Novel Molecules for the Design of Organic Conductors. Synthesis of 7,7,8,8-Tetracyano-2,5-bis(3-phenylpropyl)-p-quinodimethane and N,N'-Dicyano-2,5-bis(3-phenylpropyl)-p-quinodiimine and X-Ray Structure of the TCNQ Derivative

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The novel 7,7,8,8-tetracyano-2,5-bis(3-phenylpropyl)-p-quinodimethane 2 and N,N'-dicyano-2,5-bis(3-phenylpropyl)-p-quinodiimine 3 in which the acceptor TCNQ and DCNQI moieties are covalently linked to weak donors, phenyl rings, by three methylene units have been synthesized and studied as intended donor–acceptor–donor (D–A–D) systems. The cyclic voltammetry data reveal two one-electron reversible reduction waves to the corresponding anion-radical and dianion. The novel molecules 2 and 3 behave, in solution, as simple TCNQ and DCNQI derivatives, respectively. A structural study by X-ray diffraction on the TCNQ-type molecule 2 shows a very planar, non-distorted TCNQ ring with isolated D⋯A⋯D triplets between the central TCNQ moiety of a molecule and two phenyl rings of two other different molecules.

The syntheses of novel donor (D) and acceptor (A) molecules are of great interest in the quest for new charge-transfer complexes (CTC) showing better conducting properties, and in recent years some of the necessary requirements for such molecules have been systematized.[1] The planarity of the molecules, together with a partial degree of electron transfer, are among the necessary key conditions to arrive at segregated stacks of donors and acceptors and, thus, conductivity.[2] The synthesis of systems containing donor and acceptor moieties in the same organic molecule would amount to control over both the above requirements and the stoichiometric donor/acceptor (D/A) ratio. A very promising application of these materials has been recently suggested as the basis for unimolecular devices containing a donor and an acceptor moiety linked by a chain in which a functional group is present.[3]

Previously, the very interesting molecule 2,5-dibenzyl-7,7,8,8-tetracyano-p-quinodimethane (DBTCNQ, 1) was synthesized[4] and studied as a prototypical D–A–D system. Some derivatives containing substituents in the weakly donating phenyl ring were also included.[5]

