The Diazonium Group: an Electron Acceptor for Large Molecular Hyperpolarizabilities

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The diazonium compounds 4-dialkylamino-4′-phenylazobenzenediazonium tetrafluoroborate are synthesised and their molecular hyperpolarizabilities (β) measured with the hyper-Rayleigh scattering technique; the diazonium compounds show much larger β values than the corresponding nitro compounds.

The search for new organic materials with large non-linear optical (NLO) properties is of considerable interest.[1] The second-order NLO properties of donor–acceptor substituted π-conjugated compounds have been studied extensively. Various acceptor groups such as nitro, cyano, sulfonyl and polycyanovinyl have been used to produce a large molecular hyperpolarizability (β).

The diazonium group is well known for its strong electron-withdrawing power. In fact, no other electron-withdrawing groups known today have higher Hammett σ values than the diazonium group ($\sigma_p = 1.91$ and $\sigma_m = 1.76$).[2] Nevertheless, it has not been used as an acceptor group in NLO materials, perhaps due to its poor stability. In a joint theoretical investigation with Mhin and Kim[3] we showed that substituting the nitro group of *N,N*-dimethylamino-4-nitroaniline for a diazonium group almost doubled the hyperpolarizability. A similar theoretical result was also reported recently by Kanis *et al.*[4] Here we report the synthesis of new second-order NLO materials containing a diazonium group as an electron acceptor and the determination of their unusually large β values by the Hyper–Rayleigh scattering (HRS) technique.[5,6]

4-Dialkylamino-4′-phenylazobenzenediazonium tetrafluoroborates (alkyl = methyl, **2** or ethyl, **4**) were prepared by the coupling of *p*-nitrobenzenediazonium tetrafluoroborate and dialkylaniline, followed by reduction of the nitro group to amine with sodium sulfide, and finally by diazotization with sodium nitrite.† These compounds are stable in the solid state but decompose slowly in solution after a few hours. We also prepared the corresponding nitro compounds **1** and **3** for comparison of the β values.†

As the EFISH (electric field induced second harmonic generation) technique cannot be applied to conducting solutions, the β values of these ionic compounds were measured by the HRS technique. All measurements were performed in methanol solution with a fundamental wavelength of 1064 nm. The known β value for *p*-nitroaniline (PNA) in methanol (34.5×10^{-30} esu)[7] was used as a reference. The error on these results is approximately 15%. The measured hyperpolarizabilities β and the static β_0 obtained from the two-level approximation of these compounds as well as their absorption maxima are given in Table 1.

The diazonium compounds **2** and **4** have intense charge-transfer (CT) bands in the visible region which are strongly red-shifted compared with those of the corresponding nitro compounds **1** and **3**. Such a red shift indicates that a diazonium group induces a better charge-asymmetry than a nitro group in the π-conjugated system. Indeed, the comparison of β and β_0 values of the diazonium and corresponding nitro compounds revealed that the former have much larger hyperpolarizabilities. We attribute this observed enhancement of first hyperpolarizability (β) when a nitro group is replaced by a diazonium group to the stronger electron-withdrawing ability of the diazonium group and the more effective charge-transfer interaction between the diazonium group and the dialkylamino group.

In summary, we have demonstrated that the diazonium group is superior to a nitro group for achieving a large hyperpolarizability. It remains to be seen how various counter anions affect the β values of the diazonium salts and how one can improve the stability of this class of compounds.

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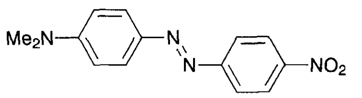
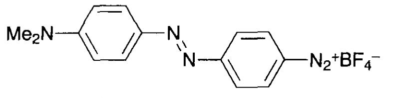
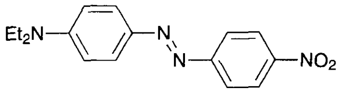
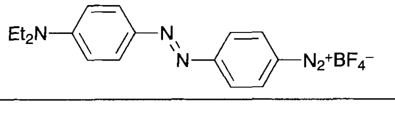
Table 1 Optical data for substituted azobenzenes measured in methanol

	Compound	λ_{max}/nm	$\beta/10^{-30}$ esu	$\beta_0/10^{-30}$ esu
1		474	610	90 (39.9)[a]
2		586	1,500	240
3		490	905	110 (49.6)[a]
4		622	1,340	320

[a] Taken from ref. 8.

Footnote

† Satisfactory elemental analyses were obtained for all the compounds. *Selected spectra data*: **1**: ^{1}H NMR ([$^2H_6$]acetone): δ 3.16 (s, 6H), 6.87 (d, *J* 9.26 Hz, 2H), 7.89 (m, 4H), 8.36 (d, *J* 9.33 Hz, 2H); **2** ^{1}H NMR ([$^2H_6$]acetone): δ 3.33 (s, 6H), 7.02 (d, *J* 9.03 Hz, 2H), 8.00 (d, *J* 9.39 Hz, 2H), 8.24 (d, *J* 9.22 Hz, 2H), 8.88 (d, *J* 9.19 Hz, 2H); IR (KBr disk): ν cm^{-1} 2235 (m, N_2^+); **3**: ^{1}H NMR ([$^2H_6$]acetone): δ 1.22 (t, 6H), 3.53 (q, 4H), 6.86 (d, *J* 9.33 Hz, 2H), 7.89 (m, 4H), 8.34 (d, *J* 9.33 Hz, 2H); **4**: ^{1}H NMR ([$^2H_6$]acetone): δ 1.26 (t, 6H), 3.63 (q, 4H), 6.97 (d, *J* 9.33 Hz, 2H), 7.93 (d, *J* 9.33 Hz, 2H), 8.16 (d, *J* 9.33 Hz, 2H), 8.81 (d, *J* 9.36 Hz, 2H); IR (KBr disk): ν cm^{-1} 2249 (m, N_2^+).

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