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Novel Conjugated Donor-π-Acceptor Molecules Based on 1,3-Diselenol-2-ylidene Units

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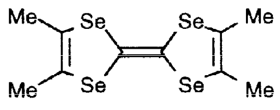
Abstract: The synthesis is described of a series of conjugated donor-π-acceptor molecules where 1,3-diselenoles are the electron donor moieties and dicyanomethylene or *N*-cyanoimine groups function as the acceptor moieties. Alkenes and aryl groups act as the conjugated spacers. The UV-VIS absorption spectra of these molecules in solution possess a low energy band resulting from intramolecular charge transfer; the wavelength of this band varies significantly with the structure of the spacer group. The solution redox properties, studied by cyclic voltammetry, reveal a reversible one-electron oxidation wave, attributed to the formation of the radical cation of the 1,3-diselenol-2-ylidene moiety, and an irreversible one-electron reduction to form the radical anion located on the dicyanomethylene or *N*-cyanoimine groups. The X-ray crystal structure of 9-(1,1-dicyanomethylene)-10-(4,5-dimethyl-1,3-diselenol-2-ylidene)-9,10-dihydroanthracene **14** is reported. The molecule is strained and adopts a "butterfly conformation" in the ground state due to unfavourable *peri*-interactions between the 1,3-diselenole selenium atoms and the *peri* hydrogens. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Molecules containing electron donor and electron acceptor units separated by a conjugated spacer group (D-π-A) have been studied extensively in the design of materials which possess interesting electronic and optical behaviour, notably intramolecular charge-transfer (ICT) and second order non-linear optical (NLO) properties.[1] These properties are dependant primarily upon three factors: i) the extent of π-conjugation, ii) the ionisation potential of the electron donor unit and iii) the electron affinity of the acceptor unit. In this context, a wide range of acceptor units have been studied, but relatively few electron donor units have been examined. Recently, we reported the use of a variety of functionalised 1,3-dithiole derivatives as the electron-donating components in D-π-A systems,[2] utilising the well-known redox behaviour of this heterocycle,[3] and building upon previous studies on 1,3-dithiole-π-A systems, which include benzo-1,3-dithiole chromophores,[4] push-pull carotenoid systems,[5] thiophene-containing systems[6] and diphenylacetylene derivatives.[7] Although the 1,3-diselenole heterocycle has enjoyed widespread attention in the field of organic molecular conductors and superconductors,[8] *e.g.* salts of tetramethyltetraselenafulvalene (TMTSF) **1**,[9] it has received very scant attention in other areas, primarily due to its relative inaccessibility. In continuation of our studies on new organoselenium systems,[10] we now report D-π-A molecules containing 1,3-diselenol-2-ylidene units.



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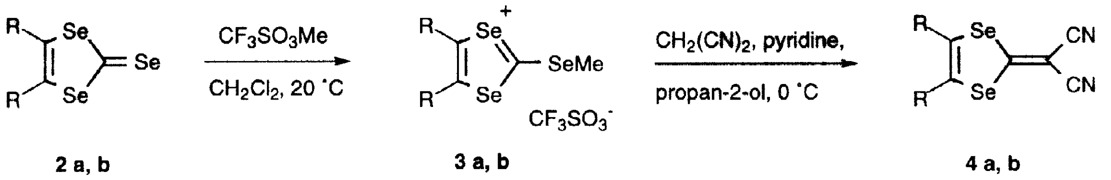
RESULTS AND DISCUSSION

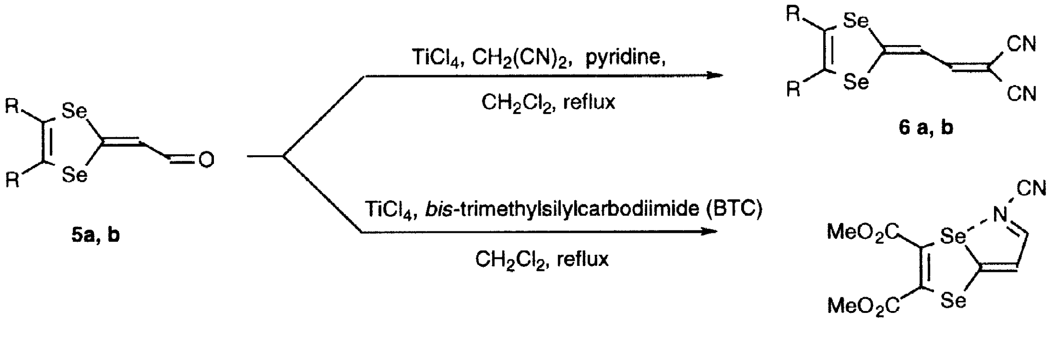
Synthesis

The synthesis of the simplest D-π-A systems **4a** and **4b**, which incorporate the dicyanomethylene acceptor group,[11] is shown in Scheme 1. This methodology is based upon the previous work of Mayer and Gebhardt[12] for the synthesis of 1,3-dithiole analogues. Thus, methylation of the selones **2a**[13] and **2b**[14] gave the 1,3-diselenonium cations **3a**[10a] and **3b**,[10b,10d] respectively, treatment of which with malononitrile, using pyridine as a base, afforded the target molecules **4a** and **4b** (53-65% yield) after the *in situ* elimination of methaneselenol.



