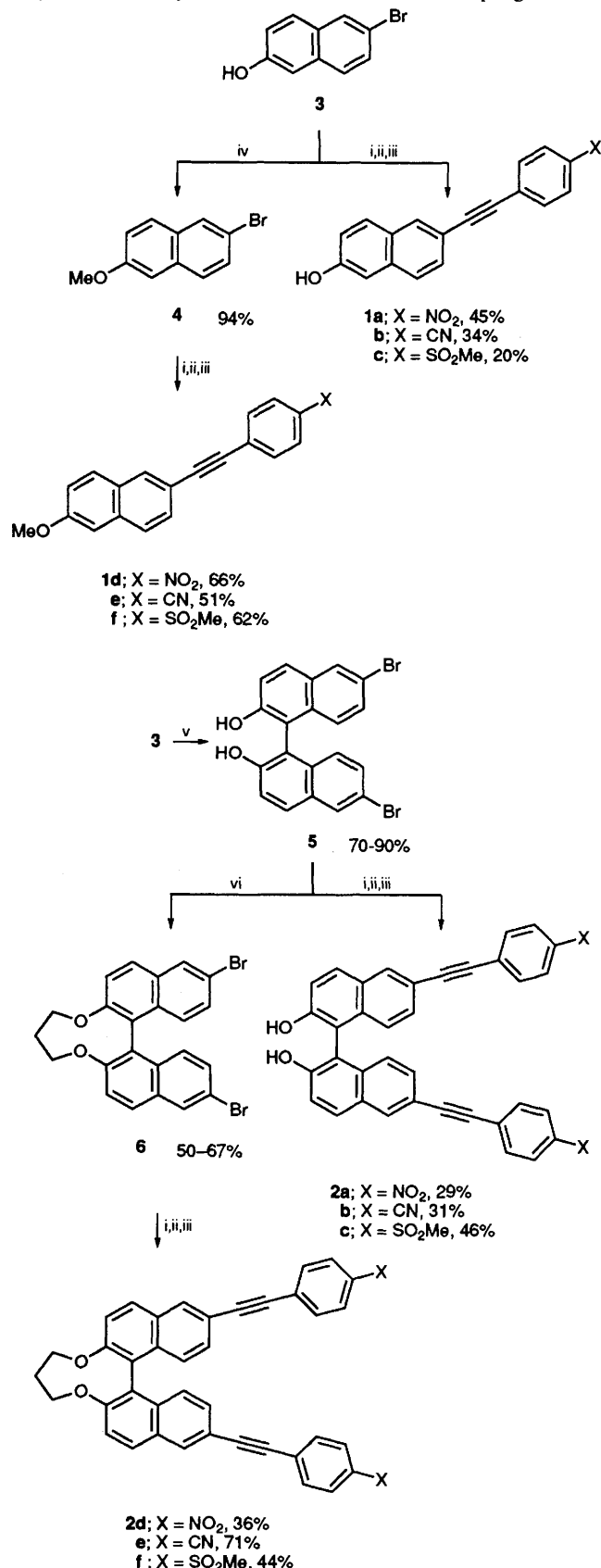
The quadratic NLO activity has been observed for five of the six materials of series **1** by the Kurtz and Perry SHG powder test performed with a 1064 nm Nd-YAG laser. The high propensity to non-centrosymmetric packing in crystalline state, which is higher than that of 4,4'-disubstituted tolanes,⁸ can be attributed to the geometrical and conformational asymmetry of these unsymmetrical diarylacetylenes. Unlike the classical donor-acceptor 4,4'-disubstituted tolane, the introduction of a naphthalene moiety into the backbone leads to a non-linear shape of the molecule. A statistical survey has also shown that most of the unsymmetrical tolanes adopt a non-planar conformation in the crystalline state.⁹ Although the optimized geometry of this class of diarylacetylenes, obtained by AM1 semi-empirical calculations is approximately planar, the energy for a twisting of 40° between a phenyl ring and a naphthyl ring requires only 0.1 kcal mol⁻¹. This is small enough to be overwhelmed by the favourable intermolecular interaction in the solid state. The ease of rotation of two phenyl rings around the triple bond has already been pointed out for a series of 4,4'-disubstituted tolanes.¹⁰ It has been suggested that an unsymmetrical tolane with

