Synthesis and non-linear properties of disubstituted diphenylacetylene and related compounds

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A variety of disubstituted diphenylacetylenes and related compounds have been synthesized by a modified Horner–Emmons reaction, and their second harmonic generation (SHG) has been evaluated by the Kurtz powder method. The diphenylacetylenes with weak electron-donating and -withdrawing groups are found to be efficient for SHG, as well as having the lowest cut-off wavelength.

In recent decades, much attention has been focused on non-linear materials from both theoretical and practical points of view. In particular, second harmonic generation (SHG) based on organic compounds is interesting because of the large non-linear susceptibilities produced by intramolecular charge transfer (ICT) in π-conjugated systems, which is substantially different from inorganic materials.[1] Most SHG active organic compounds are based on *p*-nitroaniline derivatives, despite the recent discovery of non-linear rigid ICT acetylene frameworks.[2] Disubstituted diphenylacetylene derivatives, however, have not been studied in terms of their non-linear properties, except for a few examples such as 1-(4-methoxyphenyl)-2-(4-nitrophenyl)acetylene[3,4] and 1-(4-bromophenyl)- and 1-(4-iodophenyl)-2-(4-nitrophenyl)acetylene,[5] due to the tedious preparation based on the oxidative coupling of cuprous arylacetylides with aryl iodides. Although this classical oxidative method has now been superseded by the recently developed Pd-catalysed coupling of ethynylbenzene derivatives with iodo- or bromo-substituted aromatic compounds, the latter is limited to π-conjugated systems.[6]

While searching for another preparation of diphenylacetylenes, we realised that a modified Horner–Emmons reaction has previously proved useful for triple bond formation and has afforded a variety of pyridylphenylacetylenes.[7]

Here we describe the synthesis of 4,4′-disubstituted diphenylacetylenes and related compounds based on a modified Horner–Emmons reaction, together with their SHG properties.

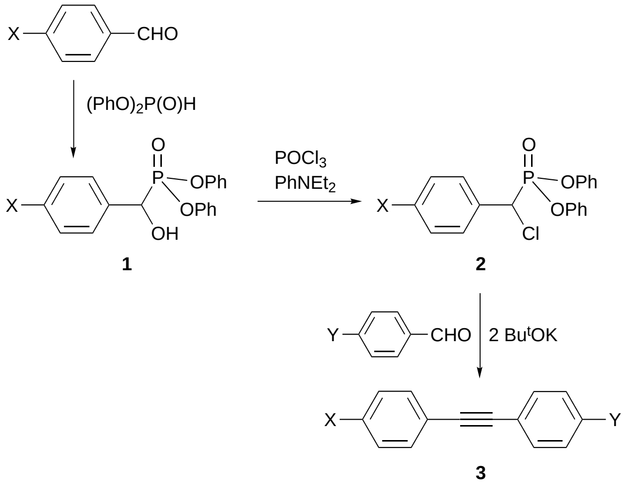
Results and Discussion

Zimmer *et al.* reported that phosphonate carbanions couple with aryl aldehydes under mild basic conditions to give chlorostilbenes or diphenylacetylenes.[8] This method, however, has not been used widely because of the sensitive reaction conditions required for the preparation of the starting hydroxy phosphonate, which is thermally liable and prone to rearrangement to the phosphate.[9] Therefore the temperature control, as well as choice of solvent, was examined.