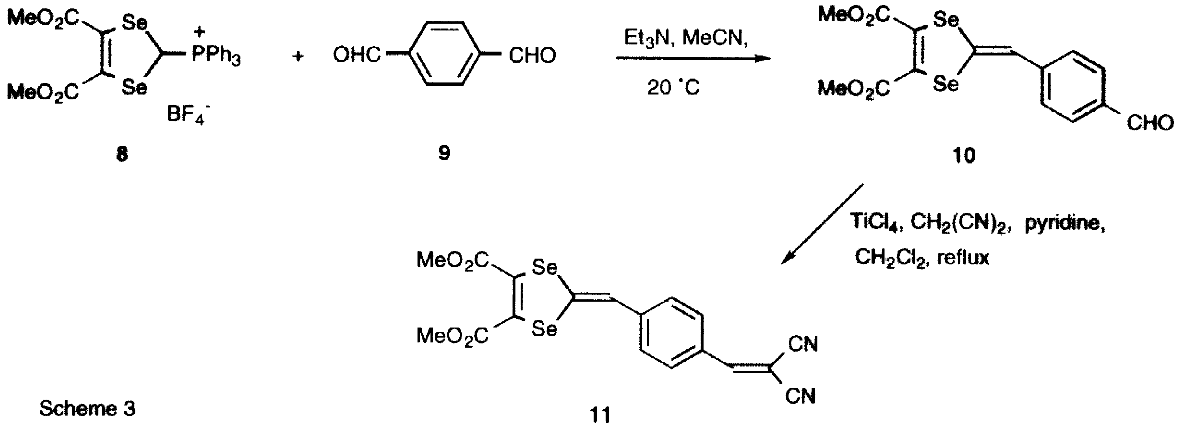
Scheme 1 **a** R = CO_2Me, **b** R = Me

Compounds **6a** and **6b**, which contain an additional double bond within the spacer unit, were prepared in *ca.* 70% yield by the reaction of Lehnert's reagent (titanium tetrachloride, malononitrile and pyridine)[15] with the conjugated aldehydes **5a**[10a,16] and **5b**,[10b] respectively, in refluxing dichloromethane (Scheme 2). Similarly, conversion of **5a** into the *N*-cyanoimine derivative **7a** (94% yield) was achieved using *bis*-trimethylsilylcarbodiimide (BTC). Comparison of the ^1H NMR spectra for compounds **6a**, **6b** and **7a** suggests that, in solution, the side chain of **6a** and **6b** adopts a very different conformation from that in **7a**. In the former compounds, the coupling constant (*J* 12 Hz) indicates an s-*trans* conformation, whereas for **7a** (*J* 4 Hz) the s-*cis* conformation is observed: such a conformation is presumably favoured for **7a** due to a close intramolecular N---Se interaction. Analogous intramolecular N---S interactions are known.[2a]



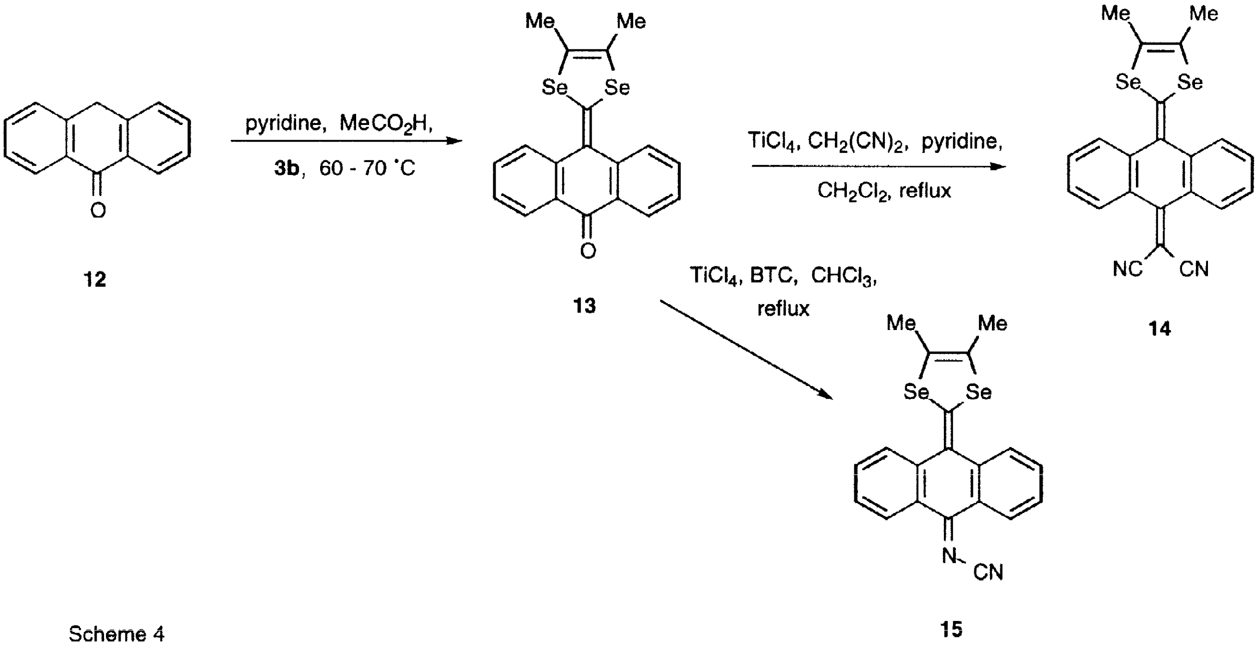
Scheme 2 **a** R = CO_2Me, **b** R = Me

It has previously been shown that aromatic spacer units within the conjugated chain between the donor and acceptor moieties can suppress intramolecular charge transfer if the intermediate obtained on excitation has a quinonoidal structure.[17] To explore this effect in our system, aldehyde **10** was synthesised in 70% yield by reaction of phosphonium salt **8**[10a,16] with terephthaldehyde **9**, and then converted into the dicyanomethylene derivative **11** (81% yield) by the standard protocol employing Lehnert's reagent (Scheme 3).



