Pergamon

Tetrahedron Letters, Vol. 35, No. 48, pp. 9073-9074, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01936-3

The Phosphonate Ester Group in Nonlinear Optical Donor-acceptor Benzenes

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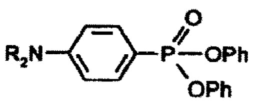
Abstract: The phosphonate ester group, typified by $P(=O)(OPh)_2$, is an effective π-electron acceptor group in donor-acceptor substituted benzenoid compounds for nonlinear optics, and has the added attractions of being easily functionalised for further fabrication into cross-linked films, and imparting transparency to simple derivatives.

We report in this Letter results of solution measurements of the quadratic hyperpolarisability, β, of two simple benzene phosphonate derivatives, 1 and 2, and conclude phosphonate may have potential as a π-electron acceptor group in nonlinear optical (NLO) materials for second harmonic generation (SHG) of blue light.



(1) R = H

(2) R = Et

Various characteristics must be designed into a molecule if it is to be optimal for application in NLO materials. The typical molecular structure for quadratic NLO is a π-conjugated system substituted by π-donor and π-acceptor groups, such as *p*-nitroaniline.[1] If the application is SHG, a further requirement is transparency at the second harmonic wavelength. Much current interest is in SHG materials for generation of blue light (ca 410nm) from semiconductor lasers (ca. 820 nm). This implies that the SHG material should be colourless, and so most nitroaniline derivatives are unsuitable. Furthermore, the molecules must be arranged noncentrosymmetrically in the bulk material phase for nonzero NLO activity. A major area of interest is electrically-poled films, where oriented dipolar molecules are locked into a noncentrosymmetric polymer matrix by means of cross-linking. This in turn implies the need for suitable functionality at both ends of the molecule to enable cross-linking.[2] Such functionality is easy to introduce into π-donor groups, but appropriately functionalised π-acceptor groups are scarcer. The methacrylate (di)ester of *N*-sulphonyl-(di)ethanolamine has recently been introduced in this role.[2]

Our search for further π-acceptor groups which combine a favourable effect on NLO properties with transparency and scope for functionalisation led us to consider the phosphonate group.[3] We are aware of only one earlier report of phosphorus-based electron-acceptors in molecules for NLO, where chiral phosphine oxide crystals and their nitroaniline co-crystals were studied for SHG.[4] However, these results gave no indication of the intrinsic molecular NLO activity, as reflected by β, of $P(=O)R_2$-based compounds.

Phosphonates **1** and **2** were prepared by a route previously reported.[5,6] Molecular hyperpolarisabilities were determined for each in acetone solution by the electric field induced second harmonic generation (EFISH) method.[7] This leads to a zero field β(0) value, reflecting the intrinsic quadratic NLO activity of the molecule.[8]

For **1**, β(0) is 3.2×10^{-30} e.s.u., and for **2**, 8.4×10^{-30} e.s.u.[9] The significance of these values becomes apparent when coupled with the optical spectra of the molecules and then compared with known values for benzenoid analogues. λ_{max}(acetone) is 276 nm for **1** and 286 nm for **2**. In general, it is found that increase in β is accompanied by an increase in λ_{max}, and there is therefore a conflict between higher NLO activity and transparency - the "transparency-efficiency trade-off".[10] In fact, a reasonable linear relationship between β and λ_{max} has been demonstrated.[11] For benzenoid compounds with λ_{max} up to about 315 nm, none has β above about 5×10^{-30} e.s.u., and it is only for derivatives with λ_{max} as bathochromic as 350 nm that β reaches that found for **2**.[11] As a specific comparison, *p*-nitroaniline has a β value of 9×10^{-30} e.s.u. and λ_{max} 378 nm.[11] Compound **1** therefore behaves much as other donor-acceptor substituted benzenes. But of more significance, phosphonate **2** is almost as NLO active as a comparable molecule whose λ_{max} is almost 100 nm higher.

Thus, donor-acceptor-substituted benzenes with phosphonate ester as the acceptor group are attractive options for SHG materials, where the relatively hypsochromic chromophore provides scope for increasing β by further chemical modification without compromising transparency with respect to the SH wavelength.[12] This is emphasised by the absorbance cut-off wavelength of ca. 350 nm for a concentrated solution of **2**. Furthermore, functionalisation of the phosphonate ester could lead to derivatives suitable for cross-linking in poled films.[13]

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6. **1**: white microcrystals from CCl_4; m.p. 99-102°C; **2**: white microcrystals from CCl_4; m.p. 116-118°C. Microanalysis and ^{1}H nmr (250 MHz; $CDCl_3$) and mass spectra were consistent with assigned structures for **1** and **2**.
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8. To extract β values, ground state dipole moments μ were also measured; for **1**: $\mu = 5.5$ D; for **2**: $\mu = 5.7$ D.
9. The EFISH measurements were done at 1.34 μm, and the dispersion enhanced β values at this wavelength are 4×10^{-30} e.s.u. and 10.9×10^{-30} e.s.u. for **1** and **2**, respectively. The error is estimated to be ±10%.
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12. In contrast, where Ph_2P acts as a phosphorus-based electron *donor* group in *p*-$Ph_2PC_6H_4CN$ (**3**) the β value is unexceptional: $\beta(0) = 2.5 \times 10^{-30}$ e.s.u.; $\beta(1.34) = 3.2 \times 10^{-30}$ e.s.u; $\mu = 4.2$ D; $\lambda_{max} = 292$ nm (acetone).
13. Molecules **1**, **2**, and **3** are SHG inactive in their crystalline phases, indicating for each that molecular dipoles cancel, possibly due to crystallisation in centrosymmetric space groups.

(*Received in UK* 15 *August* 1994; *revised* 27 *September* 1994; *accepted* 30 *September* 1994)