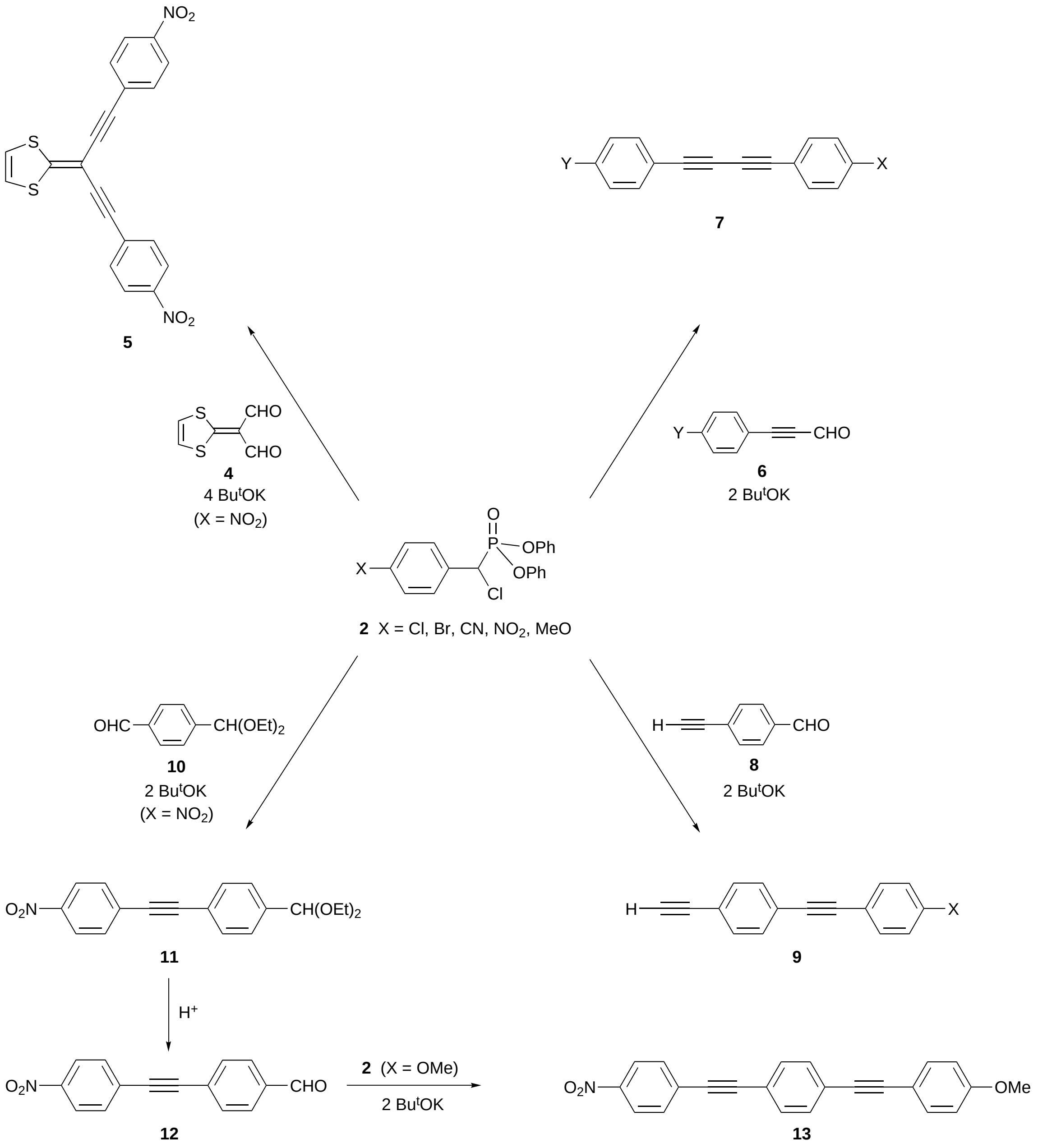
Diphenyl phosphite was allowed to react with the appropriate 4-substituted benzaldehydes in THF for a few hours below 25 °C to afford diphenyl hydroxy(aryl)methylphosphonates **1**, which were converted to the chloro compounds **2** by treatment with $POCl_3$–$PhNEt_2$ for 1 h at 90 °C. Thus, further 4-substituted benzaldehydes and **2** were subsequently treated with 2 equiv. of Bu^tOK in THF for 3 h at room temperature to afford the 4,4′-disubstituted diphenylacetylenes **3** (Scheme 1). Based on this reaction, the related compounds (**5**, **7**, **9** and **13**) were prepared from various aldehydes (Scheme 2).

Diphenylbutadiyne **7** is considered to be a potentially useful compound for third harmonic generation (THG) since some poly(diacetylene)s synthesized from butadiynes have been found to exhibit large THG properties.[10] Moreover, the terminal acetylene **9** is attractive as a potential monomer for polymerization by W, Ta[11] and/or Rh catalysts[12] into a poly(phenylacetylene) system with similar properties.