Scheme 3

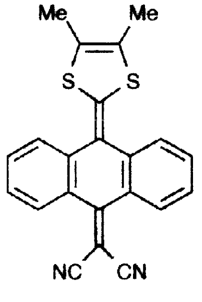
The synthetic route to compounds **14** and **15** containing the 9,10-anthracenediylidene spacer unit is outlined in Scheme 4. In contrast to compound **11**, the spacer unit in systems **14** and **15** can gain aromaticity upon intramolecular charge transfer, which should, therefore, be a favourable process. The reaction of diselenolium cation **3b** with anthrone **12** in the presence of pyridine and acetic acid, afforded ketone **13** in 86% yield, which was converted into the dicyanomethylene derivative **14** (60% yield) and the *N*-cyanoimine derivative **15** (35% yield) under standard conditions.



Scheme 4

X-Ray Molecular Structure of Compound 14

The X-ray crystal structures of the anthracenediylidene derivatives **16**[18] and **17**[19] have been determined. Both molecules are strained and adopt a "butterfly conformation" in the ground state due to unfavourable *peri*-interactions between the dithiole sulfur atoms and the *peri*-hydrogens. To determine if this buckling would be increased by the presence of the larger 1,3-diselenole unit, the X-ray structure of **14** was obtained.



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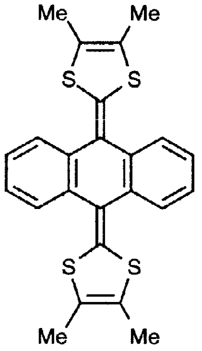

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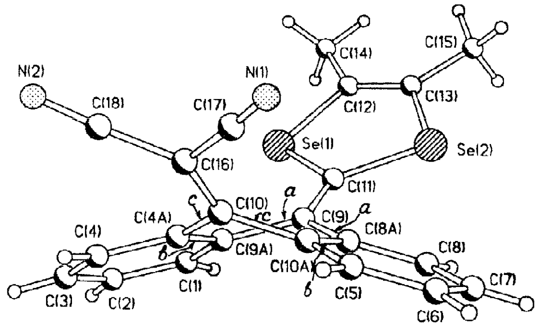

Fig.1. X-Ray molecular structure of **14**. Bond distances (Å): average Se-C 1.905(2), *a* 1.481(3), *b* 1.418(3), *c* 1.475(3), C(9)-C(11) 1.364(3), C(10)-C(16) 1.369(3), C(16)-CN 1.455(4), C(12)-C(13) 1.334(3).

The crystal of **14** is not isostructural with **16** and their molecular conformations although similar, are quantitatively different. In both structures the central anthracene-9,10-diylidene ring adopts a boat conformation: its folding along the C(8a)...C(9a) vector is larger in **14** than in **16** (32.7° *vs.* 29.2°) and so is the folding of the entire anthracene system along the C(9)...C(10) vector (36.0° compared to 33.8°) (Fig. 1). This can be attributed to increased steric repulsion between the larger chalcogen atoms in **14** and the H atoms in positions C(1) and C(8). Indeed, the difference between the corresponding Se...H and S...H distances (average 2.68 *vs.* 2.50 Å, for idealized C-H distances of 0.95 Å) is almost the same as that between the Van der Waals radii of Se (2.00 Å) and S (1.85 Å).[20] However, folding along the C(4a)...C(10a) vector is also significantly larger in **14** (32.4°) than in **16** (22.5°), without any apparent steric reason.

UV-VIS Spectroscopic and Cyclic Voltammetric Studies

The solution state UV-VIS spectra of the new D-π-A systems displayed a low energy absorption band which is attributed to ICT from the 1,3-diselenole donor unit to the acceptor unit. These data are collated in Table 1. Predictably, compounds **4a** and **4b** exhibit the highest energy charge transfer bands, due to the short conjugated pathway within these systems. The addition of a further double bond between the donor and the acceptor (*i.e.* compounds **6a** and **6b**) produced the expected bathochromic shift (*ca.* 100 - 125 nm) in the position of the ICT band. This band was also bathochromically shifted for dimethyl derivatives **4b** and **6b**, compared to their diester analogues **4a** and **6a**, reflecting the increased electron donor ability of the 1,3-diselenole ring when substituted with methyl groups instead of ester groups. It is notable that this effect of the substituents on the 1,3-diselenole ring was less evident in compounds **4a** and **4b** than in the extended systems **6a** and **6b** (bathochromic shifts of 18 and 45 nm, respectively). The data for **7a** are consistent with the decreased acceptor strength of the *N*-cyanoimine group, compared to the dicyanomethylene group.[11,21] A comparison of the data for compounds **6a** and **11**, demonstrates the effect of incorporating a benzene ring into the diene spacer unit. Although the length of the spacer is increased in **11**, effective conjugation is offset by the loss of aromaticity which would result from charge transfer through the benzene ring,[17] with the net result that the λ_{max} value of the ICT band is bathochromically shifted by only 21 nm. The lowest energy absorptions in this series of D-π-A systems are observed with compounds **14** and **15**, for which the anthracene unit attains aromaticity when charge transfer occurs. As noted previously, the ICT absorption for the *N*-cyanoimine derivative **15** shows a small hypsochromic shift compared to the dicyanomethylene analogue **14**.

