

## Studies on $\pi$ -Acceptor Molecules Containing the Dicyanomethylene Group. X-Ray Crystal Structure of the Charge-transfer Complex of Tetramethyltetrathiafulvalene and 2,3-Dicyano-1,4-naphthoquinone: (TMTTF)<sub>3</sub>-(DCNQ)<sub>2</sub>

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The reaction of tetramethyltetrathiafulvalene (TMTTF, **7**) with 2-dicyanomethyleneindane-1,3-dione (DCID, **1**) leads to isomerisation of DCID to 2,3-dicyanonaphthoquinone (DCNQ, **3**) to yield the charge-transfer complex [(TMTTF)<sub>3</sub>]<sup>2+</sup>-(DCNQ<sup>-</sup>)<sub>2</sub> **8**. The X-ray crystal structure of complex **8** reveals stacks of TMTTF molecules along the *x* direction in the sequence A . . B . . A . . A . . B . . A . . etc. The A . . A and A . . B interplanar separation distances are 3.51 Å and 3.44 Å, respectively. The DCNQ radical anions form dimers, with a remarkably short interplanar separation of 3.02 Å, which are orthogonal to the TMTTF stacks. The complex is diamagnetic. Other  $\pi$ -acceptor molecules containing the dicyanomethylene group, *viz.* compounds **2** and **10–12**, have been prepared and their redox properties studied by cyclic voltammetry. Compound **2** rearranges to compound **4** on complexation with TTF **6**. DCID derivatives **1** and **2** react with a range of amines, by displacement of one cyano group, to yield enamines **15–19**; the amphiphilic compound **18** forms Langmuir–Blodgett films which exhibit weak second harmonic generation.

As part of our continuing studies on conducting organic charge-transfer complexes, we have recently examined the properties of the electron acceptor molecule 2-dicyanomethyleneindane-1,3-dione (DCID) **1**.<sup>1</sup> Acceptor **1** had been reported by Chatterjee to form a stable radical anion,<sup>2</sup> and was, therefore, an attractive candidate for the formation of conducting complexes in combination with organic cations and  $\pi$ -electron donors, by analogy with the well-known acceptor tetracyano-*p*-quinodimethane (TCNQ) **5**.<sup>3</sup> However, we found that reaction of DCID **1** with reducing agents, *e.g.* alkali metals, and a range of metal and organic iodide salts, resulted not in radical anion salts of **1**, as claimed previously,<sup>2</sup> but, instead, radical anion salts of 2,3-dicyano-1,4-naphthoquinone (DCNQ) **3** were isolated, resulting from isomerisation of the DCID radical anion. The structure of the salt (MePPh<sub>3</sub>)<sup>+</sup>(DCNQ)<sup>-</sup>(H<sub>2</sub>O) was established by an X-ray crystal structure.<sup>1</sup> Charge-transfer complexes with donor:acceptor stoichiometries of 3:2 were isolated by mixing the  $\pi$ -electron donors tetrathiafulvalene (TTF) **6** and tetramethyl-TTF **7** with DCID **1**, and we concluded, based on spectroscopic evidence, that isomerisation of the acceptor had again occurred, and that these were complexes of the DCNQ **3** radical anion, not the DCID system **1**.<sup>1</sup> This contradicted a previous report by Fatiadi, who assumed that the complex of DCID **1** with TTF contained the DCID radical anion.<sup>4</sup>

It was, therefore, important to establish unequivocally whether or not DCID **1** had rearranged to DCNQ **3** upon complexation with the fulvalene donors TTF **6** and TMTTF **7**. We now report the X-ray crystal structure of the complex (TMTTF)<sub>3</sub>-(DCNQ)<sub>2</sub> **8** which proves that rearrangement of the anion has occurred. We also describe the synthesis and properties of other acceptors, derived from indanone and indanedione, that contain the dicyanomethylene group.

### Results and Discussion

*X-Ray Crystal Structure of (TMTTF)<sub>3</sub>-(DCNQ)<sub>2</sub> 8.*—The crystal structure of complex **8**, determined by single crystal

X-ray diffraction, is shown in Fig. 1. Selected bond lengths are listed in Table 1. The asymmetric unit of complex **8** contains one DCNQ molecule and one TMTTF molecule (A) in general positions, and half of another TMTTF molecule (B) which occupies a special position at an inversion centre. The TMTTF units form infinite stacks along the *x* direction, in the sequence . . A . . B . . A . . A . . B . . A . . etc. In both units A and B, each dithiole ring is essentially planar, but the TTF system as a whole is slightly non-planar, with the heterocycle planes inclined by 1.9° in A and (crystallographically) parallel but separated by 0.03 Å in B. In the A . . A intrastack contact, the molecules, which are related *via* an inversion centre, have their mean planes and main axes strictly parallel, but are laterally slipped with respect to each other by 1.5 Å along the direction of the C(1)–C(6) bond, and by less than 0.1 Å in the perpendicular direction [Fig. 2(a)]. Such 'longitudinal shift' giving 'ring-over-bond' overlap, is common in partially oxidised stacks of TTF and its derivatives, as in the TMTSF (tetramethyltetraselenafulvalene) stacks of the Bechgaard salts,<sup>5,6</sup> where interplanar separations in the stacks (3.49–3.69 Å) usually alternate by 0.02–0.16 Å, thus dividing a stack into dimers. The A . . A interplanar separation in complex **8** (3.51 Å) is common for the shorter (intra-dimer) contacts. The shortest S . . S contacts (3.83–3.87 Å) in complex **8** and the contact between the almost eclipsed C(6) atoms of both units (3.48 Å) exceed the sums of the Van der Waals radii (1.80 Å for S, and 1.70 Å for C).<sup>7</sup>

