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Crystal Structure of Three Compounds Related to Triphenylene and Tetracyanoquinodimethane

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The crystal structures of a charge-transfer complex of triphenylene with 1,3,5-tris(2,2-dicyanovinyl)benzene (**1**), a complex of 2,3,6,7,10,11-hexamethoxytriphenylene with 2,5-dichlorotetracyanoquinodimethane (**2**) and also 2,5-dichlorotetracyanoquinodimethane itself (**3**) have been determined. Compound **1** is triclinic, space group $P\bar{1}$, with $a=7.055(1)$, $b=11.026(2)$, $c=17.214(3)$ Å, $\alpha=96.59(3)$, $\beta=90.34(3)$, $\gamma=91.61(3)°$. Compound **2** is triclinic, space group $P\bar{1}$, with $a=12.228(2)$, $b=12.994(3)$, $c=13.702(3)$ Å, $\alpha=70.72(3)$, $\beta=83.73(3)$, $\gamma=66.06(3)°$. Compound **3** is monoclinic, space group $I2/a$ $(C2/c)$, with $a=13.692(3)$, $b=7.7183(15)$, $c=16.391(3)$ Å, $\beta=99.47(3)°$. The structures of **1** and **2** consist of mixed stacks of donors and acceptors. The structures of **2** and **3** both include 1,2-dichlorobenzene solvent molecules. Weak hydrogen bonds are present in the structures of **1** and **2**. Based on comparisons of bond lengths the electronic charge-transfer in **2** has been estimated to be about 0.3 *e*. The synthesis of 1,3,5-tris(2,2-dicyanovinyl)benzene is also reported.

As part of our structural and synthetic studies of triphenylene derivatives and related compounds we have investigated two charge-transfer salts as well as the pure acceptor for one of the salts. The constituents are shown in Fig. 1. The degree of charge-transfer is an important parameter for characterizing a charge-transfer complex. However, it is usually very difficult to obtain a reliable estimate of this quantity. A large number of studies of charge-transfer complexes have been carried out on compounds containing TCNQ (tetracyanoquinodimethane), probably the most popular electron acceptor over recent decades. Theoretical calculations by e.g. Johansen[1] have dealt with differences in electronic structure for neutral TCNQ and anions such as $TCNQ^-$. These differences imply a further electronic delocalization in $TCNQ^-$ as compared to TCNQ. Thus, the single bonds and the double bonds become more equal in the anion, and it should be possible to relate the bond lengths to the charge transferred to the acceptor. This was pointed out in an early extensive review by Herbstein[2] and later elaborated in a study by Flandrois and Chasseau,[3] who considered a large number of compounds. They proposed a linear relationship between selected bond length differences and charge transfer, which was assumed to be zero in pure TCNQ and one in the Rb^+ $TCNQ^-$ salt. Later Coppens and Row[4] as well as Kistenmacher[5] suggested a consideration of the ratios of bond lengths as a more sensitive indicator of the structural changes, and in the present study we shall adopt the Kistenmacher procedure. An extensive study for TCNQ and selected donors based upon data in the Cambridge Structural Database has also been reported.[6] A much more elaborate estimate of charge transfer can be derived from charge density studies based on very accurate X-ray diffraction data, as has been demonstrated by Coppens.[7] A different approach which has often been used assumes a linear relationship between charge transfer and the nitrile stretching frequency as observed by infrared-absorption spectroscopy.[8] Studies on charge-transfer complexes have often dealt with compounds with segregated stacks of donor and acceptor molecules (e.g. TTF–TCNQ, where TTF is tetrathiafulvalene), but mixed-stack structures also have been the subject of extensive studies. An example is the complex between TTF and chloranil, for which a temperature- or pressure-induced phase transition from an essentially neutral state to an essentially ionic state has been observed.[9]

Experimental

Preparations. NMR spectra were recorded on a 400-MHz instrument with TMS as internal reference and at 300 K. Reagent-grade solvents and chemicals were used without further purification.

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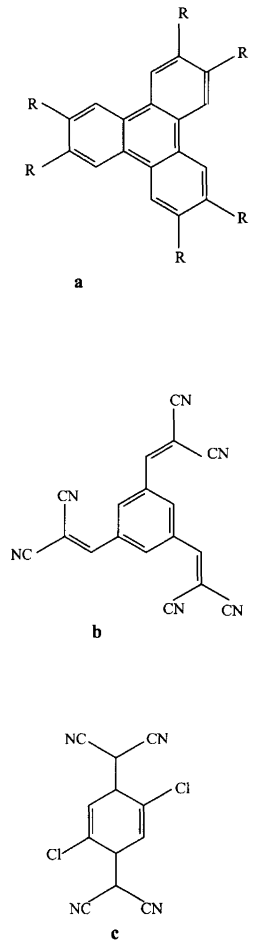

Fig. 1. Constituent molecules. Compound **1** is **a** (R = H) with **b** (1 : 1). Compound **2** is **a** ($R = OCH_3$) with **c** and solvent $C_6H_4Cl_2$ (1 : 1 : 1). Compound **3** is **c** with solvent $C_6H_4Cl_2$ (1 : 1).

