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Synthesis of Donor–Acceptor Substituted Quinonemethide Imines for Nonlinear Optical Materials

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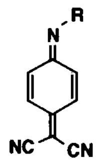
ABSTRACT

Six quinonemethide imines (4-methylene-2,5-cyclohexadien-1-imines) containing electron-donating groups such as the diphenylamino or p-*(diethylamino)-phenyl group and electron-accepting groups such as the cyano group were prepared for use in nonlinear optical materials, and their nonlinear optical properties were studied.*

INTRODUCTION

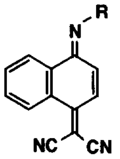
There is growing interest in the design and synthesis of new organic molecules with large second-order nonlinear optical properties for telecommunication, data storage and information processing applications.[1,2] It has been generally recognized that conjugated molecules in which an electron-donating group is separated from an electron-accepting group by a conjugated bridge possess large second-order nonlinear optical properties. Several donor–acceptor substituted organic compounds such as benzenes, stilbenes, biphenyls, azobenzenes and Schiff bases have been reported.[1,2] These compounds carry one or two phenyl rings with or without π-linkages as the conjugated bridge. It is known that quinonoid compounds have a very small energy difference between the ground and the excited states.[3] Recently, it was reported that colorants having a quinonoid structure, such as *N*,*N*-dimethylindoaniline (Phenol Blue), exhibited large second-order molecular hyperpolarizability (β).[4] Therefore, introduction of a quinonoid structure as conjugated bridge into a compound may be expected to result in enhanced charge-transfer properties and nonlinear responses. However, the number of donor–acceptor substituted quinonemethide imines having a quinonoid structure is few.[5,6]

In this paper, we describe the synthesis of *N*-(diphenylamino)- and *N*-[*p*-(diethylamino)phenyl]-4-(dicyanomethylene)-2,5-cyclohexadien-1-imines (**1a** and **1b**), *N*-(diphenylamino)- and *N*-[*p*-(diethylamino)-phenyl]-4-(dicyanomethylene)-1(4H)-naphthalenimines (**2a** and **2b**) and *N*-(diphenylamino)- and *N*-[*p*-(diethylamino)phenyl]-10-(dicyanomethylene)-9(10H)-anthracenimines (**3a** and **3b**) as new donor–acceptor substituted quinonemethide imines and some preliminary data on nonlinear optical properties, although **2b** has been previously reported.[6]



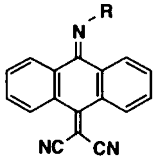
1

a: R= NPh_2
b: R= $C_6H_4NEt_2$



2

a: R= NPh_2
b: R= $C_6H_4NEt_2$



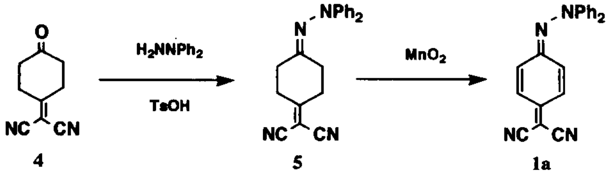
3

a: R= NPh_2
b: R= $C_6H_4NEt_2$

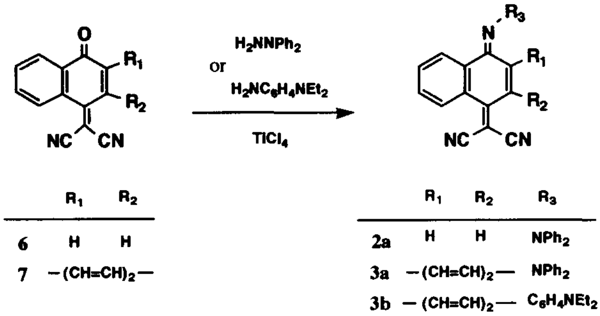
RESULTS AND DISCUSSION

Compound **1a** was prepared successfully according to the procedure shown in Scheme 1. 4-(Dicyanomethylene)cyclohexane (**4**)[7] was subjected to a dehydration reaction with 1,1-diphenylhydrazine in the presence of *p*-toluenesulfonic acid to give 4-(dicyanomethylene)cyclohexanone diphenylhydrazone (**5**) as pale brown needles in 69% yield. Compound **5** was readily oxidized with activated manganese dioxide in chloroform to give **1a** as purple needles with a metallic lustre in 53% yield.