The separation between the mean planes of units A and B, which are parallel to within 0.5°, is much shorter (3.44 Å) providing slightly shortened contacts S(1) . . C(6') 3.57, S(1) . . S(5') 3.52, S(2) . . S(5') 3.51 and S(4) . . S(6) 3.55 Å [Fig. 2(b)]. With respect to each other, units A and B exhibit no significant lateral shift; instead there is a rotation of 21° around the axis through the midpoints of their central C=C bonds. Such 'criss-cross' overlap is still favourable for electronic delocalisation along the stack (for up to 60° rotation)<sup>8</sup> and is known for some other charge-transfer salts, *e.g.* (TMTTF)<sub>3</sub>[(MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>V<sub>2</sub>Cl<sub>4</sub>O]<sub>2</sub><sup>9</sup> and (TTF)<sub>5</sub>[Hg<sub>6</sub>(SCN)<sub>16</sub>]<sub>10</sub> where rotation occurs for every third or fifth unit, respectively, in the stack. In

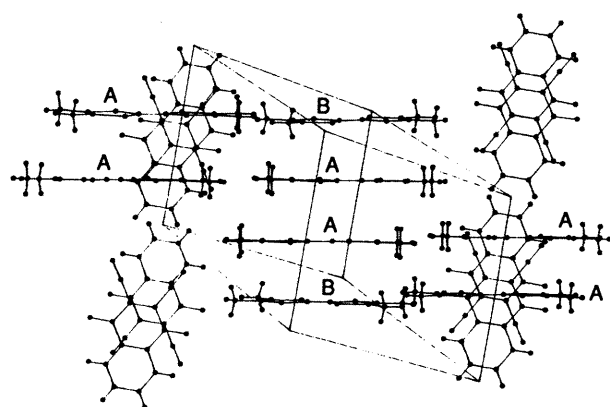
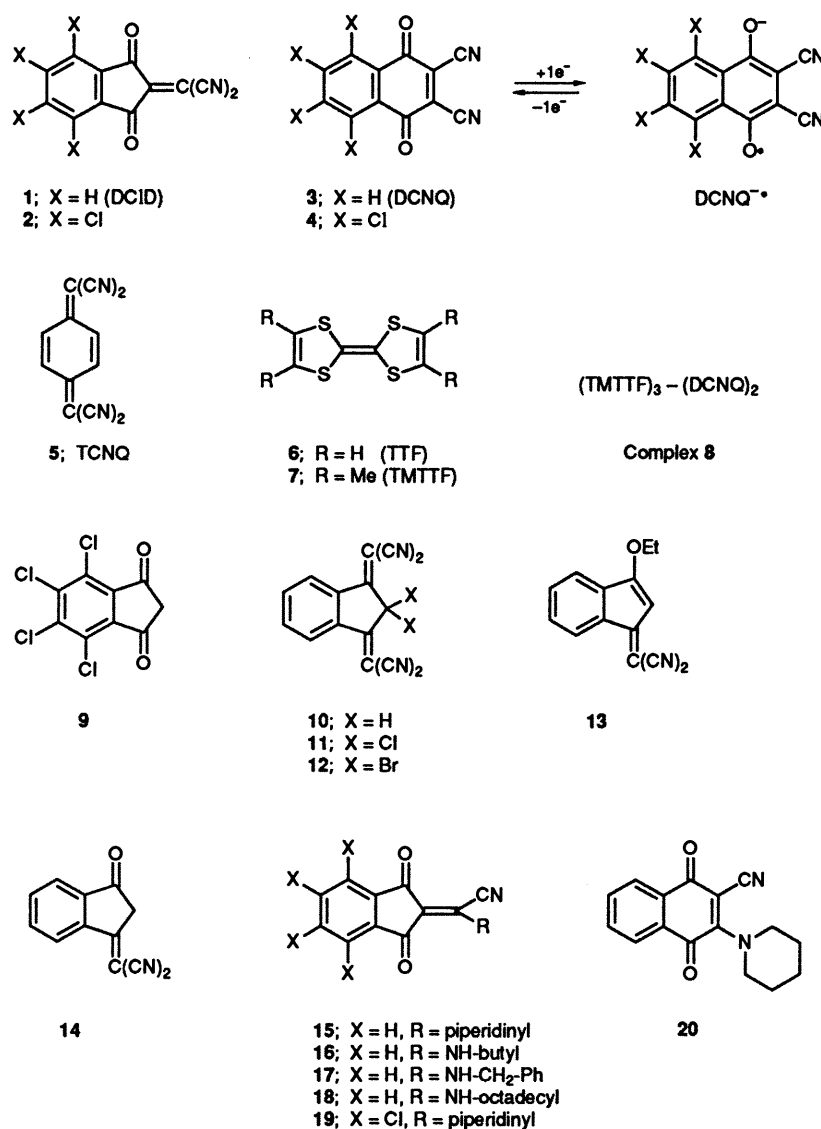


Fig. 1 Projection of the crystal structure of the complex 8, (TMTTF)<sub>3</sub>-(DCNQ)<sub>2</sub>, on the 01 $\bar{1}$  plane

(TMTTF)FeCl<sub>4</sub> criss-cross overlap is uniform along the cation stack.<sup>8</sup>

It is difficult to estimate how the average charge of +2/3 per TMTTF unit in complex 8 (which results from each DCNQ molecule accepting one electron) is distributed along the donor column. Increasing the positive charge on a TTF moiety is known to shorten the C-S bonds and to lengthen the endocyclic and the bridging C=C bonds.<sup>5,11,12</sup> A linear bond distance/

charge relationship has been proposed,<sup>5</sup> but the effect is small and for C-C distances it is comparable with esds and is overwhelmed by variations of chemically equivalent bond lengths. In the structure of complex 8, both C-C and C-S bond distances in molecule A are close to those expected for a charge of +0.5.<sup>5,6,9,11</sup> In molecule B, the average C-S distance is shorter and the C(12)=C(13) bond is longer than the corresponding bonds in molecule A, being closer to those in TMTTF<sup>•+</sup> cations.<sup>5,8,9,11,13</sup> However, the C(11)-C(11') distance in molecule B is shorter than C(1)-C(6) in A, which is not consistent with the above-mentioned rules. However, as the observed differences in C-C distances do not exceed 3 esd and these distances are usually not very informative (see above), it is possible to conclude from the more reliable C-S distances that molecules A have charges of +0.5 and molecule B of +1, which is consistent with the unique orientation of the latter in the stack.

