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

Koichi Kondo,*^a Takumi Fujitani^b and Noriaki Ohnishi^b

^aDepartment of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525, Japan ^bDepartment of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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 nonlinear 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 nonlinear 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 Although this classical oxidative method has now been superseded by the recently developed Pd-catalysed coupling of ethynylbenzene derivatives with iodo- or bromosubstituted aromatic compounds, the latter is limited to π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 $POCl_3$ -PhNEt₂ 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, Ta¹¹ and/or Rh catalysts¹² 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 3methyl-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



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-nitrophe-nyl)acetylene which were chromatographed on silica gel² 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(CH₂)_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			22
Х	Y	SHG ^a	cut-off wavelength/nm
NO,	SMe	2.7	462
NO,	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

"Relative to urea.

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



"Relative to urea.

Second harmonic generation measurements

The samples were ground with a mortar and pestle, meshed to 75 to 100 μ m and fixed on a glass slide by tape. The slide was irradiated by a Nd-YAG laser (λ =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			
Х	Y	cut-off wavelength/nm	
NO ₂	F	418	
NO,	OMe	425	
$NO_2^{\tilde{2}}$	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 cm³) was added dropwise a solution of diphenyl phosphite (18.7 g, 80 mmol) in dry THF (20 cm³) 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; $\delta_{\rm H}$ [(CD₃)₂SO] 4.65 (1H, s, OH), 5.38 (1H, d, CH, $J_{\rm HP}$ 12†), 6.90–7.41 (10H, m, aromatic H), 7.68 (2H, d, aromatic H), 8.18 (2H, d, aromatic H); $v_{\rm max}$ (KBr)/cm⁻¹ 3280s (OH), 1520s and 1330s (NO₂), 1250m (P=O), 1060m, 1020m and 960m (P–O) (Found: C, 59.15; H, 4.17; N, 3.60. C₁₉H₁₆NO₆P requires C, 59.22; H, 4.19; N, 3.64%).

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

1 (X=NO₂) (9.3 g, 24.1 mmol) was treated with 25 cm³ of POCl₃ in the presence of *N*,*N*-diethylaniline (2 cm³) for 1 h at 90 °C. After evaporation of the solvent and addition of ice–water, the reaction was extracted with CH₂Cl₂, and the extracts were washed with aqueous sodium hydrogen carbonate and dried over MgSO₄. The solvent was evaporated *in vacuo* and the residue recrystallized from ethanol to give the product (84%), mp 121 °C; $\delta_{\rm H}$ [(CO₃)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); $v_{\rm max}$ (KBr)/cm⁻¹ 1520s and 1350s (NO₂), 1270m (P=O), 1070m, 1020m and 960m (P–O) (Found: C, 56.71; H, 3.68; N, 3.37. C₁₉H₁₅NO₅PCl requires C, 56.52; H, 3.74; N, 3.47%).

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

Yield 27%, mp 117°C; $\delta_{\rm H}$ [(CD₃)₂SO] 3.85 (3H, s, CH₃), 5.20 (1H, d, CH, $J_{\rm HP}$ 14), 6.80–7.65 (14H, m, aromatic H) (Found: C, 61.35; H, 4.96. C₂₀H₁₈O₄PCl requires C, 61.78; H, 4.63%).

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

Yield 68%, mp 125 °C; $\delta_{\rm H}[(\rm CD_3)_2 \rm SO]$ 5.23 (1H, d, CH, $J_{\rm HP}$ 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. C₂₀H₁₅NO₃PCl requires C, 62.59; H, 3.94; N, 3.65%).

 $[\]dagger J$ values given in Hz.

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

Yield 56% mp 91 °C; $\delta_{\rm H}$ [(CD₃)₂SO] 5.17 (1H, d, CH, $J_{\rm HP}$ 14), 6.90–7.50 (14H, m, aromatic H) (Found: C, 57.94; H, 3.67. C₁₉H₁₅O₃PCl₂ requires C, 58.04; H, 3.85%).

