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]

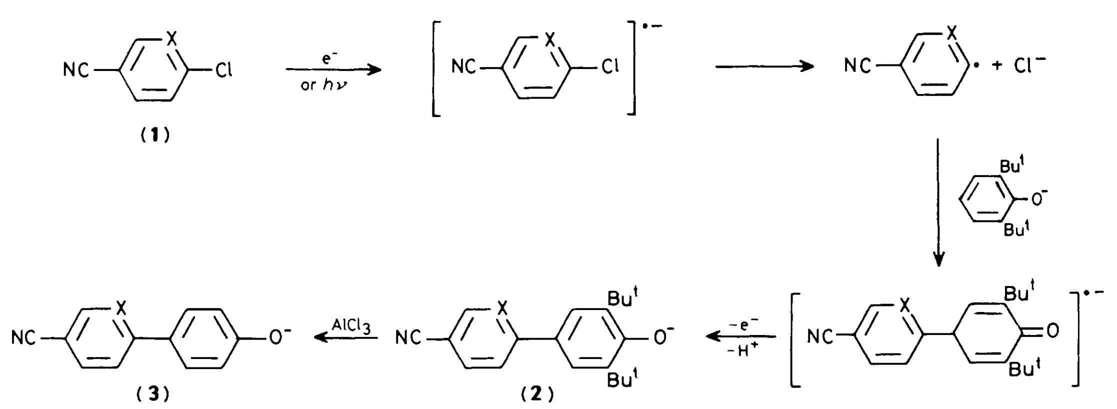
The unsymmetrical biaryls were synthesized in liquid ammonia.[8] The electrolysis was carried out in an undivided cell using a Mg soluble anode and a Pt cathode, with a constant current density of 20 mA cm^{-2} between the two electrodes.[6] Photochemical reactions were carried out using a high pressure 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	$\beta/10^{-30}$ 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^{4}V^{-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.

We acknowledge Dr. J.-F. Nicoud, Dr. R. Beugelmans and Dr. J. Zyss for helpful discussions. Thanks are due to P. Fremaux for technical support. The work was supported by grants from CNET (856B) and PIRSEM (ATP no. 2241).

Received, 27th July 1987; Com. 1087

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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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