The DCNQ anion radicals in complex 8 lie approximately parallel to the (01 $\bar{1}$ ) crystallographic plane and orthogonal to the TMTTF planes, and form centrosymmetric dimers (Fig. 3) which are arranged in infinite double ribbons along the *x* direction, intercalating the stacks of TMTTF in a chess-board order. A similar, mutually orthogonal arrangement of counterions was observed in the structures of (TMTTF)<sub>2</sub>[C<sub>4</sub>(CN)<sub>6</sub>]<sup>5</sup> and (TMTTF)<sub>3</sub>(Et<sub>2</sub>-TCNQ)<sub>2</sub>.<sup>14</sup> High polarisability of the

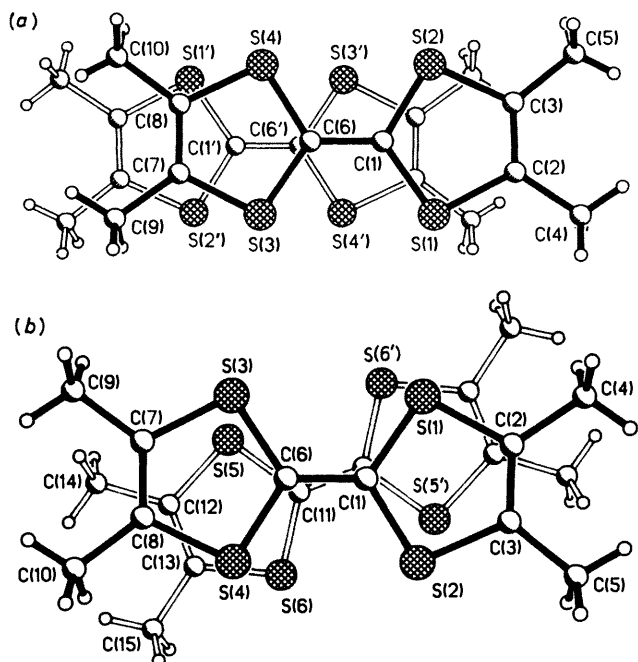


Fig. 2 Overlap of TMTTF molecules A..A (a) and A..B (b) in complex 8. Atoms related *via* an inversion centre are primed.

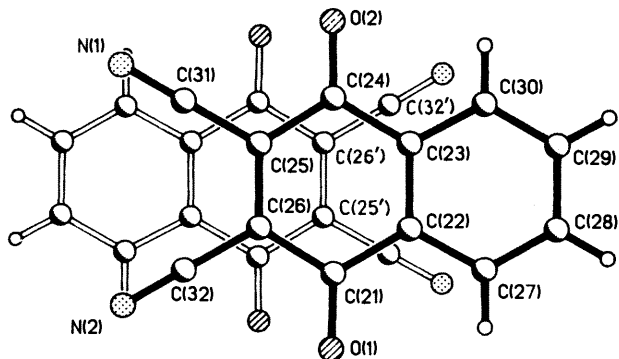


Fig. 3 Overlap of DCNQ anion radicals in complex 8. Primed atoms are symmetrically related *via* an inversion centre.

aromatic anion radical along its plane may stabilise the charge resonance interactions in the TMTTF columns. The bond distances in the DCNQ anion radical of complex 8 differ considerably from those in neutral naphthoquinone (NQ) and its derivatives.<sup>15</sup> The C–O and C(25)–C(26) bonds in complex 8 are significantly longer than in NQ's where these are localised double bonds (1.20–1.23 and 1.31–1.34 Å, respectively) and bonds C(21)–C(26) and C(24)–C(25) are shorter than the corresponding, essentially single, bonds in NQ derivatives (1.47–1.50 Å). These data correspond well to a single delocalised negative charge on each DCNQ molecule of complex 8.

The most uncommon feature of the structure is the extremely close contact between the anions in the dimer. The mean planes of their bicyclic systems (which are parallel, as imposed by crystallographic symmetry) are separated by only 3.02 Å, with the shortest intermolecular distances C(23)..*C*(32') 3.19 Å, C(24)..*C*(26') 3.09 Å and C(21)..*C*(25'), C(25)..*C*(26') 3.16 Å. Furthermore, the closest atoms of different anions, C(24) and C(26), deviate by 0.06 and 0.05 Å out of the bicyclic system plane in the same direction [C(24) outside the intradimer space and C(26) inside it]. The other eight ring atoms of the DCNQ anions are essentially coplanar, and all the substituent atoms are slightly bent outside the dimer [O(1) –0.06, O(2) –0.21, C(31) –0.07, C(32) –0.02, N(1) –0.35 and N(2) –0.09 Å]. It is noteworthy that in the crystal structure of (MePPh<sub>3</sub>)<sup>+</sup>

Table 1 Selected bond lengths (Å) for complex 8

S(1)–C(1)	1.732(3)	S(1)–C(2)	1.751(4)
S(2)–C(1)	1.728(3)	S(2)–C(3)	1.746(4)
S(3)–C(6)	1.722(3)	S(3)–C(7)	1.741(4)
S(4)–C(6)	1.731(3)	S(4)–C(8)	1.745(4)
S(5)–C(11)	1.729(3)	S(5)–C(12)	1.735(4)
S(6)–C(11)	1.709(3)	S(6)–C(13)	1.721(4)
O(1)–C(21)	1.238(5)	O(2)–C(24)	1.241(5)
N(1)–C(31)	1.144(5)	N(2)–C(32)	1.144(7)
C(1)–C(6)	1.374(5)	C(2)–C(3)	1.336(4)
C(7)–C(8)	1.339(4)	C(11)–C(11')	1.357(7)
C(12)–C(13)	1.348(4)	C(21)–C(22)	1.470(6)
C(21)–C(26)	1.444(5)	C(22)–C(23)	1.414(6)
C(22)–C(27)	1.394(5)	C(23)–C(24)	1.473(5)
C(23)–C(30)	1.390(7)	C(24)–C(25)	1.442(6)
C(25)–C(26)	1.407(5)	C(25)–C(31)	1.428(5)
C(26)–C(32)	1.426(6)	C(27)–C(28)	1.352(8)
C(28)–C(29)	1.383(8)	C(29)–C(30)	1.372(6)

