

## The Third-order Optical Non-linearity of the Phenylethynyl-substituted Benzene System

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Phenylethynyl substituted benzenes **1**, **2** and **3** are synthesized by the Pd-coupling reaction of phenylacetylene with the corresponding bromobenzene; the third-order optical non-linearity [ $\chi^{(3)}(\omega)$ ] increases with the participation of  $\pi$ -conjugation through the triple bond as determined by the degenerate four-wave mixing (DFWM) method in a chloroform solution.

Much attention has been devoted to the search for non-linear organic materials having large third-order non-linearity ( $\chi^{(3)}$ ).<sup>1</sup> Third-order non-linear organic compounds such as  $\pi$ -conjugated polymers,<sup>2</sup> organic photoconductors<sup>3</sup> and organic charge-transfer high conducting complexes<sup>4</sup> exhibit NLO effects to the order of  $10^{-9}$  to  $10^{-11}$  esu for the  $\chi^{(3)}$ .

Most of the third-order non-linearity relies on the  $\pi$ -conjugated double-bond framework. In addition to such a  $\pi$ -conjugated system, triple-bond conjugation would be another way of increasing the size of  $\chi^{(3)}$ , together with the bond alternation expected for the enhancement of non-linearity.<sup>1</sup> Although the effect of triple-bond alternation on  $\chi^{(3)}$  is still not quantitatively discussed, polydiacetylene<sup>2a,b</sup> and polyphenyleneethynylene systems<sup>2d,e</sup> seem to take advantage of it.

This paper describes the third-order non-linearity of three types of phenylethynyl substituted benzenes, **1**, **2** and **3**, which are different in the  $\pi$ -conjugation contribution of the phenylethynyl group through the triple bond to the central phenyl ring.

The compounds were synthesized by the Pd-catalysed coupling of phenylacetylene with the corresponding bromobenzene.<sup>†</sup>

The UV spectra ( $10^{-5}$  mol dm<sup>-3</sup>; CHCl<sub>3</sub>) are shown in Fig. 1. The maximum absorption of **1** at 300 nm indicates that each of the three phenylethynyl groups at *meta*-positions are not involved in  $\pi$ -conjugation, whereas **2** and **3** exhibit  $\lambda_{\max}$  at 315 and 350 nm, respectively, indicating the contribution of the phenylethynyl group to the  $\pi$ -conjugation system. X-Ray analysis of **2** reveals that two of the phenylethynyl groups substituted at *para*-positions are inclined by 11.2° from the central phenyl plane, while the other two groups at *ortho*-positions are twisted to at least 36.2°.‡ Presumably, the nearly planar  $\pi$ -conjugation with *para*-substituted phenylethynyl groups can exist, together with the non-planar conjugation through the triple bond for **2** and **3** which may be related to the shoulder absorptions at 350 and 370 nm, respectively. The relatively bathochromic shift of **3** is consistent with the larger

$\pi$ -conjugation through the triple bond which is not simply due to the planar conjugation, although the precise nature requires a detailed understanding of the X-ray analysis of **3** which has not been completed.

This behaviour is reflected in the nonlinearity of **1**, **2** and **3**, illustrated by the value of  $\chi^{(3)}(\omega)$ , determined by the degenerate four-wave mixing (DFWM) method at 532 nm in a chloroform solution.  $\chi^{(3)}(\omega)$  for **1**, **2** and **3** is  $5.6 \times 10^{-12}$ ,  $1.1 \times 10^{-11}$  and  $2.8 \times 10^{-10}$ , respectively.  $\chi^{(3)}(\omega)$  increases in the order **1** < **2** < **3**, demonstrating that the phenylethynyl groups can take part in the resonance enhancement of  $\chi^{(3)}(\omega)$  through the triple bond even if they are not in the planar arrangement. Moreover, **1**, **2** and **3** exhibit no absorbance at 532 nm that was used for the DFWM measurements, suggesting that the  $\chi^{(3)}(\omega)$  may come