Compounds **2a**, **3a** and **3b** were prepared successfully by dehydration of 4-(dicyanomethylene)-1(4H)-naphthalenone (**6**)[8] and 10-(d-cyanomethylene)-9(10H)-anthracenone (**7**)[9] with 1,1-diphenylhydrazine or *N*,*N*-diethyl-*p*-phenylenediamine using titanium tetrachloride as dehydrating reagent (Scheme 2). Compound **2a** was obtained as dark green needles



Scheme 1



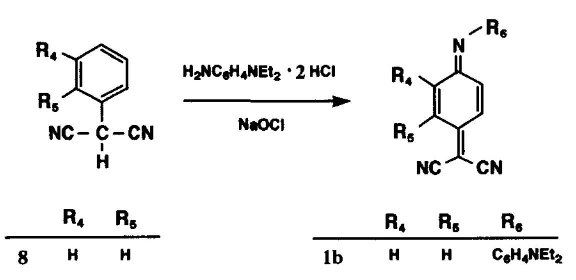
Scheme 2

with a metallic lustre in 21% yield, **3a** as red needles in 44% yield, and **3b** as red needles in a low yield (6%).

Compound **1b** was prepared from the reaction of phenylmalononitrile (**8**)[10] with *N*,*N*-diethyl-*p*-phenylenediamine dihydrochloride, using sodium hypochlorite as oxidizing reagent by the method reported by Kubo *et al.*[6] (Scheme 3). Compound **1b** was obtained as red needles in 47% yield and compound **2b** was obtained as red needles in 20% yield from 1-(dicyanomethyl)naphthalene (**9**)[11] according to the method reported by Kubo *et al.*[6]

Previously, it was reported that when *N*-cyano-4-(dicyanomethylene)-2,5-cyclohexadien-1-imine[8] and 7-(alkoxycarbonyl)-7-cyanoquinonemethides (4-[(alkoxycarbonyl)cyanomethylene]-2,5-cyclohexadien-1-one[12]) were dissolved in basic aprotic polar solvents such as tetrahydrofuran, acetone, acetonitrile, dimethyl sulfoxide and *N*,*N*-dimethylformamide (DMF), spontaneous polymerization of them occurred. However, spontaneous homopolymerizations of **1**, **2** and **3** did not occur on dissolving them in these solvents, indicating that **1**, **2** and **3** are stable in such solvents.

Second-order nonlinear optical properties for **1**, **2** and **3** were estimated by the powder second harmonic generation method,[13] that is, by comparing their second harmonic (SH) signals with that of urea at wavelength of 1064 nm. Relative intensities of their SH signals against that of



Scheme 3

urea were as small as 1/20–1/100; their second-order molecular hyperpolarizabilities (β) have not been measured yet. The third-order nonlinear optical susceptibility ($\chi^{(3)}$) of **1a** was evaluated by the Maker fringe method[14] in 1 wt% solution in DMF, giving 6×10^{-14} esu at wavelength of 1·90 nm.

EXPERIMENTAL

All melting points were measured on a Yanagitomo micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Hitachi R-600 FT NMR spectrometer using tetramethylsilane as an internal standard. IR and UV–Vis spectra were recorded on Jasco IR-700 and Jasco UVIDEC-430B spectrometers, respectively. Elemental analyses were carried out with a Yanagimoto CHN corder MT-3 instrument.

4-(Dicyanomethylene)-cyclohexanone diphenylhydrazone (5)

4-(Dicyanomethylene)-cyclohexanone (**4**)[7] (1·3 g, 8·2 mmol) and 1,1-diphenylhydrazine (1·5 g, 8·3 mmol) in 50 ml of benzene were refluxed for 1 h in the presence of *p*-toluenesulfonic acid (0·01 g) by using a Dean–Stark water separator. Solvent was then removed under reduced pressure giving a red brown solid, which was recrystallized from carbon tetrachloride to give 1·8 g (69% yield) of **5** as pale brown needles: m.p. 123–124°C; IR (KBr): 2228 (C≡N), 1588 (C=N), 1486 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$): δ 2·49 (2H, d, J = 5·4 Hz, CH$_2$), 2·67 (2H, d, J = 5·4 Hz, CH$_2$), 2·87 (4H, m, CH$_2$CH$_2$), 7·08 (10H, m, 2 × Ar H). Found: C, 77·10; H, 5·61; N, 17·29%. Calcd for $C_{21}H_{18}N_4$: C, 77·27; H, 5·57; N, 17·16%.