Table 2 Cyclic voltammetric data recorded *vs.* Ag/AgCl, Pt button electrode, scan rate 100 mV s<sup>-1</sup>, 5 × 10<sup>-4</sup> mol dm<sup>-3</sup> compound, 0.1 mol dm<sup>-3</sup> Bu<sub>4</sub>N<sup>+</sup> ClO<sub>4</sub><sup>-</sup> in acetonitrile, using a BAS 100 Electrochemical Analyser

Compound	<i>E</i> <sub>1</sub> <sup>1/2</sup> /mV	<i>E</i> <sub>2</sub> <sup>1/2</sup> /mV
1 <sup>a</sup>	+008	–979
2 <sup>b</sup>	+210	<i>c</i>
3 <sup>a</sup>	+218	–550
4 <sup>b</sup>	+400	–369
10 <sup>b</sup>	–550	<i>c</i>
11 <sup>b</sup>	–140	<i>c</i>
12 <sup>b</sup>	+007	<i>c</i>

<sup>a</sup> Reference 1. <sup>b</sup> This work. <sup>c</sup> Not observed.

(DCNQ)<sup>•-</sup> (H<sub>2</sub>O)<sup>1</sup> the DCNQ units also form dimers with essentially the same overlap mode as complex 3 (Fig. 3) and similar interplanar separation (3.04 Å), although the crystal packing in the two structures is entirely different. Usually in charge-transfer complexes,<sup>16</sup> distances between aromatic system planes less than in graphite (3.35 Å) are considered short and indicative of strong specific interactions; the distances reported herein for DCNQ are undoubtedly among the shortest ever observed.

**Magnetic Properties of (TMTTF)<sub>3</sub>–(DCNQ)<sub>2</sub>.**—Static magnetic susceptibility measurements on complex 8 were performed using a Faraday balance. The complex is diamagnetic throughout the temperature range 300–4.2 K: the observed susceptibility value of  $-6.8 \times 10^{-4} \pm 0.8 \times 10^{-4}$  emu mol<sup>-1</sup> corresponds well with the diamagnetic core contribution of  $-6.48 \times 10^{-4}$  emu mol<sup>-1</sup> calculated from the Pascal constants. This result is consistent with strongly interacting spins within the (DCNQ)<sup>•-</sup><sub>2</sub> unit, as indicated by the very short intermolecular spacing observed in the X-ray crystal structure.

**Preparation and Solution Electrochemistry of Acceptors 2 and 10–12.**—In the light of the interesting and unexpected results obtained with the acceptor DCID 1,<sup>1</sup> we have synthesised related indanone and indanedione derivatives containing one or two dicyanomethylene groups. Tetrachloro-DCID 2 was chosen for study because the presence of the chlorinated benzene ring should increase the electron affinity of the acceptor, relative to the parent system 1, thereby modifying the electronic structure of the radical anion such that rearrangement of 2 might be less facile, enabling complexes of the tetrachloro-DCID skeleton to be isolated. Tetrachloroindane-1,3-dione 9 was prepared from tetrachlorophthalic anhydride by the literature route,<sup>17</sup> and reacted with tetracyanoethane, under conditions reported previously for the synthesis of 1,<sup>18</sup> to afford

tetrachloro-DCID **2** in 76% yield. Cyclic voltammetry of **2** shows a reversible one-electron reduction at 0.21 V (*vs.* Ag/AgCl), confirming that, as expected, this derivative is a significantly stronger acceptor than derivative **1**<sup>1</sup> (Table 2).

Immediately upon mixing neutral compound **2** with either lithium iodide or methyltriphenylphosphonium iodide in acetonitrile, a colour change was observed which clearly indicated that salt formation was occurring in solution. However, in both cases a solid salt could not be isolated using work-up procedures described previously for the analogous salts derived from system **1**.<sup>1</sup> However, neutral tetrachloro-DCNQ **4** was isolated, in 30% yield, from the solution of the lithium salt using the method described previously for compound **3**.<sup>19</sup> This result establishes that the radical anion of tetrachloro-DCID **2** undergoes a rearrangement analogous to DCID **1**. A mixture of TTF **6** and acceptor **2** in acetonitrile gave a complex comprising TTF and the rearranged anion **4** in 1:1 stoichiometry, which was isolated as a black solid (21% yield); this material was identical by IR spectroscopy with that obtained using authentic acceptor **4**. Notably, the complex exhibited a very strong cyanide absorption from the tetrachloro-DCNQ radical anion at 2190 cm<sup>-1</sup>, compared with the absence of a cyanide absorption peak for both neutral tetrachloro-DCID **3** and neutral tetrachloro-DCNQ **4**. The conductivity of the complex was relatively low,  $\sigma_{\text{rt}} = 2 \times 10^{-5}$  S cm<sup>-1</sup> (two-probe, compressed pellet measurement), so the material was not investigated further.