The characteristic architectural finding in the structure of compound 1 was a packing motif of isolated triplets D⋯A⋯D formed by the central 7,7,8,8-tetracyano-p-quinomethane (TCNQ) ring of a molecule and two phenyl rings of two other neighbouring molecules. Although the donor phenyl moieties are orthogonal[4] to the acceptor TCNQ moiety, thus preventing the donors from stacking, segregated stacking was found in the acceptor moieties. Previous attempts to form fused-ring D–A–D systems with donor–acceptor moieties linked by two methylene bridges from octahydropentacene-6,13-dione 4 did not yield the D–A–D system 5 (Scheme 1). Instead, the aromatized acceptor molecule 6 was obtained.[6]
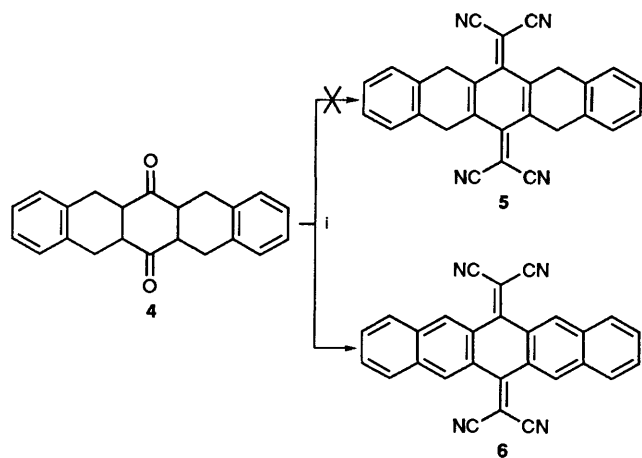
In this context we have carried out the synthesis and crystallographical and electrochemical studies of the novel molecules 7,7,8,8-tetracyano-2,5-bis(3-phenylpropyl)-p-quinodimethane 2 and N,N'-dicyano-2,5-bis(3-phenylpropyl)-p-quinodiimine 3 in which an extension of the linking chain units between the donor and the acceptor moieties has been performed. This significant structural modification should, in principle, mitigate the steric effect of the phenyl rings, now freely rotating, on the
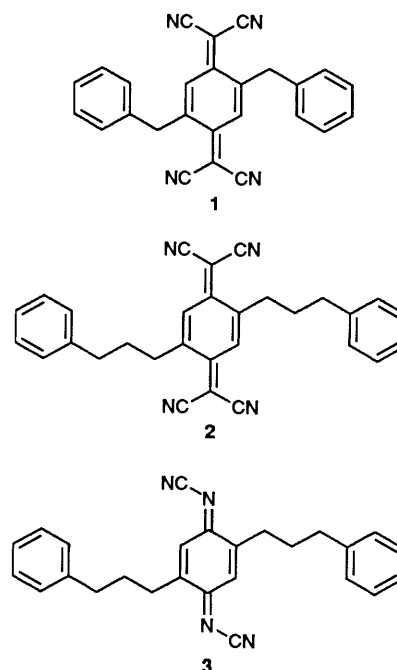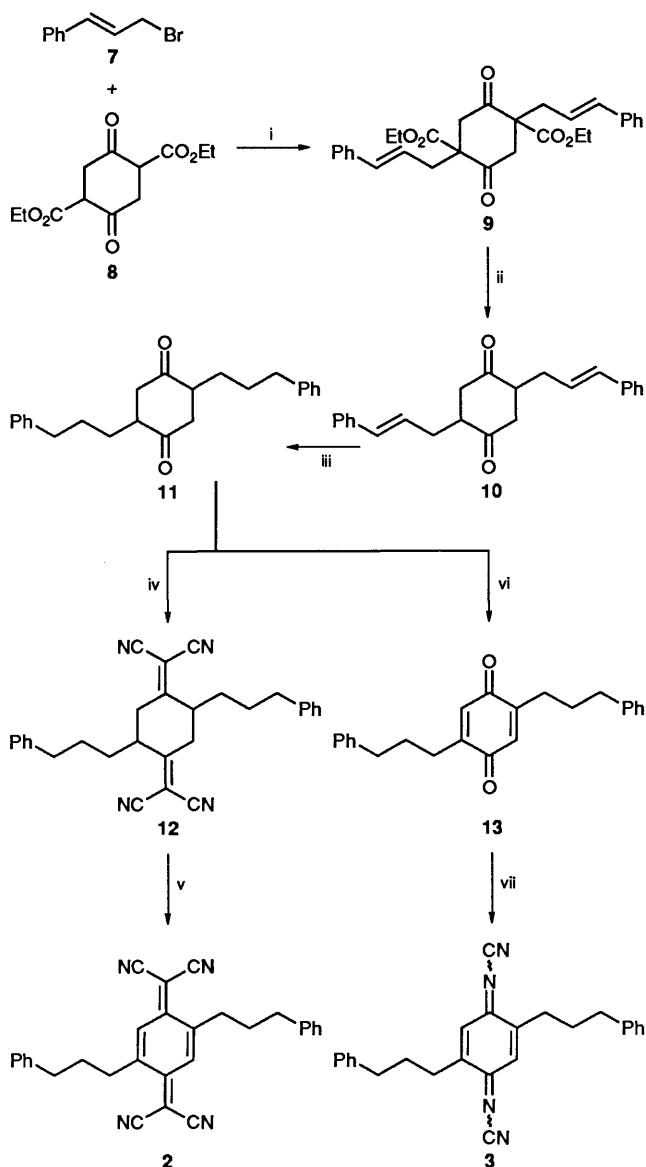

central TCNQ ring, leading to more favourable structures in comparison with compound 1.

Results and Discussion

The syntheses of the novel prototype molecules 2 and 3 were carried out in multistep processes from diketone 11 as depicted in Scheme 2. Thus, the reaction of cinnamyl bromide 7 with diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate 8 in anhydrous conditions led to the dialkylated compound 9 which was obtained as a mixture of the corresponding cis and trans derivatives (9a and 9b). The separation of these isomers could be accomplished by either fractional crystallization or chromatographic procedures (Fig. 1).

Scheme 1 *Conditions:* i, several steps

Fig. 1

was isolated. 2,6-Dialkylcyclohexane-1,4-dione **11** was finally obtained from diene **10** by catalytic hydrogenation in high yield. It is worth mentioning that attempts to obtain diketone **11** directly from diester **8** and bromo-3-phenylpropane by using the same experimental conditions as used for the cinnamyl bromide **7** were unsuccessful.