Table 1 Results of AM1 calculations and physical measurements^a

Compd.	Dipole moment, μ/D	Twist angle/degrees	Torsional angle/degrees	$\lambda_{ICT}/$ mm	SHG powder test
1a	6.4	1.3		369	+
1b	4.0	1.2		346	+++
1c	5.9	2.3		342	++
1d	7.1	1.5		365	++
1e	4.7	1		343	-
1f	6.5	2.2		338	+
2a	9.2	0.4/0.2	86.7	372	-
2b	5.9	0.2/0.7	71.9	352	+
2c	11.4	4.1/4.5	86.5	345	+
2d	10.7	0/0.2	70.4	365	-
2e	7.1	0.8/1.0	70.4	338	-
2f	12.0	4.1/4.9	70.4	334	-

^a μ (1 D $\approx 3.33564 \times 10^{-30}$ C m) is obtained from AM1 semi-empirical calculations; twist angle represents the rotation between the phenyl and naphthyl rings in the optimized geometry; torsional angle represents the dihedral angle between the two naphthyl planes in the optimized geometry. Given the broad range of sizes of crystalline particles in the samples and possible preferential orientation. UV measurements performed in THF. The powder tests were not quantified. + denotes a signal comparable to or a few times greater than that of urea; ++ and +++ refer to signals, one and two orders of magnitude greater, respectively. - denotes no visibly detectable SHG signal.

moderate dipole moment is likely to have a non-centrosymmetric crystal structure because of the comparatively strong van der Waals interactions.¹¹ Further effort in growing single crystals for X-ray structural determination is in progress.



Scheme 1 Reagents and conditions: i, HC≡C-SiMe₃, PdCl₂, CuI, PPh₃, NEt₃, 70 °C; ii, Buⁿ₄F⁻, THF, room temp.; iii, *p*-BrC₆H₄X, PdCl₂, CuI, PPh₃, NEt₃, 70 °C; iv, NaH, MeI, DMF, room temp.; v, PhCH₂(Ph)CHNH₂, CuNO₃, MeOH, room temp.; vi, Br[CH₂]₃Br, CsF, MeCN, reflux.

Concerning the bis-chromophoric molecules, a series of racemic 6,6'-bis-(phenylethynyl)-1,1'-binaphthyls (**2**) was studied. They are basically composed of two molecular units of **1**, directly connected together at the 1-position of the naphthalene moiety. In order to control the relative positions of the two chromophores within a molecule and their effect on molecular packing, the bis-ether linkage was introduced into the binaphthol framework. Although there is a red shift of λ_{ICT} for compounds **2a-c** compared with **1a-c**, the calculated β_{μ} of these bis-dipolar molecules is approximately equal to the vectorial sum of the two corresponding monomers [**2a**, β_{μ} (calc.) = 33×10^{-30} esu vs. vectorial sum of two **1a**, $\beta_{\mu} = 36 \times 10^{-30}$ esu]. On the other hand, a blue shift of λ_{ICT} for **2d-f** is observed compared with **1d-f** due to the non-coplanarity of the electron donor, alkoxy group and the naphthyl ring imposed by the strain of the nine-membered ring, as found from the computationally optimized geometry of the molecules. The destruction of π -conjugation is also reflected in β_{μ} (calc.) which is significantly smaller than the purely additive contribution of the two corresponding monomers [**2d**, β_{μ} (calc.) = 28×10^{-30} esu vs. vectorial sum of two **1d** $\beta_{\mu} = 45 \times 10^{-30}$ esu].

As the bis-naphthol framework is thermally and optically stable at ambient temperature, the bis-chromophore built onto this framework is conformationally chiral, with C₂ symmetry. In principle, the enantiomerically pure bis-tolane will pack in a non-centrosymmetric fashion, leading to SHG. Interestingly, the crystals grown from the solution of racemates **2b** and **2c** showed positive SHG signals. In order to understand this, we are preparing optically pure **2b** and **2c**. In addition, as this 2D bis-diarylacetylene system has a relatively large dipole moment with low λ_{ICT} , it is an attractive candidate for incorporations into a polymer matrix in which dipole alignment is obtained by corona poling.¹²

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