The solution redox properties of D-π-A compounds **4a, 4b, 6a, 6b, 7a, 11, 14** and **15** have been studied by cyclic voltammetry and the results are collated in Table 1. All the new compounds display a reversible one-electron oxidation wave, attributed to the formation of the radical cation of the 1,3-diselenole donor moiety, and an irreversible one-electron reduction wave, to form the radical anion located on the dicyanomethylene or

N-cyanoimine group. A comparison of the data for compounds **4a**, **4b**, **6a** and **6b** reveals that there is a large cathodic shift of the oxidation potentials by 390-470 mV with increasing donor strength. The presence of the ester substituents in compound **4a** anodically shifts the reduction potential by 450 mV compared to dimethyl analogue **4b**, but this effect is negligible (only 20 mV) for the π-extended derivatives **6a** and **6b**. It is also clear that increasing the conjugation length results in a large cathodic shift in the oxidation wave and an anodic shift in the reduction wave. The UV and CV data are, therefore, entirely consistent with an increase in electron delocalisation with increasing conjugated chain length. A comparison of the data for compounds **6a** and **11** shows that upon incorporation of a benzene ring into the conjugative spacer the oxidation potential is barely changed (15 mV anodic shift), whereas the reduction potential shows a larger (130 mV) anodic shift: this would be consistent with the benzene ring in **11** exerting little effect on the delocalisation of the radical cation, but resulting in a more localised radical anion by reducing conjugation. The data for compounds **14** and **15** demonstrate that these derivatives are considerably easier both to oxidise and to reduce than the other compounds in Table 1, which is consistent with a gain in aromaticity of the spacer unit in the radical cation and radical anion species (in agreement with their UV-VIS data, discussed above). The second reduction wave for **14** and **15** is ascribed to a one-electron reduction of the anthracene unit.[22]

The data presented in Table 1 are qualitatively similar to those of analogous 1,3-dithiole derivatives,[2a,18] although it is notable that the ICT band tends to display a very small hypsochromic shift in the 1,3-diselenole series, which is consistent with the observation that the 1,3-diselenole derivatives are consistently slightly harder to oxidise ($E_{1\text{ox}}^{1/2}$ values raised by 30-90 mV). There is no significant variation in the reduction potentials between comparable 1,3-dithiole and 1,3-diselenole series.

Table 1 Electronic absorption maxima[a] and cyclic voltammetric data[b] for D-π-A systems.

Compound	λ_{max}/nm	$E_{1\text{ox}}^{1/2}$/mV	E_{red}/mV
4a	338	+2180	-1240
4b	356	+1790	-1690
6a	437	+1580	-1050
6b	482	+1110	-1070
7a	427	+1690	-1140
11	458	+1595	-1180
14	556	+966	-920, -1300
15	552	+920	-1010, -1520

[a] In CH_2Cl_2 solution, 20 °C; [b] in dry MeCN solution, *vs.* Ag/AgCl (see Experimental section for further details).

CONCLUSIONS

The chemistry of 1,3-diselenoles has been developed to provide a series of new conjugated D-π-A chromophores, in which the donor (substituted 1,3-diselenoles) and the acceptor (dicyanomethylene or *N*-cyanoimine) units are separated by a range of conjugated spacers. The electronic spectra and redox properties of these compounds have been studied. A broad low-energy intramolecular charge transfer band is observed in the UV-VIS spectra, the wavelength of which varies with the electronic structure of the donor, spacer and acceptor fragments. The lowest energy absorptions in this series are observed for compounds **14** and **15** (λ_{max} 556 and 552 nm, respectively) where the anthracene-9,10-diylidene unit attains aromaticity when charge transfer occurs. These results establish for the first time that the 1,3-diselenole heterocycle acts as an efficient electron donor component in intramolecular charge-transfer processes. Compared to 1,3-dithiole analogues studied previously, the ICT band tends to display a very small hypsochromic shift in the 1,3-diselenole series, which is consistent with the observation that the 1,3-diselenole derivatives are consistently slightly harder to oxidise. This work should stimulate further solution and solid-state studies on new 1,3-diselenole chromophores, especially compounds (*e.g.* **14**) which, due to the presence of the large selenium atoms, are not isostructural with their 1,3-dithiole analogues.

EXPERIMENTAL

General Methods. ^{1}H and ^{13}C NMR Spectra were obtained on a Varian Gemini 200 spectrometer operating at 200.10 MHz and at 50.25 MHz, respectively. Variable temperature ^{1}H NMR spectroscopy on compound **15** was performed on a Varian VXR 400S spectrometer operating at 399.96 MHz. Mass spectra were recorded on a VG7070E spectrometer operating at 70 eV. Infra-red spectra were recorded on a Perkin-Elmer 1615 FTIR spectrometer operated from a Grams Analyst 1600. UV data were obtained using a Perkin-Elmer II UV-VIS spectrophotometer operating with 1 mL quartz cells. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. All reagents were of commercial quality and solvents were dried, where necessary, using standard procedures. All reactions were performed under an inert atmosphere of argon in pre-dried glassware. Cyclic voltammetric data were measured with iR compensation using a BAS CV50 electrochemical analyser. The experiments were carried out with 5 mL of a *ca.* 10^{-4} M solution of the compound in acetonitrile containing 0.2 M tetrabutylammonium hexafluorophosphate (Fluka, puriss, electrochemical grade) as the supporting electrolyte, at scan rate 100 mV s^{-1}. The potentials were measured *versus* a platinum wire quasi-reference electrode and corrected *versus* ferrocene/ferrocene$^+$ as $E^{1/2} = +0.36$ V by adding ferrocene to the studied solution after the experiment, and referenced *versus* Ag/AgCl.

Dimethyl 2-dicyanomethylidene-1,3-diselenole-4,5-dicarboxylate 4a. To a stirred solution of diselenonium cation **3a**[10a] (100 mg, 0.18 mmol) in anhydrous propan-2-ol (20 mL) at 0 °C were added sequentially, malononitrile (0.12 mL, 0.2 mmol) and pyridine (3 mL, excess) dropwise over 15 min. A pale yellow precipitate developed and the mixture was stirred for a further 1 h. The precipitate was removed by filtration, washed with ice-cold propan-2-ol (2 x 10 mL) and dried *in vacuo* to afford **4a** as a white solid (50 mg, 65%) mp. > 250 °C; δ_H (CDCl$_3$) 3.99 (6 H, s); ν_{max} (KBr)/ cm^{-1} 1720, 1670, 1570, 1520, 1289 and 1200; *m/z* (^{80}Se, DCI) 379 (MH$^+$, 100%); Analysis Calculated for $C_{10}H_6N_2O_4Se_2$: C, 31.74; H, 1.58; N, 7.41. Found: C, 31.82 H, 1.60 N, 7.60%; λ_{max} (CH$_2$Cl$_2$) (ε /M^{-1} cm^{-1}) 248 (8.9 x 10^3) and 338 (1.8 x 10^4) nm.