Compounds **2** and **3** were obtained from diketone **11** by following two different routes. By taking advantage of the high reactivity of the carbonyl groups in **11**, the reaction with propanedinitrile was carried out in toluene in the presence of ammonium acetate–acetic acid under azeotropic distillation of water to yield the tetracyano derivative **12**. When this reaction was carried out using β-alanine as catalyst, compound **12** was also obtained but in significantly lower yield. Finally, subsequent oxidation of compound **12** with bromine in pyridine led to compound **2**, which was obtained as a crystalline red solid in good yield.

Diketone **10** was also treated with propanedinitrile under the same reaction conditions to give the tetracyano derivative **14**. However, all attempts to oxidize compound **14** to the corresponding TCNQ derivative [bromine–pyridine; *N*-chlorosuccinimide, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)] met with failure.
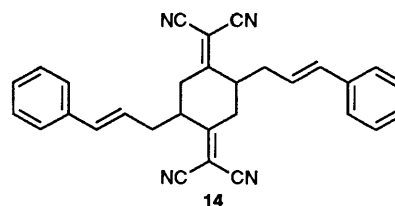
Compound **14** showed very poor solubility in common organic solvents and no NMR spectra could be recorded. Attempts to oxidize compound **10** to the *p*-benzoquinone derivative were also unsuccessful. On the other hand, the synthesis of dicyanoimine derivative **3** was carried out from diketone **11** by oxidation with DDQ to yield the 2,5-dialkylated *p*-benzoquinone **13**. Reaction of compound **13** with bis(trimethylsilyl)carbodiimide (BTC)[7] and titanium tetrachloride by following Hünig's method[8] led to *N*,*N*′-dicyano-2,5-bis(3-phenylpropyl)-*p*-quinodiimine **3** as a crystalline orange solid in moderate yield (see Scheme 2).

Electrochemistry.—Cyclic voltammetry (CV) measurements of the novel compounds **2** and **3**, together with the model parent compounds TCNQ, *N*,*N*′-dicyano-*p*-quinodiimine (DCNQI) and DBTCNQ **1** which were obtained in our laboratory to be used as references, have been carried out in dichloromethane at room temperature and using tetrabutylammonium perchlorate as supporting electrolyte (see Table 1). Compounds **2** and **3** reveal the presence of two one-electron reversible reduction waves to the corresponding anion-radical and dianion (Figs. 2 and 3).

The tetracyano derivative **2** presents a positive value for the first reduction potential. Both the first and second reduction potentials are close to the TCNQ values. The CV measurements of compound **2** do not show the presence of an oxidation wave

Scheme 2 *Reagents and conditions:* i, K_2CO_3, NaI, acetone; ii, H_2SO_4, EtOH, heat; iii, H_2, Pd/C; iv, $CH_2(CN)_2$, AcOH, $AcONH_4$; v, Br_2, pyridine; vi, DDQ; vii, BTC, $TiCl_4$, CH_2Cl_2

The mixture of isomers **9a** and **9b** was hydrolysed by heating with sulfuric acid in alcoholic solution, followed by spontaneous decarboxylation, to yield compound **10** in which only one isomer, probably the most stable *trans*-diequatorial conformer,
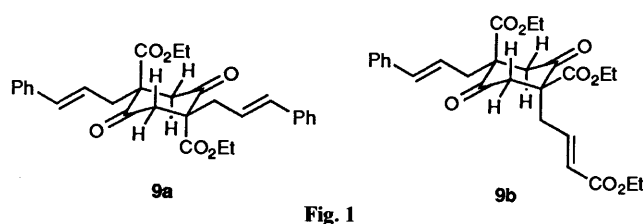
Table 1

Compound	M.p. (°C)	λ_{max}/nm (log ε)^a	ν_{CN}/cm^{-1} ^{b}	$E^1_{\frac{1}{2}}$/V^c	$E^2_{\frac{1}{2}}$/V	ΔE/V	log K
2	174–176	414 (4.6)	2217	0.14	−0.39	0.53	8.98
3	139–140	366 (4.2)	2160	0.06	−0.55	0.61	10.33
TCNQ				0.22	−0.35	0.57	9.66
DCNQI				0.21	−0.41	0.62	10.50
DBTCNQ				0.17	−0.35	0.52	8.81