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

Yield 29%, mp 107 °C; $\delta_{\rm H}$ [(CD₃)₂SO] 5.17 (1H, d, CH, $J_{\rm HP}$ 14), 6.50–7.30 (10H, m, aromatic H), 7.48 (4H, s) (Found: C, 51.84; H, 3.40. C₁₉H₁₅O₃PClBr requires C, 52.14; H, 3.45%).

1-(4-Methoxyphenyl)-2-(4-nitrophenyl)acetylene 3 (X=NO₂, Y=MeO)

Compound 2 (X=NO₂) (1.25 g, 3.07 mmol) and 4-methoxybenzaldehyde (0.60 g, 4.0 mmol) in THF (30 cm³) were treated with Bu'OK (1.0 g, 8.9 mmol) for 3 h at room temperature. After evaporation of the solvent, water (20 cm³) was added to the residue, the aqueous mixture was extracted with CH₂Cl₂, and the organic fractions were dried over MgSO₄. The solvent was removed *in vacuo* and the residue was recrystallized from ethanol to give the product in 58% yield, mp 115 °C; $\delta_{\rm H}$ (CDCl₃) 3.90 (3H, s, CH₃), 7.09–8.24 (8H, m, aromatic H); $v_{\rm max}$ (KBr)/cm⁻¹ 2210m (C=C), 1510s and 1335s (NO₂) (Found: C, 71.06; H, 4.39; N, 5.50. C₁₅H₁₁NO₃ 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; $\delta_{\rm H}$ (CDCl₃) 0.63–2.65, (8H, m, CH₂), 3.65 (3H, t, CH₃), 6.54–7.25 (8H, m, aromatic H); $\nu_{\rm max}$ (KBr)/cm⁻¹ 2940s, 2910s and 2840s (C–H), 2210m (C≡N), 2200m (C≡C) (Found: C, 82.64; H, 6.63; N, 4.57. C₂₀H₁₉NO requires C, 83.01; H, 6.62; N, 4.84%).

1-(4-Chlorophenyl)-2-(4-dimethylaminophenyl) acetylene 3 (X = Cl, Y = NMe₂)

Yield 32%, mp 150 °C; $\delta_{\rm H}$ (CDCl₃) 2.03 (6H, d, CH₃) 6.55–7.43 (8H, m, aromatic H); $v_{\rm max}$ (KBr)/cm⁻¹ 2890s, 2850s and 2800s (C–H), 2200m (C=C) (Found: C, 75.10; H, 5.37; N, 5.17. C₁₆H₁₄NCl 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; $\delta_{\rm H}$ (CDCl₃) 3.86 (3H, s, CH₃) 6.36–7.50 (8H, m, aromatic H); $v_{\rm max}$ (KBr)/cm⁻¹ 2970m, 2930m and 2840m (C–H), 2200m (C \equiv C) (Found: C, 62.48; H, 3.77. C₁₅H₁₁OBr requires C, 62.74; H, 3.86%).

3-(4-Nitrophenyl)prop-2-ynal 6 (Y = NO₂)

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 cm³). The solvent was evaporated under reduced pressure and the residue was recrystallized from benzene to give 4-(4nitrophenyl)-2-methylbut-3-yn-2-ol in 79% yield, mp 102 °C; δ_H(CDCl₃) 1.62 (6H, s, CH₃), 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 cm³), 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 cm³) 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; $\delta_{\rm H}$ (CDCl₃)

1.32 (6H, t, CH₃), 3.75 (4H, q, CH₂), 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 cm³) at 110 °C for 40 min, and the reaction was extracted with CH₂Cl₂ to give 3-(4-nitrophenyl) prop-2-ynal in 54% yield, mp 95 °C; $\delta_{\rm H}$ (CDCl₃) 7.78 (2H, d, aromatic H), 8.30 (2H, d, aromatic H), 9.50 (1H, s, CH); $\nu_{\rm max}$ (KBr)/cm⁻¹ 2260m (C=C), 1620s (C=O) (Found: C, 61.50; H, 3.05; N, 7.87. C₉H₅NO₃ requires C, 61.71; H, 2.88; N, 8.00%).