The SHG intensity of compounds **3**, **5**, **7**, **9** and **13** relative to urea was determined by the Kurtz powder method.[13] The results are summarized in Table 1 (for **3**) and Table 2 (for **5**, **7**, **9** and **13**). Table 1 shows only the SHG active phenylacetylenes out of more than seventy compounds prepared *via* the reported method. The fact that a number of diphenylacetylenes are SHG active indicates that they tend to adopt the non-centrosymmetric crystal packing essential for SHG, a suggestion that is supported by X-ray crystallographic analysis of these molecules.[14] The large number of chloro-substituted compounds that exhibit SHG also indicates that weak dipole polarization may favour non-centrosymmetric crystal packing, which can rely on a ICT structure linked to the cut-off wavelength as shown in the weak dipole–dipole interaction of SHG active 3-methyl-4-nitropyridine *N*-oxide.[15] The cut-off wavelength of the chloro-substituted compounds **3** was as low as that of stilbene derivatives.[16] In general, compounds **3** with weak electron-withdrawing and -donating groups such as Cl and



Scheme 1



Scheme 2

MeO exhibit a hypsochromic shift in the cut-off wavelength (337 nm) that arises from the weak ICT structure needed for SHG, as compared with the bathochromic shift for compounds with strong electron-withdrawing and -donating groups (590 nm for nitro and dimethylamino substitutents) (Table 3). No significant effect of the chain length of the substituted alkoxy groups on SHG was found. Additional triple bond conjugation was not significantly effective for SHG, as shown for the nitro- and methoxy-substituted compounds **3** ($X = NO_2$, $Y = MeO$): **7** ($X = MeO$, $Y = NO_2$) and **13**, in which SHG active **3** shows a decrease in the cut-off wavelength, while SHG inactive butadiyne **7** is much more highly conjugated than the extended π-conjugated diphenylacetylene type compound **13** (Tables 1 and 2). SHG active **5** is of interest because of its triangular structure, which is similar to SHG active Λ-type methanediamine derivatives.[17]

Sample manipulation affects SHG significantly. For example, 1-(4-methylthio- and 1-(4-methoxy-phenyl)-2-(4-nitrophenyl)acetylene which were chromatographed on silica gel[2] and recrystallized from methylcyclohexane,[3] respectively, are 50 to 65 times as active as urea. However, when recrystallized from ethanol, as in our study, they are only twice as active as urea. Such solvent effects may be due to crystal polymorphism related to crystal packing, which can vary when different solvents are used during crystallization. Further studies involving X-ray crystallography are currently in progress.

Experimental

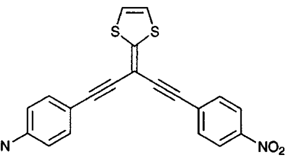
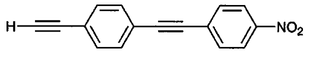
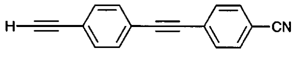
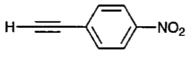
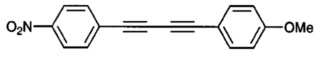
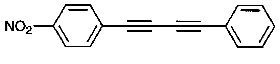
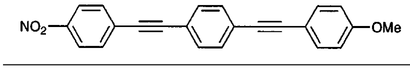
THF was distilled over sodium and $LiAlH_4$. 4-Alkoxybenzaldehydes were obtained by the reaction of 4-hydroxybenzaldehyde with the relevant alkyl bromide [$Me(CH_2)_nBr$; $n = 4$–11] in DMF in the presence of sodium hydride at 50 °C for 24 h. 6,6-Diformyl-1,4-dithiafulvene **4**,[18] 4-ethynylbenzaldehyde **8**[19] and 4-(diethoxymethyl)benzaldehyde **10**[20] were prepared by literature methods. 4-Substituted 3-phenyprop-2-ynal **6** was obtained by the formylation of 4-substituted ethynylbenzene,[21] which was derived from 4-substituted trimethylsilylethynylbenzene[6a] or 4-aryl-2-methylbut-3-yn-2-ol.[22]