^{a} Solvent CH_2Cl_2. ^{b} FT-IR spectrometer. ^{c} Working electrode: glassy carbon; sweep rate 20 mV s^{-1}.
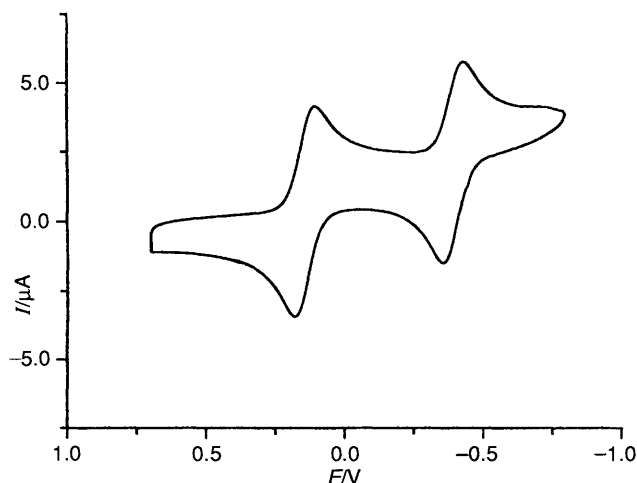

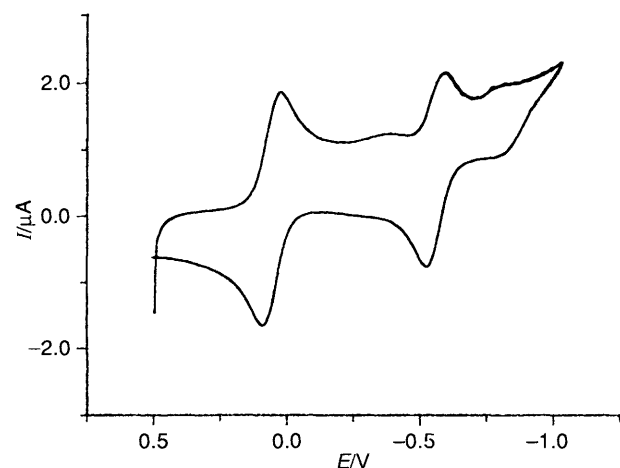**Fig. 2** Cyclic voltammogram of compound **2** at a scan rate of 20 mV s^{-1}

Fig. 3 Cyclic voltammogram of compound **3** at a scan rate of 20 mV s^{-1}

corresponding to the cation-radical in the range 0–2.0 V. These facts show that the presence of substituents on the central TCNQ ring in compound **2** does not alter its electrochemical properties significantly. This suggests that compound **2** behaves in solution essentially as a 2,5-substituted TCNQ derivative. This is confirmed by the absence in the UV spectrum of an electronic transfer band from the weakly donating phenyl ring to the acceptor TCNQ moiety.[9],* This finding is similar to others for bis-tetrathiafulvalenes (bis-TTF) systems in which intermolecular effects have been observed only when single atoms or shorter spacer groups are bridging the TTF units.[10]

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* A charge-transfer band near 700 nm has been detected in the UV spectrum of a donor–acceptor system linked by two heteroatomic bridges.[9]
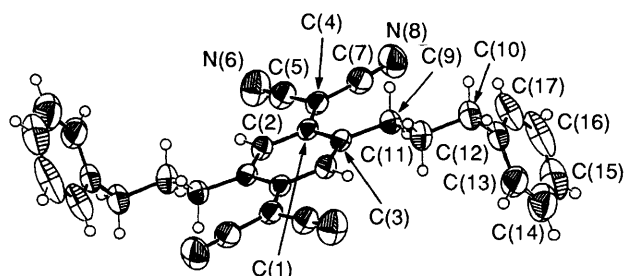

Fig. 4 An ORTEP view[13] of the molecular structure of compound **2**, showing the atomic numbering

The same electrochemical behaviour is shown by the DCNQI derivative **3**, which exhibits a slightly poorer ability as an acceptor than does compound **2** and is also very similar to the parent DCNQI. The values obtained for log K from the ΔE-values[11] are analogous to those for the parent compounds TCNQ and DCNQI and are indicative of thermodynamically stable anion-radicals due to the absence of steric hindrance in these compounds. These values for log K are higher than those corresponding to the previously described TCNQ and DCNQI benzene-fused derivatives in which an increase in benzannelation results in a decrease in the thermodynamic stability of the anion-radical.[12]

Crystallographic Study.—As mentioned above, the ability to form organic conductors is strongly dependent on the formation of segregated stacks of donor and acceptor moieties. On the other hand, we wondered if a modification of the chain length linking the acceptor and the donor would bear any influence on the stacking motif in comparison with compound **1**. The structure of compound **2** was determined by single-crystal X-ray diffraction. Attempts to obtain a single crystal of compound **3** were unsuccessful.