We were also interested in studying the acceptors **10–12** containing the 1,3-bis(dicyanomethylene)indane framework. Their syntheses had been reported previously by Russian workers (albeit somewhat inconclusively) but their redox properties had not been examined. Reaction of 1,3-indandione with two equivalents of malononitrile in ethanol, with ammonium acetate as base, as described,<sup>20</sup> gave compound **10** in 41% yield. During early attempts to prepare **10**, the new, bright red compound **13** was isolated in low yield. The mechanism of formation of **13** presumably involves addition of ethoxide ion, produced *in situ*, to the carbonyl group of intermediate **14**,<sup>21</sup> followed by elimination. The 2,2-dichloro- and 2,2-dibromo-derivatives **11** and **12** were obtained from **10** by reaction with *N*-chlorosuccinimide and *N*-bromosuccinimide, respectively.<sup>20a</sup>

Electrochemical redox properties of acceptors **10–12** were determined by cyclic voltammetry and the data are collated in Table 1; all three compounds display a single irreversible reduction wave. Compound **10** is a considerably weaker acceptor than DCID **1**, and, as would be expected, the acceptor strength of system **10** is increased by halogen substitution at the 2 position. Surprisingly, dibromo derivative **12** is a markedly stronger acceptor than dichloro derivative **11** (the value of  $E_1$  is more positive by *ca.* 0.2 V for the former compound). This is not the case with halo-substituted quinones and derivatives of TCNQ **5**, for which the attachment of both chloro and bromo substituents increases the electron affinity by essentially the same amount.<sup>22,23</sup> However, it has been noted by Torrance *et al.* that salts of TTF **6** with both fluoranil and chloranil are neutral, while TTF-bromanil has an ionic ground state.<sup>24,25</sup> This phenomenon was attributed to the more polarisable bromine atoms stabilising the ionic ground state. A similar effect could contribute to the observed solution reduction potentials of compounds **11** and **12**. Additionally, steric effects could complicate the situation for the series of derivatives **10–12**, where the dicyanomethylene groups in the neutral molecules may not be co-planar with one another, or with the benzene ring. Unfortunately, crystals of **10–12** suitable for X-ray analysis could not be obtained. Acceptor **10** forms a 1:1 complex with TTF **6** which has a room temperature conductivity value in the semiconductor regime,  $\sigma_{\text{rt}} = 3 \times 10^{-4}$  S cm<sup>-1</sup> for compressed

pellets. All attempts to complex TTF with both dichloro- and dibromo-derivatives, **11** and **12**, respectively, in a range of solvents, failed, probably due to steric effects in the acceptors.

*The Reaction of DCID Derivatives 1 and 2 with Amines: Formation of Donor- $\pi$ -Acceptor Systems.*—We sought to substitute one cyano group of compounds **1** and **2** with an amine substituent to yield 'push-pull' systems which might hold promise as materials for non-linear optics, by virtue of the conjugation between electron donor (amine) and acceptor (carbonyl and cyano) moieties.<sup>26</sup> Molecular second-order hyperpolarisability ( $\beta$ ) is related to charge-transfer properties and electron delocalisation *via*  $\pi$ -electron conjugation. Materials with large values of  $\beta$  will not exhibit second-order non-linearity unless the molecules crystallise in a non-centrosymmetric space group. However, for amphiphilic donor- $\pi$ -acceptor molecules, non-centrosymmetric alignment and bulk second-order optical effects can be achieved by Langmuir-Blodgett deposition.<sup>27</sup>

Piperidine, butylamine, benzylamine and octadecylamine reacted with compound **1** to furnish the highly conjugated enamine derivatives **15–18**, respectively, in 40–65% yields.<sup>28</sup> For each enamine derivative, two carbonyl stretching frequencies were observed in the IR spectra at *ca.* 1700 and 1650 cm<sup>-1</sup>, which is reminiscent of the carbonyl doublet seen for 2-aryl-methyleneindane-1,3-dione.<sup>29</sup> The cyanide absorption of DCID **1** occurs as a very weak peak at 2230 cm<sup>-1</sup>; it shows little change in the enamine derivatives **15** and **16** (2230–2240 cm<sup>-1</sup>) and is absent altogether in derivatives **17** and **18**. The UV spectra of compounds **15–18** show a bathochromic shift compared to DCID **1**, indicative of intramolecular charge transfer. Tetrachloro-DCID **2** reacted similarly with piperidine to produce derivative **19**. We established that DCID had not rearranged to DCNQ derivatives upon reaction with the amines stated above, by reacting DCNQ **3** with piperidine, under identical conditions. Product **20**, thereby obtained, was clearly different (melting point and IR spectroscopic comparison) from compound **15**, confirming that structures **15–19** are correct.

Powdered samples of compounds **15–19**, gave no SHG effects, when investigated by means of the Kurtz powder technique, using a Q-switched Nd:YAG laser.<sup>30</sup> Compound **18**, which carries a long hydrophobic side chain, formed a monolayer film at the air-water interface of a Langmuir-Blodgett trough. Multilayers of **18** could be assembled on silica glass slides by Z-type deposition onto a hydrophilically treated quartz slide; a ten-layer film exhibited an SHG signal that was weak relative to the standard urea, against which most materials are compared.<sup>31</sup> Further studies on LB films of compound **18** are in progress.

## Conclusions

The results obtained in this study have shown that the electron acceptor DCID **1** rearranges to DCNQ **3** upon formation of a charge-transfer complex with TTF **6** or TMTTF **7**. The X-ray crystal structure of the complex TMTTF<sub>3</sub>-DCNQ<sub>2</sub> **8** reveals unusual packing modes of both donor and acceptor species. Acceptors **10–12** have been shown to be weaker acceptors than DCID **1** as judged by cyclic voltammetry. The new push-pull systems **15–19** have been synthesised and the amphiphilic derivative **18** forms Langmuir-Blodgett films which exhibit a weak SHG signal.

## Experimental

*General.*—Details of general procedures have been reported previously.<sup>1</sup>

**Complex of Tetramethyltetrathiafulvalene and 2,3-Dicyanophthalquinone, (TMTTF)<sub>2</sub> (DCNQ)<sub>2</sub> 8.**—A hot solution of TMTTF 7 (25 mg, 0.096 mmol) dissolved in acetonitrile (5 cm<sup>3</sup>) was added to a hot solution of DCID 1<sup>1</sup> (20 mg, 0.096 mmol) in acetonitrile (5 cm<sup>3</sup>) and the mixture was cooled slowly to 0 °C. The black, highly crystalline complex, (TMTTF)<sub>3</sub> (DCNQ)<sub>2</sub> was filtered and dried *in vacuo* (29 mg, 75%) (Found: C, 53.9; H, 3.5; N, 4.3. C<sub>54</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>S<sub>12</sub> requires: C, 54.1; H, 3.7; N, 4.7%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2195 (C≡N, which is largely obscured by a broad charge-transfer band) 1580, 1553, 1522, 1427, 1300 (very broad), 1080, 920, 880, 782, 692 and 455.