N-(diphenylamino)-4-(dicyanomethylene)-2,5-cyclohexadien-1-imine (1a)

Compound **5** (1·4 g, 4·2 mmol) was dissolved in 60 ml of chloroform and then into the solution were added activated manganese dioxide (7·0 g) and 3A molecular sieves (6·0 g). The mixture was refluxed with stirring for 15 min, cooled, and then filtered. Solvent was removed from the filtrate under reduced pressure, giving a purple solid which was dissolved in a small amount of chloroform. The resulting solution was passed through a silica-gel column using chloroform as an eluent. The purple band was eluted and solvent removed, giving a product which was recrystallized from a mixture of benzene and hexane to give 0·7 g (53% yield) of **1a** as purple needles with a metallic lustre: m.p. 164–165°C; IR (KBr): 2202 (C≡N), 1604 (C=N), 1485 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$):

δ 5·92 (2H, d, J = 10·2 Hz, quinonoid H), 6·83 (2H, d, J = 10·2 Hz, quinonoid H), 7·39 (10H, m, 2 × Ar H); UV ($CHCl_3$): 287 ($\varepsilon = 7{\cdot}3 \times 10^3$) and 544 ($\varepsilon = 4{\cdot}2 \times 10^4$) nm. Found: C, 78·56; H, 4·18; N, 17·26%. Calcd for $C_{21}H_{14}N_4$: C, 78·24; H, 4·38; N, 17·38%.

N-(diphenylamino)-4-(dicyanomethylene)-1(4H)-naphthalenimine (2a)

4-(Dicyano-methylene)-1(4H)-naphthalenone (**6**)[8] (1·5 g, 7·3 mmol) and 1,1-diphenylhydrazine (4·0 g, 21·8 mmol) were dissolved in 25 ml of THF and into the resulting solution was added titanium tetrachloride (0·7 g, 3·6 mmol) in 10 ml of pentane at room temperature. The mixture was stirred at room temperature for 1 h and then refluxed for 1·5 h. The reaction mixture was placed under reduced pressure to remove THF, to give a dark green solid which was extracted with chloroform. The extract was washed with water and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove solvent, giving a dark green solid which was dissolved in a small amount of chloroform. The resulting solution was passed through a silica-gel column using chloroform as an eluent. A dark green band was eluted, yielding, after further recrystallization of the product from a mixture of benzene and hexane, 0·55 g (21% yield) of **2a** as dark green needles with a metallic lustre: m.p. 196–197°C; IR (KBr): 2202 (C≡N), 1583 (C=N), 1433 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$): δ 6·36 (1H, d, J = 9·6 Hz, quinonoid H), 7·05 (1H, d, J = 9·6 Hz, quinonoid H), 7·40 (13H, m, Ar H), 8·78 (1H, m, Ar H); UV ($CHCl_3$): 558 ($\varepsilon = 3{\cdot}7 \times 10^4$) nm. Found: C, 80·78; H, 4·19: N, 15·03%. Calcd for $C_{25}H_{16}N_4$: C, 80·63; H, 4·33; N, 15·04%.

N-(diphenylamino)-10-(dicyanomethylene)-9(10H)-anthracenimine (3a)

Compound **3a** was obtained as red needles in 44% yield from the reaction of 10-(dicyanomethylene)-9(10H)-anthracenone (**7**)[9] with 1,1-diphenylhydrazine in a process similar to that for **2a**: m.p. 208–209°C; IR (KBr): 2222 (C≡N), 1580 (C=N), 1487 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$): δ 7·18 (10H, s, 2 × Ar H), 7·78 (4H, m, Ar H), 8·39 (4H, m, Ar H): UV ($CHCl_3$): 265 ($\varepsilon = 6{\cdot}5 \times 10^3$) and 530 ($\varepsilon = 1{\cdot}7 \times 10^4$) nm. Found: C, 82·70; H, 4·25: N, 13·05%. Calcd for $C_{29}H_{18}N_4$: C, 82·44; H, 4·29; N, 13·26%.