The crystallographical data for compound **2** show a central TCNQ ring totally planar [maximum deviation from least-square plane 0.001(2) Å in C-2] with the two phenyl rings nearly orthogonal to the TCNQ moiety and in a *trans* conformation as depicted in Fig. 4. The crystal packing is built of unlimited sheets on (101) planes (see Fig. 5), where molecules are held by Ph⋯Ph interactions; that is, there is a stacking pattern between the central ring and two phenyl rings, defining isolated triplets D–A–D (Fig. 6); besides this, donor moieties are linked forming a herringbone pattern along the *b*-axis. An apparent stacking of acceptor moieties may be observed for compound **2** in Fig. 5; however, the distance between centroids (8.63 Å) reveals a non-significant interaction between the acceptor TCNQ moieties due, probably, to the orthogonally arranged phenyl rings (Fig. 5).

In conclusion, we have developed a useful synthetic strategy to introduce longer chains between donor and acceptor moieties and have shown that a higher number of methylene units linking the donor and acceptor, in compounds of the D–A–D type, does not lead to significant modifications of the molecular
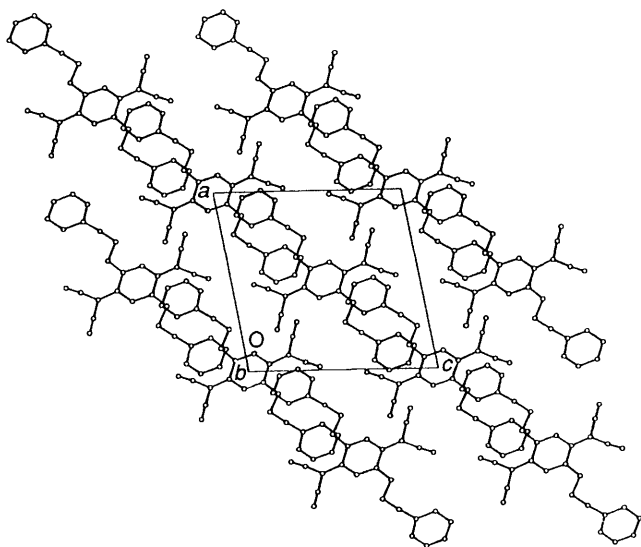
Fig. 5 Stacking pattern of compound **2**, showing the relationship between the acceptor moieties of neighbouring molecules
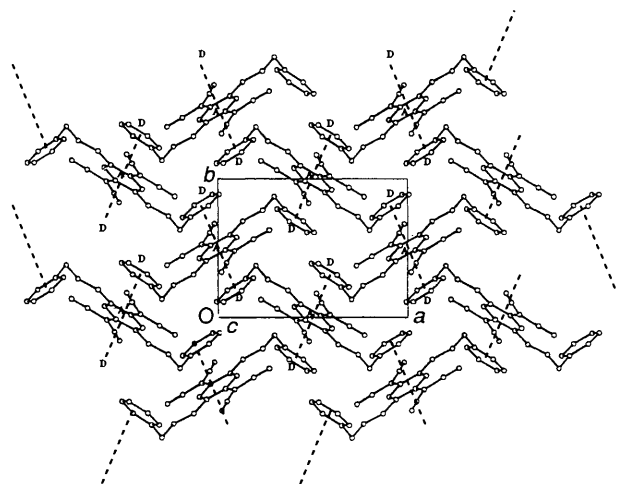

Fig. 6 Crystal packing of compound **2**, as projected along the c-axis,[14] showing the intermolecular interactions in a sheet

structure. On the other hand, these compounds behave in solution as simple TCNQ and DCNQI derivatives with electrochemical properties similar to those of the parent TCNQ and DCNQI molecules. Work is in progress to explore if the presence of stronger donors could increase the driving force towards properly segregated stacks in the crystal packing.

Experimental

Apparatus and Chemicals.—All m.p.s were measured on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 257, and FTIR spectra on a Bruker IFs 114 c spectrometer. UV spectra were recorded on a Perkin-Elmer Lambda 3 instrument. ^1H NMR and ^{13}C NMR spectra were determined with a Varian XL-300 spectrometer, and elemental analyses were performed on a Perkin-Elmer CHN 2400 apparatus. Catalytic hydrogenation was carried out in a Parr apparatus.