4,5-Dimethyl-2-dicyanomethylidene-1,3-diselenole 4b. Following the procedure for preparation of **4a**, diselenonium cation **3b**[10b,10d] (85 mg, 0.19 mmol), anhydrous propan-2-ol (20 mL), malononitrile (0.12 mL, 0.2 mmol) and pyridine (3 mL, excess) afforded **4b** as a yellow solid (30 mg, 53%) mp. > 250 °C; δ_H (CDCl$_3$) 2.30 (6 H, s); ν_{max} (KBr)/ cm^{-1} 2209, 2201, 1457, 1439 and 1389; *m/z* (^{80}Se, DCI) 276 (M$^+$, 100%); Analysis Calculated for $C_8H_6N_2Se_2$: C, 33.10 H, 2.07; N, 9.65. Found: C, 33.18 H, 2.01 N, 9.46%; λ_{max} (CH$_2$Cl$_2$) (ε /M^{-1} cm^{-1}) 250 (7.9 x 10^3) and 356 (1.6 x 10^4) nm.

Dimethyl 2-(1,1-dicyanoprop-1-enylidene)-1,3-diselenole-4,5-dicarboxylate 6a. To a solution of aldehyde **5a**[10a,16] (125 mg, 0.35 mmol) in anhydrous dichloromethane (50 mL) was added sequentially, titanium tetrachloride (0.9 mL of a 1 M solution in dichloromethane, 0.9 mmol), malononitrile (0.22 mL, 3.5 mmol) and pyridine (0.28 mL, 3.5 mmol). The resultant yellow solution was heated under reflux for 24 h during which time a yellow precipitate formed. The mixture was then cooled, the solid was isolated by filtration and purified by column chromatography on silica gel with dichloromethane as eluent, followed by recrystallisation from hexane:dichloromethane (10:1 v/v) to afford **6a** as an orange solid (100 mg, 70%) mp. 220 - 222 °C; δ_H (CDCl$_3$) 7.12 (1 H, d, *J* 12 Hz), 7.05 (1 H, d, *J* 12 Hz) and 3.90 (6 H, s); ν_{max} (KBr)/ cm^{-1} 2218, 1693, 1573, 1533, 1285 and 1215; *m/z* (^{80}Se, DCI) 422 (MNH$_4^+$, 100%) and 404 (MH$^+$, 70%); HRMS $C_{12}H_8N_2O_4Se_2$ requires 403.8814, observed 403.8788; λ_{max} (CH$_2$Cl$_2$) (ε /M^{-1} cm^{-1}) 275 (8.6 x 10^3) and 437 (3.3 x 10^4) nm.

4,5-Dimethyl 2-(1,1-dicyanoprop-1-enylidene)-1,3-diselenole 6b. To a solution of aldehyde **5b**[10b] (44 mg, 0.15 mmol) in anhydrous dichloromethane (50 mL) were added sequentially, titanium tetrachloride (0.37 mL of a 1 M solution in dichloromethane, 0.37 mmol), malononitrile (0.1 mL, 1.7 mmol) and pyridine (0.12 mL, 1.6 mmol). The resultant orange solution was heated under reflux for 72 h, then the reaction mixture was cooled and the solvent removed *in vacuo*; purification of the crude solid by silica gel chromatography with dichloromethane as eluent, followed by recrystallisation from hexane:dichloromethane (10:1 v/v) afforded **6b** as a red solid (36 mg, 73%) mp. 235 - 236 °C; δ_H ($CDCl_3$) 7.16 (1 H, d, *J* 12 Hz), 7.04 (1 H, d, *J* 12 Hz), 2.16 (3H, s) and 2.13 (3 H, s); ν_{max} (KBr)/ cm^{-1} 2210, 1654, 1578, 1442 and 1035; *m/z* (^{80}Se, DCI) 334 (MNH_4^+, 30%) and 317 (MH^+, 100%); Analysis Calculated for $C_{10}H_8N_2Se_2$: C, 38.24 H, 2.54 N, 8.92. Found: C, 38.09 H, 2.57 N, 8.60%; λ_{max} (CH_2Cl_2) (ε /M^{-1} cm^{-1}) 274 (6.3 x 10^3), 295 (5.3 x 10^3) and 482 (3.4 x 10^4) nm.

2-(4,5-Dimethoxycarbonyl-1,3-diselenol-2-ylidene)-*N*-cyanoethanimine 7a. To a solution of aldehyde **5a** (122 mg. 0.34 mmol) in anhydrous dichloromethane (10 mL) were added sequentially, titanium tetrachloride (0.40 mL of a 1 M solution in dichloromethane, 0.40 mmol) and *bis*-trimethylsilylcarbodiimide (BTC) (0.09 mL, 0.40 mmol). The resulting solution was heated under reflux for 48 h, then cooled, and water (50 mL) and dichloromethane (50 mL) were added. The organic fraction was collected and washed sequentially with water (50 mL) and brine (50 mL), dried ($MgSO_4$) and the solvent removed in *vacuo*. Purification of the resulting crude solid, by silica gel chromatography using dichloromethane as eluent, afforded **7a** as an orange solid (119 mg, 94%) mp. 150 - 152 °C; δ_H ($CDCl_3$) 8.58 (1 H, d, *J* 4 Hz), 7.18 (1 H, d, *J* 4 Hz), 3.92 (3 H, s) and 3.90 (3 H, s); δ_C ($CDCl_3$) 168.43, 162.31, 161.87, 161.30, 143.67, 135.85, 116.38, 112.97, 53.86, 53.72; ν_{max} (KBr)/ cm^{-1} 2189, 1732, 1689, 1482 and 1227; *m/z* (^{80}Se, DCI) 381 (MH^+, 100%); Analysis Calculated for $C_{10}H_8N_2O_4Se_2$: C, 32.09 H, 2.35 N, 6.98%. Found: C, 32.19 H, 2.35 N, 6.98; λ_{max} (CH_2Cl_2) (ε/M^{-1} cm^{-1}) 269 (4.3 x 10^3) and 427 (1.3 x 10^4) nm.

