Selective Electrochemical and Photochemical Syntheses of Unsymmetrical Biaryls and Their Non-linear Optical Properties

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A selective synthesis of unsymmetrically substituted electron donor/electron acceptor biaryls is described which is based on an electrochemically or photochemically induced $S_{RN}1$ reaction; the optical hyperpolarizability coefficients β are determined in solution for the various reaction products and found to be of the same order of magnitude as that of 4-nitro-aniline.

Biaryls which are unsymmetrically substituted with electron acceptors and electron donors are among the most suitable molecular subunits for non-linear optical properties which require (i) a high polarizability of the molecules constituting the material, (ii) a good transparency in the frequency region usually employed for second harmonic generation (SHG) (1.06—0.53 μm).[1] It has been found that the highly polarizable biphenyl subunit permits the variation of the amount of acceptor–donor charge transfer by changing the angle between the two substituted aromatic rings.[2] This paper describes the synthesis of unsymmetrical biaryls based on a chemically,[3] photochemically,[4] or electrochemically[5] induced $S_{RN}1$ mechanism, in which a phenoxy-derivative acts as a nucleophile[6a] towards a halogeno-cyano-disubstituted aromatic derivative (**1**). The mechanism involved in the electrochemically induced process is the subject of a separate publication.[6b] The non-linear optical properties of the condensation products were determined in solution by the electric field-induced second harmonic generation method.[7]

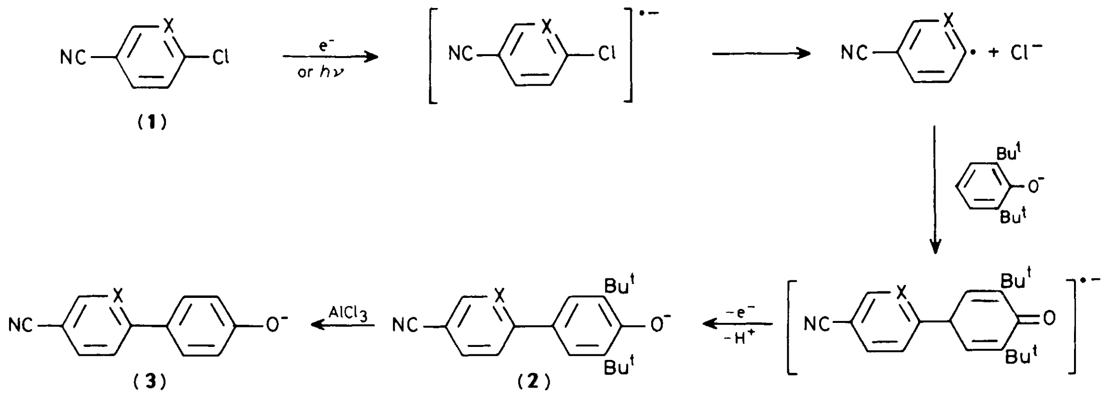
The unsymmetrical biaryls were synthesized in liquid ammonia.[8] The electrolysis was carried out in an undivided cell using a Mg soluble anode and a Pt cathode, with a constant current density of 20 mA cm^{-2} between the two electrodes.[6] Photochemical reactions were carried out using a high pressure Hg lamp. In both cases the first step involved the reduction of the cyano-halogeno-disubstituted derivative (**1**) to form a radical-anion which in turn yielded the corresponding radical by elimination of the halide. The highly reactive radical then condensed with the 2,6-di-t-butyl-phenoxide ion to give the coupling product, Scheme 1.

The corresponding phenols (**2a**) and (**2b**) were obtained by protonation using an ammonium salt. In the case of the pyridine derivative, a 1 : 1 mixture of pyridine and pyridine *N*-oxide was obtained. The overall chemical yield based on the starting chloro-cyano-derivative was *ca.* 20% by the electrochemical method for both (**2a**), mixed with its *N*-oxide, and

Table 1. Wavelength of the charge transfer band ($\lambda_{max.}$) and hyperpolarizability coefficients (β) determined at 1.06 μm.[a]

	$\lambda_{max.}$/nm	β/10^{-30} e.s.u.[b]	Ref.
p-H_2N–C_6H_4–NO_2	320	20	16
		35	17
p-MeO–C_6H_4–CN	247	5	18
p-MeO–C_6H_4–NO_2	314	14—17	18
p-H_2N–C_6H_4–CN	269	13	18
(**2a**)	329	23 ± 5	This work
(**2b**)	300	17 ± 4	,,
(**3b**)	292	21 ± 6	,,
p-NC–C_6H_4–C_6H_4–OMe-p	292	20	,,

[a] The permanent dipole moments were calculated by the bond additivity method.[18] An estimate of the accuracy is given when possible. [b] β (MKS in 10^{-40} m^4V^{-1}) = 4.189 × 10^{-10} β (CGS in e.s.u.).



a; X = N
b; X = CH

Scheme 1

(**2b**).[†] The yields increased to 70% under photochemical activation. The electrochemical yield was also increased to 70% in the case of (**2b**) by using 4,4′-bipyridyl as redox catalyst.[9]

Compounds (**2a**) and (**2b**), on treatment with $AlCl_3$ in toluene, gave the corresponding de-t-butylated molecules (**3**).[10]

The above methods of preparation were more suitable than alternative purely chemical routes.[11]

The non-linear optical properties of (**2a**), (**2b**), and (**3b**) and some closely related derivatives were determined in acetone solutions (Yag-Nd laser; 1.06 μm) (Table 1). The hyperpolarizability coefficient β depends on the donor and acceptor strength of the substituents and, hence, on the maximum absorption wavelength of the charge transfer band.[12] The donor and acceptor groups may be ranked in the order $-OH < -OMe < -NH_2$ and $-CN < -NO_2$.[13] It can be seen from Table 1 that *p*-nitro-aniline is *ca.* 5 times more effective than the corresponding methoxy-cyano-compound. The use of the biphenyl subunit as a polarizable relay group allows us to achieve the same efficiency (20—25 10^{-30} e.s.u.) because of the increase of the conjugation length.[14] 4-Hydroxy-4′-cyano-biphenyl derivatives are then as efficient as standard nitro-aniline compounds at the wavelength studied (1.06 μm) but with a better transparency. Cyano-pyridine moieties lead to slightly higher β values as compared to the corresponding substituted benzene derivatives.

The molecular units synthesized are shown to offer a good efficiency–transparency trade-off in non-linear optical applications. The ionization of the phenol derivatives into the corresponding phenoxide anions should significantly reinforce their electron donor strength[15] and thus yield higher hyperpolarizabilities. A modification of the electric field-induced SHG in solution is currently under study to allow us to measure the hyperpolarizabilities of such salts.

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[†] Yields of isolated products. The crude residue obtained after evaporation of the volatile material was extracted with dichloromethane and purified by chromatography over SiO_2. (**2a**), (**2a**)-N-oxide, and (**2b**) were recrystallized from heptane.

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