**4,5,6,7-Tetrachloro-2-dicyanomethyleneindane-1,3-dione 2.**—Tetracyanoethylene (428 mg, 3.3 mmol) was added to a warm solution of 4,5,6,7-tetrachloroindane-1,3-dione<sup>17</sup> (427 mg, 1.5 mmol) dissolved in absolute ethanol (80 cm<sup>3</sup>). The mixture was then stirred at room temperature for 30 min. The resulting yellow precipitate was filtered, washed with cold ethanol and dried *in vacuo*, to afford compound 2 (410 mg, 79%). M.p. 250 °C (decomp.); EI *m/z*: M<sup>+</sup> absent (Found: C, 41.4; H, 8.4. C<sub>12</sub>N<sub>2</sub>Cl<sub>4</sub>O<sub>2</sub> requires: C, 41.6; H, 8.1%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1750, 1710, 1628, 1540, 1382, 1372, 1295, 1210, 1182, 1138, 935, 800, 741, 640 and 340.

**Complex of Tetrathiafulvalene and 2,3-Dicyano-5,6,7,8-tetrachlorophthalquinone.**—Hot saturated solutions of 2 (20 mg, 5.8 × 10<sup>-5</sup> mol) and TTF 6 (12 mg, 5.8 × 10<sup>-5</sup> mol) in dry acetonitrile, were mixed and allowed to cool to room temperature. The resulting black precipitate was filtered off and dried in a desiccator over silica gel, yielding the complex (6.5 mg, 21%). M.p. > 250 °C (decomp) [Found: C, 39.0; H, 0.6; N, 5.0. C<sub>18</sub>H<sub>4</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub> (a 1:1 complex) requires: C, 39.3; H, 0.7; N, 5.1%];  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3090, 2190, 2160, 1655, 1637, 1535, 1493, 1470, 1435, 1342, 1320, 1300, 1250, 1183, 1128, 1087, 830, 760, 750, 735, 690 and 490.

**1,3-Bis(dicyanomethylene)indane 10.**—A solution of indane-1,3-dione (2.4 g, 16 mmol), malononitrile (2.7 g, 41 mmol) and ammonium acetate (1.25 g, 16 mmol) dissolved in absolute ethanol (30 cm<sup>3</sup>) was heated at reflux for 30 min. After cooling to room temperature, water (25 cm<sup>3</sup>) was added and the solution acidified with concentrated hydrochloric acid. The brown precipitate was filtered off and washed with water. Recrystallisation from glacial acetic acid afforded compound 10 (1.6 g, 41%) as a yellow-brown solid. M.p. 249–253 °C; EI *m/z*: 242 (M<sup>+</sup>); CI (Bu<sup>+</sup>) *m/z* 243 (Found: C, 74.1; H, 2.4; N, 23.1. C<sub>15</sub>H<sub>6</sub>N<sub>4</sub> requires: C, 74.4; H, 2.5; N, 23.1%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2920, 2895, 2870, 2230 (C≡N, very strong), 1595, 1575, 1475, 1455, 1385, 1340, 1315, 1280, 1275, 1220, 1195, 1150, 1070, 905, 785, 620 and 390;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  8.64–8.60 (2 H, m, *J*<sub>AB</sub> 6, *J*<sub>AB'</sub> 3), 7.90–7.86 (2 H, m, *J*<sub>BA</sub> 6, *J*<sub>BA'</sub> 3) and 4.27 (2 H, s).\*

**3-Ethoxy-2-dicyanomethylene-1H-indene 13.**—A solution of indane-1,3-dione (2.0 g, 13.7 mmol), malononitrile (2.25 g, 34 mmol) and ammonium acetate (300 mg, 3.9 mmol) dissolved in absolute ethanol (100 cm<sup>3</sup>) was heated at reflux for 24 h. The solvent was removed *in vacuo*, leaving a purple solid from which a red product was extracted with boiling light petroleum (b.p. 40–60 °C). Eluting the extract with chloroform through a short alumina column, followed by vacuum sublimation (*ca.* 120 °C, 0.001 mbar Hg) afforded compound 13 (20 mg, 4%) as a bright red powder. M.p. 140–143 °C; EI *m/z*: 222 (M<sup>+</sup>); CI (Bu<sup>+</sup>) *m/z*: 223 (Found: C, 75.7; H, 4.2; N, 12.8. C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O requires: C,

75.7; H, 4.5; N, 12.6%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3100, 2225, 1610, 1545, 1455, 1400, 1382, 1360, 1300, 1265, 1230, 1138, 1100, 1085, 1018, 1005, 875, 805, 755, 676 and 640;  $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$  8.00 (1 H, m), 7.2 (3 H, m), 5.6 (1 H, s), 4.2 (2 H, q, *J* 7.1) and 1.5 (3 H, t, *J* 7).

**2,2-Dichloro-1,3-bis(dicyanomethylene)indane 11.** Compound 10 (267 mg, 1.1 mmol), *N*-chlorosuccinimide (294 mg, 2.2 mmol) benzoyl peroxide (10 mg) and dry carbon tetrachloride (25 cm<sup>3</sup>) under an atmosphere of nitrogen were heated at reflux for 4 h. After cooling to 20 °C the precipitate was collected, washed with water and recrystallised from glacial acetic acid to yield compound 11 (239 mg, 70%) as pale green needles. M.p. 265 °C (decomp.); CI *m/z*: 311 (Found: C, 57.6; H, 1.1; N, 18.3. C<sub>15</sub>H<sub>4</sub>Cl<sub>2</sub>N<sub>4</sub> requires: C, 57.9; H, 1.3; N, 18.0%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ : 2230, 1605, 1570, 1325, 1275, 1225, 1200, 1100, 824, 807, 758 and 655;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ : 8.79–8.75 (2 H, dd, *J*<sub>AB</sub> 6.0, *J*<sub>AB'</sub> 3.0) and 8.07–8.04 (2 H, dd, *J*<sub>BA</sub> 6.0, *J*<sub>BA'</sub> 3.0).