1-(4,5-Dimethoxycarbonyl-1,3-diselenol-2-ylidenemethyl)-4-formylbenzene 10. To a stirred solution of phosphonium salt **8**[10a,16] (400 mg, 0.2 mmol) in anhydrous acetonitrile (50 mL) was added sequentially triethylamine (0.03 mL, 0.22 mmol) and terephthaldehyde **9** (53 mg, 0.4 mmol). The resultant solution was stirred at 20 °C for 16 h whereupon the solvent was removed *in vacuo* to leave a brown residue, purification of which was achieved by column chromatography on silica gel using dichloromethane as eluent to give **10** as a yellow solid (60 mg, 70%) mp. 128 - 130 °C; δ_H ($CDCl_3$) 9.98 (1 H, s), 7.89 (2 H, d, *J* 8 Hz), 7.35 (2 H, d, *J* 8 Hz), 6.52 (1 H, s), 3.86 (3 H, s) and 3.64 (3 H, s); ν_{max} (KBr)/ cm^{-1} 1736, 1718, 1581, 1566, 1238 and 1162; *m/z* (^{80}Se, DCI) 433 (MH^+, 100%); Analysis Calculated for $C_{15}H_{12}O_5Se_2$: C, 41.70 H, 2.27. Found: C, 42.00 H, 2.48%; λ_{max} (CH_2Cl_2) (ε /M^{-1} cm^{-1}) 221 (4.1 x 10^3) and 401 (4.4 x 10^4) nm.

1-(4,5-Dimethoxycarbonyl-1,3-diselenol-2-ylidenemethyl)-4-(2,2-dicyanoethenyl)benzene 11. To a solution of aldehyde **10** (51 mg, 0.12 mmol) in anhydrous dichloromethane (50 mL) was added sequentially, titanium tetrachloride (0.30 mL of a 1 M solution in dichloromethane, 0.30 mmol), malononitrile (0.07 mL, 1.18 mmol) and pyridine (0.07 mL, 1.18 mmol). The resultant yellow solution was heated under reflux for 48 h, cooled and the solvent removed *in vacuo*. The residue was purified by chromatography on silica gel with dichloromethane as the eluent, followed by recrystallisation from dichloromethane:hexane (1:10 v/v) to yield **11** as a red solid (46 mg, 81%) mp. 165 - 166 °C; δ_H ($CDCl_3$) 7.65 (2 H, d, *J* 12 Hz), 7.24 (2 H, d, *J* 12 Hz), 6.87 (1 H, s), 3.90 (3 H, s) and 3.88 (3 H, s); ν_{max} (KBr)/ cm^{-1} 2251, 1643, 1633, 1599, 1554 and 1421; *m/z* (^{80}Se, DCI) 481 (MH^+, 100%); Analysis Calculated for $C_{18}H_{12}N_2O_4Se_2$: C, 45.00 H, 2.91 N, 5.83 Found: C, 44.88 H, 3.08 N, 5.69%; λ_{max} (CH_2Cl_2) (ε/M^{-1} cm^{-1}) 229 (4.8 x 10^3) and 458 (3.2 x 10^4) nm.

9-(4,5-Dimethyl-1,3-diselenol-2-ylidene)-9,10-dihydroanthracen-10-one 13. To a stirred solution of anthrone **12** (140 mg, 0.72 mmol) in pyridine:acetic acid (40 mL, 3:1 v/v) was added diselenonium cation **3b** (350 mg, 0.74 mmol) to give a deep red solution which was heated at 60-70 °C for 16 h. The solvent was then removed *in vacuo* and the residue extracted into dichloromethane (200 mL). The organic solution was washed sequentially with water (2 x 100 mL) and aqueous sodium bicarbonate (1 M, 2 x 50 mL), dried ($MgSO_4$) and the solvent removed *in vacuo* to afford a red solid. Purification by column chromatography on silica using dichloromethane:hexane (1:1 v/v) as the eluent, followed by recrystallisation from the same solvent mixture afforded **13** as thin red needles (264 mg, 86%) mp. > 250 °C; δ_H ($CDCl_3$) 8.24 (2 H, d, *J* 8 Hz), 7.76 (2 H, d, *J* 8 Hz), 7.64 (2 H, t, *J* 8 Hz), 7.44 (2 H, t, *J* 8 Hz) and 2.00 (6 H, s); δ_C ($CDCl_3$) 183.7, 140.7, 135.8, 131.9, 130.5, 127.0, 126.7, 125.7, 125.4, 125.1 and 14.8; ν_{max} (KBr)/ cm^{-1} 1655, 1593, 1495, 1301, 771 and 687; *m/z* (^{80}Se, DCI) 419 (MH^+, 100%); Analysis Calculated for $C_{19}H_{14}OSe_2$: C, 54.83 H, 3.39. Found: C, 54.49 H 3.28%; λ_{max} (CH_2Cl_2) (ε/M^{-1} cm^{-1}) 249 (1.2 x 10^4), 275 (9.7 x 10^3), 380 (2.1 x 10^3) and 475 (7.6 x 10^3) nm.