1-(4-Ethynylphenyl)-2-(4-nitrophenyl)acetylene 9 (X = NO₂)

Compound **2** (X=NO₂) (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 cm³) for 3 h at room temperature. After evaporation of the solvent, the residue was extracted with CH₂Cl₂, and the solution dried over MgSO₄. The solvent was removed and the residue recrystallized from ethanol to give the product in 44% yield, mp 211 °C; $\delta_{\rm H}$ (CDCl₃) 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); $v_{\rm max}$ (KBr)/cm⁻¹ 3240m (C–H), 2200m (C=C), 1500s and 1335s (NO₂) (Found: C, 77.62; H, 3.60; N, 5.58. C₁₆H₉NO₂ requires C, 77.72; H, 3.67; N, 5.67%).

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

Mp 207 °C; $\delta_{\rm H}$ (CDCl₃) 3.10 (1H, s, CH), 7.38 (4H, m, aromatic H), 7.52 (4H, m, aromatic H); $v_{\rm max}$ (KBr)/cm⁻¹ 3225m (C–H), 2220m (C=N), 2200 (C=C) (Found: C, 89.63; H, 3.80; N, 6.05. C₁₇H₉N requires C, 89.84; H, 3.99; N, 6.16%).

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

Compound 2 (X=NO₂) (1.61 g, 4 mmol) and 6,6-diformyl-1,4dithiafulvene (0.30 g, 1.7 mmol) were treated with Bu^tOK (1.0 g, 9.2 mmol) in THF (50 cm²) for 4 h at room temperature. After evaporation of the solvent, the residue was extracted with CH₂Cl₂ and the solution dried over MgSO₄. The solvent was removed and residue recrystallized from ethanol to give the product in 15% yield, mp 115 °C; $\delta_{\rm H}$ (CDCl₃) 7.15–8.25 (8H, m, aromatic H); $v_{\rm max}$ (KBr)/cm⁻¹ 2200m (C=C), 1510s and 1330s (NO₂) (Found: C, 58.52; H, 2.85; N, 6.52. C₂₀H₁₂N₂O₄S₂ 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 $Bu^{t}OK$ (1.2 g, 10.7 mmol) in THF (30 cm³) for 3 h at room temperature. After evaporation of the solvent the residue was stirred with 1 м hydrochloric acid (50 cm³) for 30 min, then the reaction was extracted with CH₂Cl₂, and the organic fractions dried over MgSO₄. The solvent was removed under reduced pressure, and the residue recrystallized from ethanol to give 1-(4formylphenyl)-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; $\delta_{\rm H}$ (CDCl₃) 6.75–7.50 (8H, m, aromatic H), 7.55 (2H, d, aromatic H), 8.10 (2H, d, aromatic H); $v_{max}(KBr)/cm^{-1}$ 2200m (C=C), 1505s and 1335s (NO₂) (Found: C, 78.05; H, 4.18; N, 3.85. C₂₃H₁₅NO₃ requires C, 78.17; H, 4.28; N, 3.96%).

1-(4-Methoxyphenyl)-4-(4-nitrophenyl)buta-1,3-diyne 7 (X = MeO, Y = NO₂)

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 cm³) for 4 h at room temperature. After evaporation of the solvent, the residue was dissolved

in CH₂Cl₂ and dried over MgSO₄. The solvent was removed in vacuo and the residue was recrystallized from benzene to give the title compound in 20% yield, mp 244 °C; $\delta_{\rm H}({\rm CDCl}_3)$ 3.98 (3H, s, CH₃), 6.89 (2H, d, aromatic H), 7.57 (2H, d, aromatic H), 7.75 (2H, d, aromatic H), 8.33 (2H, d, aromatic H); $v_{max}(KBr)/cm^{-1}$ 2200m (C=C), 1510s and 1335s (NO₂) (Found: C, 73.30; H, 3.98; N, 4.80. C₁₇H₁₁NO₃ requires C, 73.64; H, 4.00; N, 5.05%).

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