**2,2-Dibromo-1,3-bis(dicyanomethylene)indane 12.**—Compound 10 (300 mg, 1.24 mmol), *N*-bromosuccinimide (441 mg, 2.48 mmol) and azo(isobutyronitrile) (AIBN) (10 mg) in dry carbon tetrachloride (25 cm<sup>3</sup>) were heated at reflux for 1 h. Work-up as described for compound 11, gave compound 12 (304 mg, 61%) as pale yellow needles. M.p. 270 °C (decomp.); EI *m/z*: M<sup>+</sup> absent; CI (Bu<sup>+</sup>) *m/z*: 399 (60), 400 (13), 401 (100), 402 (22), 403 (59), 404 (11) (Found: C, 45.3; H, 1.0; N, 14.0. C<sub>15</sub>H<sub>4</sub>Br<sub>2</sub>N<sub>4</sub> requires: C, 45; H, 1.0; N, 14.0%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2230, 1595, 1560, 1460, 1320, 1273, 1200, 1175, 800, 785, 710, 633 and 526;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  8.79–8.78 (2 H, dd, *J*<sub>AB</sub> 6.0, *J*<sub>AB'</sub> 3.1) and 8.03–7.99 (2 H, dd, *J*<sub>BA</sub> 6.0, *J*<sub>BA'</sub> 3.1).

**Tetrathiafulvalene Complex with 1,3-bis(dicyanomethylene)indane.**—A hot, saturated solution of compound 10 (25 mg, 0.1 mmol) dissolved in dry acetonitrile (4 cm<sup>3</sup>), was added to a hot, saturated solution of TTF 6 (21 mg, 0.1 mmol) in dry acetonitrile (4 cm<sup>3</sup>). The mixture was cooled to room temperature and the solvent allowed partially to evaporate. The resulting precipitate was filtered and dried *in vacuo*, yielding a black complex (30 mg, 65%). M.p. > 260 °C [Found: C, 56.4; H, 2.2; N, 12.5. C<sub>21</sub>H<sub>10</sub>N<sub>4</sub>S<sub>4</sub> (a 1:1 complex) requires: C, 56.5; H, 2.2; N, 12.6%];  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2230, 1600, 1572, 1485, 800, 795, 780, 760, 660, 650, 620, 438 and 390.

**Amine-substituted 2-Dicyanomethyleneindane-1,3-diones 15–19: General Procedure.**—A mixture of compound 1 or 2, the amine (1 equivalent) and dry tetrahydrofuran (THF) was heated at reflux for 1–1.5 h. The reaction mixture was then stirred at room temperature for 20 h. The solvent was removed *in vacuo*, and column chromatography on alumina of the resulting solid, eluting with chloroform, yielding the desired product (as the first fraction). Recrystallisation afforded analytically pure samples.

**Piperidino(1,3-dioxindan-2-ylidene)acetonitrile 15.** Compound 1 (342 mg, 1.6 mmol) and piperidine (136 mg) in THF (15 cm<sup>3</sup>) yielded compound 15 (224 mg, 52%) as an orange solid, which was recrystallised from toluene–hexane (1:1 v/v). M.p. 125–129 °C; EI *m/z*: M<sup>+</sup> absent; CI *m/z*: 267 (Found: C, 72.6; H, 5.4; N, 10.2. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires: C, 72.2; H, 5.3; N, 10.5%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2950, 2900, 2850, 2230 (C≡N, extremely weak), 1690, 1655, 1590, 1540, 1470, 1435, 1365, 1350, 1333, 1290, 1267, 1250, 1203, 1170, 1155, 1130, 1100, 1070, 1050, 1015, 1005, 920, 895, 860, 830, 805, 788, 740, 710, 670, 660, 565, 553, 530, 430 and 345;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ : 7.78–7.60 (4 H, m), 3.94 (4 H, br s) and 1.90–1.79 (6 H, m).

**Butylamino(1,3-dioxindan-2-ylidene)acetonitrile 16.** Compound 1 (250 mg, 1.2 mmol) and butylamine (88 mg) in dry

\* *J*-Values are given in Hz.

THF (20 cm<sup>3</sup>) yielded compound **16** (193 mg, 63%) as a light yellow solid. M.p. 110–111 °C (from hexane). EI *m/z*: M<sup>+</sup> absent; CI (Bu<sup>+</sup>) *m/z*: 255 (Found: C, 70.9; H, 5.7; N, 10.8. C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires: C, 70.9; H, 5.5; N, 11.0%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3190, 2955, 2860, 2240 (C≡N, weak), 1700, 1650, 1540br, 1465, 1383, 1350, 1327, 1305, 1250, 1210, 1182, 1165, 1145, 1110, 1080, 1030, 990, 872, 810, 735, 710, 690, 665, 530, 400 and 350;  $\delta_{\text{H}}(60 \text{ MHz}; \text{CDCl}_3)$ : 7.7 (4 H, m), 3.6 (2 H, t, *J* 6.5), 2.0–1.4 (4 H, m) and 0.95 (3 H, t).

**Benzylamino(1,3-dioxindan-2-ylidene)acetonitrile 17.** Compound **1** (353 mg, 1.7 mmol) and benzylamine (181 mg) in THF (20 cm<sup>3</sup>) yielded compound **17** (272 mg, 55%) as a golden yellow solid. M.p. 163–166 °C [from toluene–hexane (1:1 v/v)]; EI *m/z*: 288 (M<sup>+</sup>); CI *m/z*: 289 (Found: C, 74.9; H, 4.3; N, 9.5. C<sub>18</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> requires: C, 75.0; H, 4.2; N, 9.7%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1705, 1660, 1575, 1480, 1455, 1365, 1335, 1260, 1121, 1155, 1025, 1012, 875, 815, 760, 705, 660, 600 and 540;  $\delta_{\text{H}}(60 \text{ MHz}; \text{CDCl}_3)$ : 7.58 (4 H, m), 7.26 (5 H, s) and 4.73 (2 H, s).