9-(1,1-Dicyanomethylene)-10-(4,5-dimethyl-1,3-diselenol-2-ylidene)-9,10-dihydroanthracene 14. To a stirred solution of ketone **13** (50 mg, 0.06 mmol) in chloroform (50 mL) was added sequentially, titanium tetrachloride (1 mL of a 1 M solution in dichloromethane, 1 mmol), malononitrile (0.06 mL, 1 mmol) and pyridine (0.1 mL, 1 mmol). The resultant brown solution was heated under reflux for 24 h with periodic addition of malononitrile and pyridine until no starting material was evident (TLC analysis). The solution was allowed to cool and diluted with water (200 mL), the organic portion was separated and the aqueous phase extracted with dichloromethane (3 x 100 mL). The combined organic fractions were washed with water (100 mL), dried ($MgSO_4$) and the solvent removed *in vacuo*. The resultant black oil was purified by chromatography on silica gel using chloroform:hexane (4:1 v/v) as the eluent to afford **14** as black needles (35 mg, 60%) mp. > 250 °C; δ_H ($CDCl_3$) 8.12 (2 H, d, *J* 8 Hz), 7.81 (2 H, d, *J* 8 Hz), 7.57 (2 H, t, *J* 8 Hz), 7.42 (2 H, t, *J* 8 Hz) and 2.05 (6 H, s); ν_{max} (KBr)/ cm^{-1} 3054, 2305, 1421, 1665, 747 and 705; *m/z* (^{80}Se, DCI) 467 (MH^+, 90%), 276 (100%); HRMS $C_{22}H_{14}N_2Se_2$ requires 465.9487, observed 465.9481; λ_{max} (CH_2Cl_2) (ε/M^{-1} cm^{-1}) 253 (1.1 x 10^4), 322 (9.2 x 10^3) and 556 (5.2 x 10^3) nm. Crystals suitable for X-ray analysis were grown from hexane:dichloromethane (2:1 v/v).

9-*N*-Cyanoimino-10-(4,5-dimethyl-1,3-diselenol-2-ylidene)-9,10-dihydroanthracene 15. To a stirred solution of ketone **13** (50 mg, 0.06 mmol) in chloroform (50 ml) was added sequentially, titanium tetrachloride (1 mL of a 1 M solution in dichloromethane, 1 mmol) and *bis*-trimethylsilylcarbodiimide (BTC) (0.27 mL, 1.2 mmol). The resultant black solution was heated under reflux for 48 h with periodic addition of BTC until no starting material was evident (TLC analysis). The solution was allowed to cool and the solvent removed *in vacuo*. The resultant black oil was purified by chromatography on silica gel using chloroform:cyclohexane (3:2 v/v) as the eluent to afford **15** as a black solid (20 mg, 35%) mp. > 250 °C; δ_H ($CDCl_3$, -30 °C) 8.84 (1 H, d, *J* 8 Hz), 8.20 (1 H, d, *J* 8 Hz), 7.88 (1 H, d, *J* 8 Hz), 7.70 - 7.65 (3 H, m), 7.51 (1 H, t, *J* 8 Hz), 7.43 (1 H, t, *J* 8 Hz) and 2.05 (6 H, s); δ_C ($CDCl_3$) 173.5, 150.4, 150.3, 150.2, 149.9, 138.9, 138.7, 132.5, 126.9, 126.7, 126.3, 124.9, 115.7, 26.7 and 14.9; ν_{max} (KBr)/ cm^{-1} 2180, 1644, 1552, 1095, 975 and 721; *m/z* (^{80}Se, DCI) 443 (MH^+, 100%); HRMS $C_{20}H_{14}N_2Se_2$ requires 441.9487, observed 441.9491; λ_{max} (CH_2Cl_2) (ε/M^{-1} cm^{-1}) 256 (1.1 x 10^4), 315 (7.7 x 10^3) and 552 (5.2 x 10^3) nm.

X-Ray Crystallographic Data for 14: $C_{22}H_{14}N_2Se_2$, M=464.27, T=150 K, monoclinic, space group $P2_1/c$, a=15.795(1), b=8.685(1), c=14.368(1) Å, β=112.39(1)°, V=1822.4(3) Å^3, Z=4, D_x=1.69 g cm^{-3}, graphite-monochromated Mo-K_α radiation, $\bar{\lambda}$=0.71073 Å, μ=40.7 cm^{-1}, crystal size 0.4×0.32×0.03 mm, 16116 reflections (5058 unique) measured with a Siemens CCD area detector; R_{int}=0.165 before, 0.033 after face-indexing (integration) absorption correction ($T_{min,max}$=0.25, 0.88), full-matrix least-squares on F^2 of all data to wR=0.066 (non-H atoms aniso-, H isotropic, 291 variables); for 4331 data with $I>2\sigma(I)$, R(F)=0.029; $\Delta\rho_{min,max}$=0.48, -0.47 eÅ^{-3}. Atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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REFERENCES

1 Reviews: (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, **1991**; (b) Denning, R. G. *J. Mater. Chem.* **1995**, *5*, 365; (c) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155; (d) Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. *J. Mater. Chem.* **1997**, *7*, 2175.

2 (a) Moore, A. J.; Bryce, M. R.; Batsanov, A. S.; Green, A.; Howard, J. A. K.; McKervey, M. A.; McGuigan, P.; Ledoux, I.; Ortí, E.; Viruela, R.; Viruela, P. M.; Tarbit, B. *J. Mater. Chem.* **1998**, *8*, 1173; (b) Perepichka, I. F.; Perepichka, D. F.; Bryce, M. R.; Goldenberg, L. M.; Kuz'mina, L. G.; Popov, A. F.; Chesney, A.; Moore, A. J.; Howard, J. A. K.; Sokolov, N. I. *Chem. Commun*, **1998**, 819.