Table 1 Relative SHG powder efficiency of **3**

3			
X	Y	SHG^a	cut-off wavelength/nm
NO_2	SMe	2.7	462
NO_2	OMe	2.0	425
CN	OC_5H_{11}	7.5	373
CN	OC_6H_{13}	0.1	375
CN	OC_7H_{15}	4.0	375
CN	F	0.1	350
CN	Br	0.1	406
CN	NMe_2	0.1	457
CN	NEt_2	0.1	474
Cl	SMe	0.1	360
Cl	OMe	0.1	337
Cl	OEt	0.1	343
Cl	OPr	0.1	332
Cl	OBu	0.1	346
Cl	OC_5H_{11}	0.1	337
Cl	OC_6H_{13}	2.8	350
Cl	OC_7H_{15}	0.1	348
Cl	OC_8H_{17}	0.8	347
Cl	$OC_{10}H_{25}$	0.9	342
Cl	$OC_{12}H_{25}$	0.5	383
Cl	F	0.1	320
Cl	NMe_2	4.7	433
Cl	NEt_2	0.1	427
Br	OMe	1.4	347
Br	OC_6H_{13}	0.1	352
Br	OC_7H_{15}	0.1	351
Br	OC_8H_{17}	0.1	428
Br	NEt_2	0.1	433

^{a}Relative to urea.

Table 2 Relative SHG powder efficiency of extended π-conjugated systems

extended π-conjugated system	SHG^a	cut-off wavelength/nm
	0.1	520
	5.0	483
	1.0	475
	1.5	467
	0	485
	0	456
	0	470

^{a}Relative to urea.

Second harmonic generation measurements

The samples were ground with a mortar and pestle, meshed to 75 to 100 μm and fixed on a glass slide by tape. The slide was irradiated by a Nd-YAG laser ($\lambda = 1064$ nm, pulse width 350 ps, power density 5 GW cm^{-2}, spot size 0.8 mm) and the intensity of SHG light (532 nm) was monitored by a photodiode and compared with the SHG intensity of urea.

Table 3 Cut-off wavelength for varied substitution in compound **3**

3		
X	Y	cut-off wavelength/nm
NO_2	F	418
NO_2	OMe	425
NO_2	NEt_2	590
CN	F	350
CN	OMe	374
CN	NEt_2	474
Br	F	324
Br	OMe	347
Br	NEt_2	433
Cl	F	320
Cl	OMe	337
Cl	NEt_2	427

Cut-off wavelength

The cut-off wavelength was determined from 95% of the transmittance, which was measured for a 1 mM MeCN solution of the compounds.

Diphenyl hydroxy(4-nitrophenyl)methylphosphonate 1 ($X=NO_2$)

To a solution of 4-nitrobenzaldehyde (12 g, 80 mmol) in dry THF (30 cm^3) was added dropwise a solution of diphenyl phosphite (18.7 g, 80 mmol) in dry THF (20 cm^3) over 30 min, and the reaction was stirred for 3 h at room temperature. After evaporation of the solvent, the residue was recrystallized from ethanol to give the product (65%), mp 125 °C; $\delta_H[(CD_3)_2SO]$ 4.65 (1H, s, OH), 5.38 (1H, d, CH, J_{HP}12†), 6.90–7.41 (10H, m, aromatic H), 7.68 (2H, d, aromatic H), 8.18 (2H, d, aromatic H); ν_{max}(KBr)/cm^{-1} 3280s (OH), 1520s and 1330s (NO_2), 1250m (P=O), 1060m, 1020m and 960m (P–O) (Found: C, 59.15; H, 4.17; N, 3.60. $C_{19}H_{16}NO_6P$ requires C, 59.22; H, 4.19; N, 3.64%).

Diphenyl chloro(4-nitrophenyl)methylphosphonate 2 ($X=NO_2$)

1 ($X=NO_2$) (9.3 g, 24.1 mmol) was treated with 25 cm^3 of $POCl_3$ in the presence of *N*,*N*-diethylaniline (2 cm^3) for 1 h at 90 °C. After evaporation of the solvent and addition of ice–water, the reaction was extracted with CH_2Cl_2, and the extracts were washed with aqueous sodium hydrogen carbonate and dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue recrystallized from ethanol to give the product (84%), mp 121 °C; $\delta_H[(CO_3)_2SO]$ 5.64 (1H, d, CH, J_{HP} 15), 7.20–7.65 (10H, m, aromatic H), 8.08 (2H, d, aromatic H), 8.52 (2H, d, aromatic H); ν_{max}(KBr)/cm^{-1} 1520s and 1350s (NO_2), 1270m (P=O), 1070m, 1020m and 960m (P–O) (Found: C, 56.71; H, 3.68; N, 3.37. $C_{19}H_{15}NO_5PCl$ requires C, 56.52; H, 3.74; N, 3.47%).