**Octadecylamino(1,3-dioxindan-2-ylidene)acetonitrile 18.** Compound **1** (396 mg, 1.9 mmol) and octadecylamine (511 mg) in THF (20 cm<sup>3</sup>) were heated at reflux for 5 h, and then stirred at room temperature for 18 h. Purification using repeated silica gel column chromatography, eluting the first column with ether–hexane (4:1 v/v) and the second column with hexane–ethyl acetate (1:1 v/v) provided a pure sample of compound **18** (389 mg, 45%) as a pale yellow solid. M.p. 90–94 °C; EI *m/z*: M<sup>+</sup> absent (Found: C, 77.1; H, 9.7; N, 5.7. C<sub>29</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub> requires: C, 77.3; H, 9.3; N, 6.2%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3200, 2915, 2850, 1700, 1655, 1570, 1465, 1350, 1329, 1200, 1150 and 733;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  9.85 (1 H, br s), 7.87–7.67 (4 H, m), 3.66 (2 H, q, *J* 6.8), 1.74 (2 H, quintet, *J* 7.0), 1.25 (30 H, m) and 0.88 (3 H, t, *J* 6.5).

**Piperidino(4,5,6,7-tetrachloro-1,3-dioxindan-2-ylidene)acetonitrile 19.** Piperidine (51 mg, 0.6 mmol) was added to a mixture of compound **2** (209 mg, 0.6 mmol) partially dissolved in dry THF (20 cm<sup>3</sup>). Drying the yellow precipitate in a desiccator yielded analytically pure compound **19** (128 mg, 53%). M.p. 240–244 °C (decomp.); EI *m/z*: 404 (M<sup>+</sup>) (Found: C, 47.6; H, 2.4; N, 6.9. C<sub>16</sub>H<sub>10</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub> requires: C, 47.5; H, 2.5; N, 6.9%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2940, 2860, 1705, 1663, 1565, 1550, 1453, 1440, 1360, 1300, 1270, 1255, 1200, 1190, 965, 777 and 733;  $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$  4.03 (2 H, br s), 3.86 (2 H, br s), 1.92 (4 H, m) and 1.83 (2 H, m).

**3-Piperidino-1,4-dioxo-1,4-dihydro-2-naphthonitrile 20.**—A mixture of 2,3-dicyano-1,4-naphthoquinone **3** (140 mg, 0.67 mmol), piperidine (57 mg, 0.67 mmol) and dry THF (10 cm<sup>3</sup>) was heated at reflux for 3 h. The solvent was then removed *in vacuo*. Purification of the solid residue by alumina column chromatography, eluting with chloroform–hexane (4:1 v/v), followed by recrystallisation from methanol yielded compound **20** (16 mg, 9%) as an orange-red solid. M.p. 114–117 °C (decomp.); EI *m/z*: 266 (M<sup>+</sup>); CI *m/z*: 267 (Found: C, 71.8; H, 5.7; N, 9.9. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires: C, 72.2; H, 5.3; N, 10.5%);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2920, 2850, 2210, 1680, 1625, 1590, 1550, 1413, 1405, 1340, 1338, 1315, 1290, 1260, 1210, 1172, 1020, 930, 737 and 715;  $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$  8.21–7.50 (4 H, m), 4.06–3.66 (4 H, m) and 2.10–1.47 (6 H, m).

**Crystal Structure Determination of Complex 8.**—Black crystals of **8** were grown from acetonitrile solution, and a prismatic crystal of dimensions 0.17 × 0.20 × 0.40 mm was selected for data collection on a Siemens R3m/V diffractometer at room temperature.

**Crystal Data.** C<sub>54</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>S<sub>12</sub> or [(C<sub>10</sub>H<sub>12</sub>S<sub>4</sub>)<sub>3</sub>]<sup>2+</sup>(C<sub>8</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>. *M* = 1197.7, triclinic, space group *P* $\bar{1}$ , *a* = 10.527(3), *b* = 11.853(3), *c* = 11.996(3) Å,  $\alpha$  = 68.51(2),  $\beta$  = 69.58(2),

$\gamma$  = 82.58(2)°, *U* = 1305.1(6) Å<sup>3</sup> (from 12 pairs of Friedel-equivalent reflections with 24° ≤ 2θ ≤ 32°), *D<sub>c</sub>* = 1.52 g cm<sup>-3</sup>, *Z* = 1, *F*(000) = 620, λ(Mo-Kα) = 0.710 69 Å (graphite monochromated), μ = 5.55 cm<sup>-1</sup>.

By the Wyckoff (limited ω) scan technique 5243 independent reflections with 2θ ≤ 55° were measured, of which 4174 with *I* > 2σ(*I*) were used in calculations after semi-empirical absorption correction based on 360 ψ-scans from 10 reflections (maximum and minimum transmission factors 0.8885 and 0.7686, respectively).

The structure was solved by direct method and refined by full-matrix least-squares using the SHELXTL PLUS set of programs. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms in isotropic approximation, converging at *R* = 0.050, *R<sub>w</sub>* = 0.059 and *S* = 1.91 for 422 refined parameters and weighting scheme ω<sup>-1</sup> = σ<sup>2</sup>(*F*) + 0.0004 *F*<sup>2</sup>. The final difference map showed no feature above 0.73 e Å<sup>-3</sup> which itself may be due to slight disorder of TMTTF molecule B.

Full lists of atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre.\*

### Acknowledgements

We thank the SERC for funding this work, the Royal Society for financial support (to A. S. B.), and Professor A. M. Kini for informing us of references relevant to the X-ray crystal structure.

\* For details of the CCDC deposition scheme, see 'Instructions for Authors (1993)', *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

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Paper 2/06730G  
Received 21st December 1992