N-[*p*-(diethylamino)phenyl]-10-(dicyanomethylene)-9(10H)-anthracenimine (3b)

Compound **3b** was obtained as red needles in 6% yield from the reaction of **7** with *N,N*-diethyl-*p*-phenylenediamine in a process similar to that for

2a: m.p. 117–118°C; IR (KBr): 2206 (C≡N), 1614 (C=N), 1462 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$): δ 1·26 (6H, t, *J* = 7·2 Hz, 2 × CH_3), 3·52 (4H, q, *J* = 7·2 Hz, 2 × CH_2), 6·72 (2H, d, *J* = 9·0 Hz, Ar H), 7·28 (4H, s, Ar H), 7·30 (2H, d, *J* = 9·0 Hz, Ar H), 7·82 (4H, m, Ar H); UV ($CHCl_3$): 495 (ε = 6·7 × 10^4) nm. Found: C, 80·44; H, 5·61: N, 13·95%. Calcd for $C_{27}H_{22}N_4$: C, 80·57; H, 5·52; N, 13·91%.

N-[*p*-(diethylamino)phenyl]-4-(dicyanomethylene)-2,5-cyclohexadien-1-imine (1b)

Phenylmalononitrile[10] (0·8 g, 5·6 mmol) and *N,N*-diethyl-*p*-phenylenediamine dihydrochloride (2·7 g, 11·3 mmol) were dissolved in 30 ml of water containing sodium hydroxide (0·7 g, 17·5 mmol). Into the solution was added 10% aq. sodium hypochlorite (21 g) and the mixture was then stirred for 10 min at room temperature. The reaction mixture was extracted with chloroform, the extract washed with water, dried over anhydrous magnesium sulfate and then evaporated under reduced pressure to give a red solid, which was then dissolved in a small amount of chloroform. The resulting solution was passed through a silica-gel column using chloroform as eluent. The red band was eluted and yielded, after recrystallization from hexane, 0·76 g (47% yield) of **1b** as red needles: m.p. 107–107·5°C; IR (KBr): 2202 (C≡N), 1603 (C=N), 1515 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$): δ 1·21 (6H, t, *J* = 7·2 Hz, 2 × CH_3), 3·43 (4H, q, *J* = 7·2 Hz, 2 × CH_2), 6·74 (2H, d, *J* = 9·0 Hz, Ar H), 7·50 (2H, m, quinonoid H), 7·58 (2H, d, *J* = 9·0 Hz, Ar H), 8·13 (2H, m, quinonoid H); UV ($CHCl_3$): 272 (ε = 1·6 × 10^4) and 468 (ε = 2·4 × 10^4) nm. Found: C, 75·01; H, 5·98: N, 18·16%. Calcd: C, 75·47; H, 6·00; N, 18·53%.

N-[*p*-(diethylamino)phenyl]-4-(dicyanomethylene)-1(4H)-naphthalenimine (2b)

Compound **2b** was obtained as red needles in 20% yield by using 1-(dicyanomethyl)naphthalene[11] in a process similar to that for **1b**: m.p. 138–139°C (140–141°C[6]); IR (KBr): 2200 (C≡N), 1606 (C=N), 1515 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$): δ 1·21 (6H, t, *J* = 7·2 Hz, 2 × CH_3), 3·40 (4H, q, *J* = 7·2 Hz, 2 × CH_2), 6·78 (2H, d, *J* = 9·0 Hz, Ar H), 7·35 (1H, d, *J* = 10 Hz, quinonoid H), 7·60 (2H, *J* = 9·0 Hz, Ar H), 7·62 (1H, d, *J* = 6·0 Hz, Ar H), 7·95 (1H, d, *J* = 10 Hz, quinonoid H), 7·98 (1H, d, *J* = 6·0 Hz, Ar H), 8·10 (1H, m, Ar H), 9·05 (1H, m, Ar H); UV ($CHCl_3$): 328 (ε = 1·1 × 10^4) and 468 (ε = 2·5 × 10^4) nm. Found: C, 78·81; H, 5·28; N, 15·90%. Calcd for $C_{23}H_{20}N_4$: C, 78·38; H, 5·72; N, 15·90%.

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