Diphenyl chloro(4-methoxyphenyl)methylphosphonate 2 (X=MeO)

Yield 27%, mp 117 °C; $\delta_H[(CD_3)_2SO]$ 3.85 (3H, s, CH_3), 5.20 (1H, d, CH, J_{HP} 14), 6.80–7.65 (14H, m, aromatic H) (Found: C, 61.35; H, 4.96. $C_{20}H_{18}O_4PCl$ requires C, 61.78; H, 4.63%).

Diphenyl chloro(4-cyanophenyl)methylphosphonate 2 (X=CN)

Yield 68%, mp 125 °C; $\delta_H[(CD_3)_2SO]$ 5.23 (1H, d, CH, J_{HP} 15), 6.80–7.30 (10H, m, aromatic H), 7.65 (4H, m, aromatic H) (Found: C, 62.26; H, 3.92; N, 3.68. $C_{20}H_{15}NO_3PCl$ requires C, 62.59; H, 3.94; N, 3.65%).

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† *J* values given in Hz.

Diphenyl chloro(4-chlorophenyl)methylphosphonate 2 (X = Cl)

Yield 56% mp 91 °C; $\delta_H[(CD_3)_2SO]$ 5.17 (1H, d, CH, J_{HP} 14), 6.90–7.50 (14H, m, aromatic H) (Found: C, 57.94; H, 3.67. $C_{19}H_{15}O_3PCl_2$ requires C, 58.04; H, 3.85%).

Diphenyl bromo(4-bromophenyl)methylphosphonate 2 (X = Br)

Yield 29%, mp 107 °C; $\delta_H[(CD_3)_2SO]$ 5.17 (1H, d, CH, J_{HP} 14), 6.50–7.30 (10H, m, aromatic H), 7.48 (4H, s) (Found: C, 51.84; H, 3.40. $C_{19}H_{15}O_3PClBr$ requires C, 52.14; H, 3.45%).

1-(4-Methoxyphenyl)-2-(4-nitrophenyl)acetylene 3 (X = NO_2, Y = MeO)

Compound **2** (X = NO_2) (1.25 g, 3.07 mmol) and 4-methoxybenzaldehyde (0.60 g, 4.0 mmol) in THF (30 cm^3) were treated with Bu^tOK (1.0 g, 8.9 mmol) for 3 h at room temperature. After evaporation of the solvent, water (20 cm^3) was added to the residue, the aqueous mixture was extracted with CH_2Cl_2, and the organic fractions were dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was recrystallized from ethanol to give the product in 58% yield, mp 115 °C; $\delta_H(CDCl_3)$ 3.90 (3H, s, CH_3), 7.09–8.24 (8H, m, aromatic H); $\nu_{max}(KBr)/cm^{-1}$ 2210m ($C\equiv C$), 1510s and 1335s (NO_2) (Found: C, 71.06; H, 4.39; N, 5.50. $C_{15}H_{11}NO_3$ requires C, 71.14; H, 4.38; N, 5.53%).

1-(4-Cyanophenyl)-2-(4-pentyloxyphenyl)acetylene 3 (X = CN, Y = $C_5H_{11}O$)

Yield 34%, mp 83 °C; $\delta_H(CDCl_3)$ 0.63–2.65, (8H, m, CH_2), 3.65 (3H, t, CH_3), 6.54–7.25 (8H, m, aromatic H); $\nu_{max}(KBr)/cm^{-1}$ 2940s, 2910s and 2840s (C–H), 2210m ($C\equiv N$), 2200m ($C\equiv C$) (Found: C, 82.64; H, 6.63; N, 4.57. $C_{20}H_{19}NO$ requires C, 83.01; H, 6.62; N, 4.84%).

1-(4-Chlorophenyl)-2-(4-dimethylaminophenyl)acetylene 3 (X = Cl, Y = NMe_2)

Yield 32%, mp 150 °C; $\delta_H(CDCl_3)$ 2.03 (6H, d, CH_3) 6.55–7.43 (8H, m, aromatic H); $\nu_{max}(KBr)/cm^{-1}$ 2890s, 2850s and 2800s (C–H), 2200m ($C\equiv C$) (Found: C, 75.10; H, 5.37; N, 5.17. $C_{16}H_{14}NCl$ requires C, 75.14; H, 5.52; N, 5.48%).