Cyclovoltammetric measurements were performed on an EG & G PAR Versastat potentiostat using 250 Electrochemical Analysis software. A Metrohm 6.084.C10 glassy carbon electrode was used as indicator electrode in voltammetric studies.

Diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate **8**, cinnamyl bromide **7**, malononitrile, DDQ and BTC were commercially available, and were used without further purification.

Diethyl 1,4-*Dicinnamyl*-2,5-*dioxocyclohexane*-1,4-*dicarboxylate* **9**.—A mixture of diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate **8** (6.4 g, 25 mmol), cinnamyl bromide **7** (13.0 g, 66 mmol), anhydrous potassium carbonate (4.9 g) and sodium iodide (0.4 g) in dry acetone (30 cm³) was refluxed for 72 h. The reaction was monitored by TLC [hexane–ethyl acetate (3:1)] and formation of both isomers was observed. After cooling of the reaction mixture, the precipitated salts were filtered off and the solvent was evaporated under reduced pressure. The residual yellow solid was recrystallized from diethyl ether–methanol (1:9) and a solid (6.5 g, 53%) was obtained as a mixture of two isomers. The mixture of *cis* and *trans* isomers was separated by flash chromatography [hexane–ethyl acetate (7:1)].

The first fraction proved to be the trans-*isomer*. Further purification was accomplished by recrystallization from methanol. M.p. 129–131 °C (Found: C, 73.7; H, 8.9. $C_{30}H_{32}O_6$ requires C, 73.8; H, 8.9%); δ_H(300 MHz; CDCl₃) 7.2 (10 H, m), 6.38 (2 H, d), 6.05 (2 H, m), 4.10 (4 H, q), 3.0 (2 H, d), 2.8 (2 H, d), 2.7 (4 H, m) and 1.15 (6 H, t); ν_{max}(KBr)/cm⁻¹ 3100–2990, 1725, 1600, 1210, 765 and 710.

Then, the corresponding cis-*isomer* was collected, and recrystallized from methanol. M.p. 117–118 °C (Found: C, 73.7; H, 8.8%); δ_H(300 MHz; CDCl₃) 7.30 (10 H, m), 6.42 (2 H, d), 5.95 (2 H, m), 4.2 (4 H, q), 3.2 (2 H, d), 2.6 (2 H, d), 2.8 (4 H, m) and 1.25 (6 H, t); ν_{max}(KBr)/cm⁻¹ 3100–2990, 1720, 1600, 1200, 750 and 700.

2,5-*Dicinnamylcyclohexane*-1,4-*dione* **10**.—Diethyl 1,4-dicinnamyl-2,5-dioxocyclohexane-1,4-dicarboxylate **9** (4.0 g, 8.2 mmol) was suspended in 4 mol dm⁻³ H₂SO₄ (100 cm³)–ethanol (150 cm³). Upon heating, the homogeneous solution obtained was refluxed for 66 h. A solid precipitated and, upon cooling, the precipitate was filtered off (1.8 g). The filtrate was refluxed for another 24 h and, after cooling, a second crop (0.8 g) was collected. The combined precipitates (2.6 g, 90%) were recrystallized from ethanol to give *dione* **10** as a solid, m.p. 134 °C (Found: C, 83.7; H, 6.9. $C_{24}H_{24}O_2$ requires C, 83.7; H, 7.0%); δ_H(CDCl₃; 300 MHz) 7.16 (10 H, m), 6.41 (2 H, d), 6.15 (2 H, m) and 2.96–2.32 (10 H, m); ν_{max}(KBr)/cm⁻¹ 3020, 2910, 1705, 965, 745 and 695.

2,5-*Bis*(3-*phenylpropyl*)*cyclohexane*-1,4-*dione* **11**.—A solution of diene **10** (1.0 g, 2.9 mmol) in ethyl acetate (200 cm³) was treated with 10% Pd–C under H₂ (2.7 atm) at room temperature for 1 h. After removal of the catalyst, the solvent was evaporated off under reduced pressure and a solid was obtained (0.98 g, 95%). Further purification was accomplished by recrystallization from ethanol to give *compound* **11**, m.p. 105–107 °C (Found: C, 82.6; H, 8.0. $C_{24}H_{28}O_2$ requires C, 82.8; H, 8.05%); δ_H(300 MHz; CDCl₃) 7.28–7.13 (10 H, m), 2.76–2.40 (9 H, m) and 1.9–1.3 (9 H, m); ν_{max}(KBr)/cm⁻¹ 3100–3020, 2920, 2860, 1720, 755 and 705.