2,3,6,7,10,11-Hexamethoxytriphenylene was prepared from veratrole as described by Krebs *et al.*[10]

2,5-Dichloro-7,7,8,8-tetracyano-p-*quinodimethane* was prepared as described by Wheland and Martin,[11] and crystals were grown from dichlorobenzene.

CT complex formation. Equimolar amounts of 2,3,6,7,10,11-hexamethoxytriphenylene and 2,5-dichloro-7,7,8,8-tetracyano-*p*-quinodimethane, both dissolved in 1,2-dichloromethane, were mixed, and after cooling brown crystals of the CT complex were formed.

1,3,5-Tris(2,2-dicyanovinyl)benzene. Benzene-1,3,5-tricarbaldehyde (1.62 g, 10 mmol), prepared according to the literature procedure,[12] and malononitrile (1.98 g, 30 mmol) were dissolved in 1,2-dimethoxyethane (50 mL). The mixture was cooled to 0 °C, and one drop of piperidine was added. The reaction was slightly exothermic and the product precipitated. The mixture was stirred for another 30 min at 20 °C, and the solvent was removed under reduced pressure. Recrystallization from MeCN resulted in a colorless powder in 95% yield (2.91 g): m.p. >250 °C (decomp); ^{1}H NMR (DMSO-d_6) δ 8.78 (s, 3 H), 8.48 (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 159.2, 134.4, 133.2, 113.4, 112.0, 85.9; Anal. Calcd. for $C_{18}H_6N_3$: C, 70.58; H, 1.97; N, 27.44. Found: C, 70.38; H, 2.08; N, 27.54; MS *m/z* 306 (100), 280 (40) 254 (15).

CT complex formation. Equimolar amounts of triphenylene and 1,3,5-tris(2,2-dicyanovinyl)benzene were dissolved in boiling MeCN, and upon cooling the CT complex crystallized as bright yellow needles.

Crystal structure determinations. Suitable single crystals were mounted in a thin protecting layer of oil on glass fibers and transferred to the cold stream of nitrogen (Oxford Cryostream) on the diffractometer. A Siemens SMART CCD diffractometer was used, and data were collected at 120(2) K. An almost complete sphere of reciprocal space was covered by a combination of several sets of exposure frames, each set with a different φ angle for the crystal and each frame covering a scan of 0.3° in ω. Data collection, integration of frame data and conversion to intensities corrected for Lorenz, polarization and absorption effects were performed using the programs SMART,[13] SAINT[13] and SADABS.[14] Structure solution, refinement of the structures, structure analysis and production of crystallographic illustrations were carried out using the programs SHELXS97,[15] SHELXL97,[16] PLATON[17] and SHELXTL.[18] In all of the structures H atoms were included in calculated positions. In the final refinements the H atom positions were allowed to refine in the structures of **1** and **3**. A summary of crystal data, X-ray data collection parameters and structural refinement results is given in Table 1. The final atomic coordinates and equivalent isotropic displacement parameters for non-H atoms are given Tables 2–4. During the final refinements of the structure of **2** a rather high residual electron density peak appeared close to the 3,6 positions of the 2,5-dichloro-TCNQ molecules. This was interpreted as orientational/positional disorder of the latter molecules, and it was modeled by assigning a minor fraction of the Cl atoms to the alternate 3,6 positions. This fraction refined to 0.171 and 0.081 in the two molecules, respectively, cf. Table 3. The same kind of disorder has been reported for the crystal structure of the 4,4-diethylmorpholinium salt of 2,5-dichloro-TCNQ.[19] The rather high values of R and R_{int} for **3** may be due to some crystal decomposition (loss of solvent) during crystal mounting. Tables of anisotropic displacement parameters, coordinates of H atom positions as well as lists of observed and calculated structure factors are available from the authors on request.

Results and discussion

Structure of **1**. Figure 2 shows a perspective view of the two moieties of the structure. Triphenylene in this structure is approximately planar, but several atoms deviate by about 0.1 Å from the average plane. Similar but less pronounced deviations have been observed in crystals of pure triphenylene[20,21] The bond lengths are also very

Table 1. Crystal data and refinement parameters.

	1	2	3
Chemical formula	$C_{36}H_{18}N_6$	$C_{36}H_{26}Cl_4N_4O_6$	$C_{18}H_6Cl_4N_4$
Formula weight	534.56	752.41	420.07
Temperature/K	120(2)	120(2)	120(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*I* 2/*a* (*C* 2/*c*)
a/Å	7.0549(14)	12.282(2)	13.692(3)
b/Å	11.026(2)	12.994(3)	7.7183(15)
c/Å	17.214(3)	13.702(3)	16.391(3)
α/°	96.59(3)	70.72(3)	90
β/°	90.34(3)	83.73(3)	99.47(3)
γ/°	91.61(3)	66.06(3)	90
V/Å^3	1329.6(5)	1877.5(6)	1708.5(6)
Z, D_x/g cm^{-3}	2, 1.335	2, 1.331	4, 1.633
Radiation/Å	0.71073 (Mo *K*α)	0.71073 (Mo *K*α)	0.71073 (Mo *K*α)
μ/mm^{-1}	0.082	0.364	0.703
Crystal size /mm	0.25 × 0.07 × 0.05	0.37 × 0.08 × 0.03	0.13 × 0.08 × 0.05
Transmission range	0.996–0.980	0.991–0.877	0.966–0.914
θ-Range for data collection/°	1.19–26.39	1.58–26.44	2.52–26.65
No. of measured reflections	12910	19971	8387
No. of unique reflections	5350	7627	1769
Completeness of unique refl.	0.982	0.985	0.982
R_{int}	0.0447	0.0834	0.2228
Data/restraints/parameters	5350/0/436	7627/0/515	1769/0/130
No. of refl. with $I > 2\sigma(I)$	3622	4062	940
R [F, $I > 2\sigma(I)$]	0.0532	0.0659	0.0846
R_w (F^2)	0.1262	0.1761	0.2285
Goodness-of-fit (*S*)	1.038	0.967	0.966
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.19, −0.24	0.97, −0.61	0.61, −1.16