1-(4-Bromophenyl)-2-(4-methoxyphenyl)acetylene 3 (X = Br, Y = MeO)

Yield 26%, mp 155 °C; $\delta_H(CDCl_3)$ 3.86 (3H, s, CH_3) 6.36–7.50 (8H, m, aromatic H); $\nu_{max}(KBr)/cm^{-1}$ 2970m, 2930m and 2840m (C–H), 2200m ($C\equiv C$) (Found: C, 62.48; H, 3.77. $C_{15}H_{11}OBr$ requires C, 62.74; H, 3.86%).

3-(4-Nitrophenyl)prop-2-ynal 6 (Y = NO_2)

4-Bromonitrobenzene (50 g, 247 mmol) and 2-methylbut-3-yn-2-ol (25 g, 297 mmol) were refluxed for 2 h in triethylamine (500 cm^3). The solvent was evaporated under reduced pressure and the residue was recrystallized from benzene to give 4-(4-nitrophenyl)-2-methylbut-3-yn-2-ol in 79% yield, mp 102 °C; $\delta_H(CDCl_3)$ 1.62 (6H, s, CH_3), 2.17 (1H, s, OH), 7.50 (2H, d, aromatic H), 8.13 (2H, d, aromatic H). The alcohol (15 g, 73 mmol) and Bu^tOK (2 g, 17.8 mmol) were refluxed for 50 min in Bu^tOH (50 cm^3), the solvent was evaporated under reduced pressure and the residue was recrystallized from ethanol to give 1-ethynyl-4-nitrobenzene in 67% yield, which can also be prepared from 1-bromo-4-nitrobenzene and trimethylsilylacetylene.[6a] Thus, 1-ethynyl-4-nitrobenzene (1.48 g, 10.0 mmol) and triethyl orthoformate (30 cm^3) were heated in the presence of zinc iodide (0.14 g, 0.4 mmol) at 140 °C for 2 h to remove ethanol by distillation. The residue was distilled under reduced pressure to give 3-(4-nitrophenyl)prop-2-ynal diethyl acetal (bp 150 °C at 1 torr) in 60% yield; $\delta_H(CDCl_3)$ 1.32 (6H, t, CH_3), 3.75 (4H, q, CH_2), 5.50 (1H, s, CH), 7.60 (2H, d, aromatic H), 8.15 (2H, d, aromatic H). The acetal (3 g, 12 mmol) was hydrolysed with 0.5 M sulfuric acid (50 cm^3) at 110 °C for 40 min, and the reaction was extracted with CH_2Cl_2 to give 3-(4-nitrophenyl)prop-2-ynal in 54% yield, mp 95 °C; $\delta_H(CDCl_3)$ 7.78 (2H, d, aromatic H), 8.30 (2H, d, aromatic H), 9.50 (1H, s, CH); $\nu_{max}(KBr)/cm^{-1}$ 2260m ($C\equiv C$), 1620s (C=O) (Found: C, 61.50; H, 3.05; N, 7.87. $C_9H_5NO_3$ requires C, 61.71; H, 2.88; N, 8.00%).

1-(4-Ethynylphenyl)-2-(4-nitrophenyl)acetylene 9 (X = NO_2)

Compound **2** (X = NO_2) (2.01 g, 4.9 mmol) and 4-ethynylbenzaldehyde **8** (0.65 g, 4.9 mmol) were treated with Bu^tOK (1.20 g, 10.7 mmol) in THF (30 cm^3) for 3 h at room temperature. After evaporation of the solvent, the residue was extracted with CH_2Cl_2, and the solution dried over $MgSO_4$. The solvent was removed and the residue recrystallized from ethanol to give the product in 44% yield, mp 211 °C; $\delta_H(CDCl_3)$ 3.23 (1H, s, CH), 7.52 (2H, d, aromatic H), 7.70 (2H, d, aromatic H), 8.13 (2H, d, aromatic H), 8.28 (2H, d, aromatic H); $\nu_{max}(KBr)/cm^{-1}$ 3240m (C–H), 2200m ($C\equiv C$), 1500s and 1335s (NO_2) (Found: C, 77.62; H, 3.60; N, 5.58. $C_{16}H_9NO_2$ requires C, 77.72; H, 3.67; N, 5.67%).