1,4-*Bis*(*dicyanomethylene*)-2,5-*bis*(3-*phenylpropyl*)*cyclohexane* **12**.—A mixture of 2,5-bis(3-phenylpropyl)cyclohexane-1,4-dione **11** (0.3 g, 0.86 mmol), propanedinitrile (0.22 g, 3.3 mmol), ammonium acetate (0.07 g) and acetic acid (0.2 cm³) was dissolved in toluene (25 cm³). The solution was refluxed for 24 h under azeotropic elimination of water from the reaction mixture (Dean–Stark). After cooling, the resulting solution was washed with water, dried over magnesium sulfate, and the solvent was evaporated off under reduced pressure almost to dryness. Ethanol was added and a solid precipitated out. It was collected by filtration (0.17 g, 44%) and was recrystallized from acetonitrile to give the *tetranitrile* **12**, m.p. 188–190 °C (Found: C, 81.0; H, 6.4; N, 12.5. $C_{30}H_{28}N_4$ requires C, 81.1; H, 6.3; N, 12.6%); δ_H(CDCl₃; 300 MHz) 7.40–7.25 (10 H, m), 3.4–2.5 (9 H,

m) and 1.8–1.4 (9 H, m); ν_{max}(KBr)/cm^{-1} 3040, 3010, 2900, 2840, 2220, 1580, 1430, 730 and 685.

2,5-*Bis*(3-*phenylpropyl*)*tetracyano*-p-*quinodimethane* **2**.—To a cold (0 ° C) suspension of 1,4-bis(dicyanomethylene)-2,5-bis-(3-phenylpropyl)cyclohexane **12** (0.3 g, 0.68 mmol) in dry acetonitrile (4 cm^3) was added a solution of bromine (0.25 g, 1.6 mmol) in dry acetonitrile (2 cm^3) by syringe. Then a solution of pyridine (0.22 g, 2.8 mmol) in dry acetonitrile (0.8 cm^3) was added dropwise. The reaction mixture was stirred at room temperature for 3 h and the reaction was monitored by TLC. Water (5 cm^3) was added and the reaction mixture was stirred for another 3 h. The solid that precipitated out was filtered off, and washed with cold diethyl ether. The red solid thus obtained (0.25 g, 83%) was recrystallized from acetonitrile to give *compound* **2**, m.p. 174–176 °C (Found: C, 81.7; H, 5.6; N, 12.9. $C_{30}H_{24}N_4$ requires C, 81.8; H, 5.45; N, 12.7%); δ_H(300 MHz; CDCl$_3$) 7.35–7.15 (12 H, m), 3.0 (4 H, t), 2.8 (4 H, t) and 1.95 (4 H, quint.); ν_{max}(KBr)/cm^{-1} 3050, 2920, 2850, 2217, 1600, 750 and 700; λ_{max}(CH$_2$Cl$_2$)/nm 414 (log ε 4.6).

X-Ray Crystallographic Data at Room Temperature for Compound **2**.—$C_{30}H_{24}N_4$, $M_r = 440.546$, Monoclinic, $P2_1/n$, $a = 11.9204(2)$, $b = 8.6257(1)$, $c = 12.3834(2)$ Å, $\beta = 101.160(1)°$, $V = 1249.21(3)$ Å^3, $Z = 2$, so the asymmetric unit comprises just half a molecule of the compound, an inversion centre lies in the middle of the central ring (see structure **2**), $D_c = 1.17$ g cm^{-3}, $F(000) = 464$, $\mu = 5.13$ cm^{-1}. Refined cell parameters were obtained from setting angles of 75 reflections. A prismatic orange monocrystal (0.43 × 0.23 × 0.17 mm) was used for the analysis.

Data collection. Automatic four-circle diffractometer (Philips PW 1100) with graphite-oriented monochromated Cu-Kα radiation. The intensity data were collected using the $\omega/2\theta$ scan mode between $2 < \theta < 65°$; two standard reflections were measured every 90 min with no intensity variation. A total of 2109 reflections were measured and 1758 were considered as observed [$I > 3\sigma(I)$ criterion]. The data were corrected for Lorentz and polarization effects).