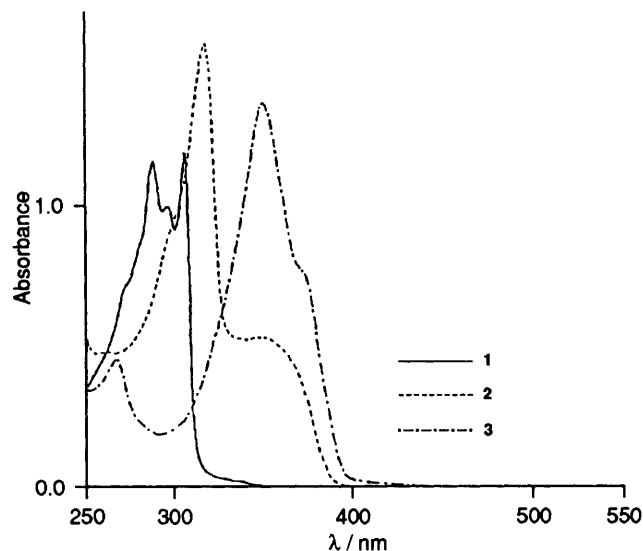
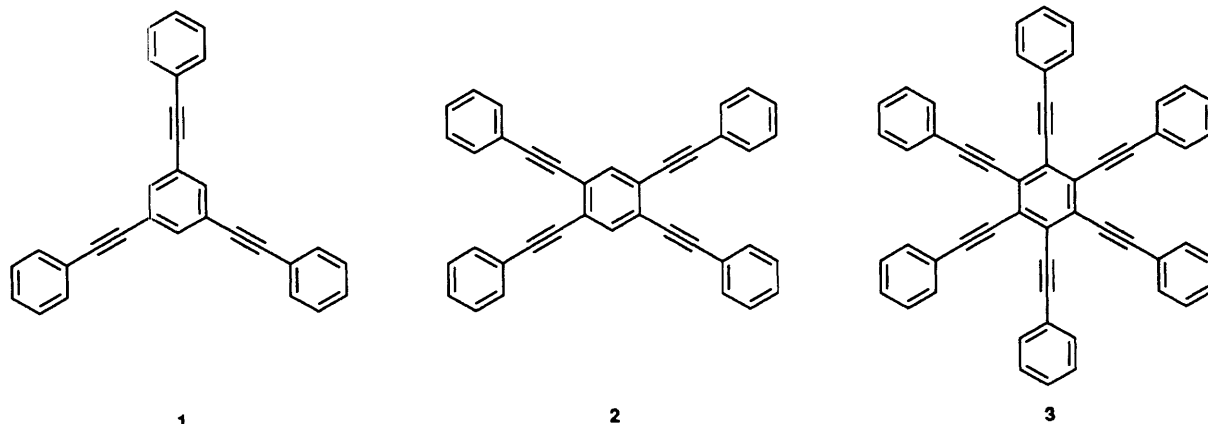


Fig. 1 UV spectra for **1**, **2** and **3**



from almost the non-resonant region which has not been observed with other non-linear organic compounds.

Received, 23rd September 1994; Com. 4/05809G

#### Footnotes

† *General procedure*: Hexabromobenzene (1 mol) and phenylacetylene (6.93 mol) were refluxed in *N,N,N,N*-tetramethylethylenediamine (20 ml) for 8 h under  $N_2$  in the presence of  $PdCl_2(PPh_3)_2$  (0.01 mmol),  $PPh_3$  (0.02 mmol) and  $CuI$  (0.02 mmol). After removal of the insoluble material, the solvent was removed *in vacuo* and the residue recrystallized from toluene to give the product **3** in 15% yield, mp 169 °C (169–170 °C lit.<sup>5</sup>);  $^1H$  NMR (270 MHz,  $CDCl_3$ )  $\delta$  7.52–7.78 (m, 30H); IR  $\nu/cm^{-1}$  (KBr) 2190s, 760m and 650m.

‡ *Crystal data* for **2**: monoclinic, space group;  $C2/c$ ,  $Z = 4$ ,  $R = 0.074$ ,  $a = 30.99$ ,  $b = 4.96$ ,  $c = 18.80$  Å,  $\beta = 112.06^\circ$ .

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