1-(4-Cyanophenyl)-2-(4-ethynylphenyl)acetylene 9 (X = CN)

Mp 207 °C; $\delta_H(CDCl_3)$ 3.10 (1H, s, CH), 7.38 (4H, m, aromatic H), 7.52 (4H, m, aromatic H); $\nu_{max}(KBr)/cm^{-1}$ 3225m (C–H), 2220m ($C\equiv N$), 2200 ($C\equiv C$) (Found: C, 89.63; H, 3.80; N, 6.05. $C_{17}H_9N$ requires C, 89.84; H, 3.99; N, 6.16%).

6,6-Bis[2-(4-nitrophenyl)ethynyl]-1,4-dithiafulvene 5

Compound **2** (X = NO_2) (1.61 g, 4 mmol) and 6,6-diformyl-1,4-dithiafulvene (0.30 g, 1.7 mmol) were treated with Bu^tOK (1.0 g, 9.2 mmol) in THF (50 cm^2) for 4 h at room temperature. After evaporation of the solvent, the residue was extracted with CH_2Cl_2 and the solution dried over $MgSO_4$. The solvent was removed and residue recrystallized from ethanol to give the product in 15% yield, mp 115 °C; $\delta_H(CDCl_3)$ 7.15–8.25 (8H, m, aromatic H); $\nu_{max}(KBr)/cm^{-1}$ 2200m ($C\equiv C$), 1510s and 1330s (NO_2) (Found: C, 58.52; H, 2.85; N, 6.52. $C_{20}H_{12}N_2O_4S_2$ requires C, 58.81; H, 2.96; N, 6.86%).

1-(4-Methoxyphenylethynyl)-4-(4-nitrophenylethynyl)benzene 13

Compound **2** (X = NO_2) (2.01 g, 5.01 mmol) and compound **10** (1.0 g, 4.81 mmol) were treated with Bu^tOK (1.2 g, 10.7 mmol) in THF (30 cm^3) for 3 h at room temperature. After evaporation of the solvent the residue was stirred with 1 M hydrochloric acid (50 cm^3) for 30 min, then the reaction was extracted with CH_2Cl_2, and the organic fractions dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue recrystallized from ethanol to give 1-(4-formylphenyl)-2-(4-nitrophenyl)acetylene **12** (X = NO_2) in 60% yield. Compound **12** (X = NO_2) (0.15 g, 1 mmol) and compound **2** (X = MeO) (0.39 g, 1 mmol) were similarly treated with Bu^tOK (0.23 g, 2.02 mmol) to give the final product in 20% yield, mp 193 °C; $\delta_H(CDCl_3)$ 6.75–7.50 (8H, m, aromatic H), 7.55 (2H, d, aromatic H), 8.10 (2H, d, aromatic H); $\nu_{max}(KBr)/cm^{-1}$ 2200m ($C\equiv C$), 1505s and 1335s (NO_2) (Found: C, 78.05; H, 4.18; N, 3.85. $C_{23}H_{15}NO_3$ requires C, 78.17; H, 4.28; N, 3.96%).

1-(4-Methoxyphenyl)-4-(4-nitrophenyl)buta-1,3-diyne 7 (X = MeO, Y = NO_2)

3-(4-Nitrophenyl)prop-2-ynal (0.175 g, 1 mmol) and compound **2** (X = MeO) (0.388 g, 1 mmol) were treated with Bu^tOK (0.25 g, 2.2 mmol) in THF (30 cm^3) for 4 h at room temperature. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was recrystallized from benzene to give the title compound in 20% yield, mp 244 °C; $\delta_H(CDCl_3)$ 3.98 (3H, s, CH_3), 6.89 (2H, d, aromatic H), 7.57 (2H, d, aromatic H), 7.75 (2H, d, aromatic H), 8.33 (2H, d, aromatic H); $\nu_{max}(KBr)/cm^{-1}$ 2200m (C≡C), 1510s and 1335s (NO_2) (Found: C, 73.30; H, 3.98; N, 4.80. $C_{17}H_{11}NO_3$ requires C, 73.64; H, 4.00; N, 5.05%).

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