3 Reviews: (a) Narita, M.; Pittman, C. V. *Synthesis* **1976**, 489; (b) Krief, A. *Tetrahedron* **1986**, *42*, 1237; (c) Schukat, G.; Richter, A. M.; Fanghänel, E. *Sulfur Reports* **1987**, *7*, 155; (d) Schukat, G.; Fanghänel, E. *Sulfur Reports* **1993**, *13*, 254; (e) Hansen, T. K.; Becher, J. *Adv. Mater.* **1993**, *5*, 288.

4 Katz, H. E.; Singer, K. D.; Sohn, J. E.; Dirk, C. W.; King, L. A.; Gordon, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 6561.

5 (a) Blanchard-Desce, M.; Ledoux, I.; Lehn, J.-M.; Malthete, J.; Zyss, J. *J. Chem. Soc., Chem. Commun.* **1988**, 737; (b) Barzoukas, M.; Blanchard-Desce, M.; Josse, D.; Lehn, J.-M.; Zyss, J. *Chem. Phys.* **1989**, *133*, 323.

6 Jen, A. K.-Y.; Rao, V. P.; Drost, K. J.; Wong, K. Y.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1994**, 2057.

7 Kondo, K.; Fujitani, T.; Ohnishi, N. *J. Mater. Chem.* **1997**, *7*, 429.

8 (a) Cowan, D.; Kini, A. in *The Chemistry of Organic Selenium and Tellurium Compounds*, Patai, S. J. Ed.; Wiley, Chichester, **1987**, Vol. 2, p. 463; (b) Burgin, T.; Miebach, T.; Huffman, J. C.; Montgomery, L. K.; Paradis, J. A.; Rovira, C.; Whangbo- M-H.; Magonov, S. N.; Khan, S. I.; Strouse, C. E.; Overmeyer, D. L.; Schirber, J. E. *J. Mater. Chem.* **1995**, *5*, 1659; (c) Takimiya, K.; Oharuda, A.; Morikami, A.; Aso, Y.; Otsubo, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 619; (d) Kushch, N. D.; Buravov, L. I.; Pesotskii, S. I.; Lyubovskii, R. B.; Yagubskii, E. B.; Kaplunov, M. G.; Golubev, E. V.; Narymbetov, B. Zh.; Khasanov, S. S.; Zorina, L. V.; Rozenberg, L. P.; Shibaeva, R. P.; Kobayashi, A. K.; Kobayashi, H. *J. Mater. Chem.* **1998**, *8*, 897.

9 Bechgaard, K.; Jacobsen, C. S.; Mortensen, K.; Pedersen, M. J.; Thorup, N. *Solid State Commun.* **1980**, *33*, 1119.

10 (a) Chesney, A.; Bryce, M. R.; Chalton, M. A.; Batsanov, A. S.; Howard, J. A. K.; Fabre, J.-M.; Binet, L.; Chakroune, S. *J. Org. Chem.* **1996**, *61*, 2877; (b) Bryce, M. R.; Chesney, A.; Yoshida, S.; Moore, A. J.; Batsanov, A. S.; Howard, J. A. K. *J. Mater. Chem.* **1997**, *5*, 381; (c) Binet, L.; Fabre, J. M.; Montginoul, C.; Simonsen, K. B.; Becher, J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 783; (d) Binet, L.; Fabre, J. M.; Becher, J. *Synthesis* **1997**, 26.

11 For reviews of dicyanomethylene and *N*-cyanoimine groups as electron acceptors see: (a) Hünig, S. *J. Mater. Chem.* **1995**, *5*, 1469; (b) Martín, N.; Segura, J. L.; Seoane, C. *J. Mater. Chem.* **1997**, *7*, 1661.

12 Mayer, R.; Gebhardt, B. *Chem. Ber.* **1964**, *97*, 1298.

13 Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1976**, *41*, 883.

14 Bechgaard, K.; Cowan, D. O.; Bloch, A. N.; Henriksen, L. *J. Org. Chem.* **1975**, *40*, 746.

15 (a) Lehnert, W. *Tetrahedron Lett.* **1970**, 4723; (b) Lehnert, W. *Synthesis* **1974**, 667.

16 Sugimoto, T.; Awaji, H.; Sugimoto, I.; Misaki, Y.; Kawase, T.; Yoneda, S.; Yoshida, Z.; Kobayashi, T.; Anzai, H. *Chem. Mater.* **1989**, *1*, 535.

17 (a) Gorman, C. B.; Marder, S. R. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 625; (b) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature* **1997**, *388*, 845.

18 Batsanov, A. S.; Bryce, M. R.; Coffin, M. A.; Green, A.; Hester, R. E.; Howard, J. A. K.; Lednev, I. K.; Martín, N.; Moore, A. J.; Moore, J. N.; Ortí, E.; Sánchez, L.; Savirón, M.; Viruela, P. M.; Viruela, R.; Ye, T-Q. *Chem. Eur. J.* in press.

19 Bryce, M. R.; Moore, A. J.; Hasan, M.; Ashwell, G. J.; Fraser, A. T.; Clegg, W.; Hursthouse, M. B.; Karaulov, A. I. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1450.

20 Pauling, L. *The Nature of the Chemical Bond*, 3rd Edition, Cornell Univ. Press, Ithaca, **1960**.

21 Illescas, B.; Martín, N.; Segura, J. L.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela, R. *J. Mater. Chem.* **1995**, *5*, 1563.

22 Martín, N.; Sánchez, L.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela, R. *J. Org. Chem.* **1998**, *63*, 1268.