Structure solution and refinement. The structure was solved by direct methods using SIR88 [15] and successive Fourier synthesis. H-atoms were included in a mixed refinement, except those in the phenyl system which were considered as fixed contributors. A convenient weighting scheme was applied to obtain a flat dependence in $\langle w^2F \rangle$ vs. $\langle F_o \rangle$ and $\langle \sin \theta/\lambda \rangle$.[16] Final R (R_w) value was 6.0 (7.4). Atomic scattering factors were taken from International Tables for X-Ray Crystallography[17] and calculations were performed using XTAL,[18] XRAY80,[19] HSEARCH[20] and PARST.[21],*

2,5-*Bis*(3-*phenylpropyl*)-p-*benzoquinone* **13**.—To a solution of 2,5-bis(3-phenylpropyl)cyclohexane-1,4-dione **11** (0.5 g, 1.43 mmol) in dry tetrahydrofuran (15 cm^3) was added a solution of DDQ (1.44 g, 0.34 mmol) in dry acetonitrile (29 cm^3) dropwise. The reaction mixture was refluxed under inert atmosphere (argon) for 24 h. After cooling to room temperature, the solvent was eliminated under reduced pressure and a black solid (1.9 g) was obtained. The solid was submitted to flash chromatography [hexane–ethyl acetate (1 : 4)] to yield a pure orange solid (0.36 g, 73%). Further purification was accomplished by recrystalliz-ation in acetic acid to give *compound* **13**, m.p. 100 °C (Found: C, 83.6; H, 6.9. $C_{24}H_{24}O_2$ requires C, 83.7; H, 7.0%); δ_H(CDCl$_3$; 300 MHz) 7.32–7.16 (10 H, m), 6.52 (2 H, s), 2.68 (4 H, t) and

1.83 (4 H, quint.); ν_{max}(KBr)/cm^{-1} 3090, 2940, 2900, 2880, 1640, 1625, 745 and 720.

N,N′-*Dicyano*-2,5-*bis*(3-*phenylpropyl*)-p-*quinodiimine* **3**.—To a cold solution (ice-bath) of the quinone **13** (0.12 g, 0.35 mmol) in dry chloroform (20 cm^3) were added titanium tetrachloride (0.12 cm^3, 1.2 mmol) and then BTC (0.28 cm^3, 1.02 mmol) under argon. The reaction mixture was refluxed for 5 h and, after cooling, was poured onto water (20 cm^3)–dichloro-methane (20 cm^3). The organic phase was separated from the aqueous phase and was dried over magnesium sulfate. The solvent was evaporated off under reduced pressure until ~ 10 cm^3 and then n-hexane was added. The yellow pure solid that precipitated out (46 mg, 34%) was recrystallized from aceto-nitrile to give *compound* **3**, m.p. 139–140 °C (Found: C, 79.7; H, 6.0; N, 14.1. $C_{26}H_{24}N_4$ requires C, 79.6; H, 6.1; N, 14.3%); δ_H(CDCl$_3$; 300 MHz) 7.31–7.15 (12 H, m), 2.71 (4 H, t), 2.62 (4 H, t) and 1.92 (4 H, quint.); ν_{max}(KBr)/cm^{-1} 3000, 2900, 2840, 2145, 1550, 1520, 700 and 630; λ_{max}(CH$_2$Cl$_2$)/nm 336 (log ε 4.2).

1,4-*Dicinnamyl*-2,5-*bis*(*dicyanomethylene*)*cyclohexane* **14**.—To a solution of 2,5-dicinnamylcyclohexane-1,4-dione **10** (0.95 g, 2.7 mmol) and propanedinitrile (0.69 g, 10.5 mmol) in toluene (66 cm^3) were added ammonium acetate (0.20 g) and acetic acid (0.6 cm^3). The reaction mixture was refluxed with azeotropic elimination of water (Dean–Stark) for 24 h. At room tempera-ture, the solution was washed with plenty of water and then was dried over magnesium sulfate. The solvent was evaporated off under reduced pressure to 20 cm^3 and a solid precipitated out (0.15 g, 13%). *Compound* **14** had m.p. 236 °C (Found: C, 81.7; H, 5.6; N, 12.6. $C_{30}H_{24}N_4$ requires C, 81.8; H, 5.45; N, 12.7%); ν_{max}(KBr)/cm^{-1} 3020, 2940, 2230, 1600, 980, 750 and 700.

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