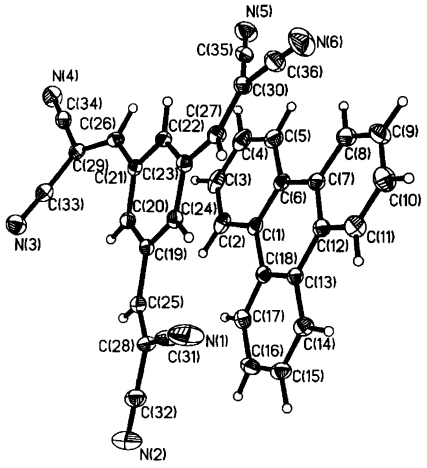

Fig. 2. View of triphenylene molecule (right) and acceptor molecule (left) in **1** with atomic labels.

similar to the values reported by the latter studies. The acceptor molecule differs considerably from planarity in a propeller-like fashion, which is clearly seen from the packing diagram in Fig. 3. The donor and acceptor molecules are almost parallel and stack alternately along the short *a*-axis. The stacking is somewhat slipped, with translations in the planes of the molecules. The packing is stabilized by weak hydrogen bonds from H atoms attached to C(25), C(26) and C(27) to N atoms of the cyano groups (H···N distances: 2.40, 2.45 and 2.36 Å).

Structure of **2.** The constituent molecules with atomic labels are shown in Fig. 4 (ignoring the partial disorder described above). The asymmetric unit consists of one donor molecule, two separate half-parts of dichloro-TCNQ and one dichlorobenzene solvent molecule which implies an overall composition of 1 : 1 : 1. The two dichloro-TCNQ molecules are each centered on an inversion center. The hexamethoxytriphenylene donor molecules are almost planar ignoring the methyl H atoms. As in the previous structure the flat donor and acceptor molecules form mixed stacks, as seen from the packing displayed in Fig. 5. The molecules are situated in common planes transverse to the stacking. Perpendicular to these planes are planes containing solvent molecules which separate the mixed donor–acceptor layers. Weak hydrogen bonds C–H···N (N···H 2.49 and 2.57 Å) and C–H···O (O···H 2.40 and 2.54 Å) appear to be present, but the geometry is not exactly known, since H atom positions were not refined in this structure.

Structure of **3.** The dichloro-TCNQ molecule as well as the dichlorobenzene solvent molecule with atomic labels are displayed in Fig. 6. The asymmetric unit contains one half of each molecule. As seen from the packing in Fig. 7 the structure may be described as planes containing both kinds of molecules. The only notable intermolecular interactions seem to be related to the short N···Cl contacts within these planes, N(1)···Cl(2) of 3.205(6) Å and N(2)···Cl(1) of 3.138(6) Å. Perpendicular to the

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

Atom	x/a	y/b	z/c	U_{eq}[a]
C(1)	9551(3)	6835(2)	3120(1)	20(1)
C(2)	9180(3)	7827(2)	3691(1)	25(1)
C(3)	8719(3)	7637(3)	4447(1)	30(1)
C(4)	8603(3)	6459(3)	4660(1)	34(1)
C(5)	8908(3)	5474(2)	4111(1)	28(1)
C(6)	9389(3)	5634(2)	3329(1)	21(1)
C(7)	9638(3)	4588(2)	2738(1)	21(1)
C(8)	9524(3)	3373(2)	2925(1)	28(1)
C(9)	9632(4)	2390(2)	2361(2)	32(1)
C(10)	9852(4)	2580(2)	1578(2)	33(1)
C(11)	10028(3)	3756(2)	1378(1)	28(1)
C(12)	9954(3)	4786(2)	1948(1)	20(1)
C(13)	10259(3)	6034(2)	1744(1)	19(1)
C(14)	10797(3)	6260(2)	979(1)	24(1)
C(15)	11165(3)	7429(2)	799(1)	26(1)
C(16)	11030(3)	8421(2)	1372(1)	25(1)
C(17)	10510(3)	8225(2)	2119(1)	23(1)
C(18)	10103(3)	7044(2)	2322(1)	19(1)
C(19)	5395(3)	7527(2)	2081(1)	18(1)
C(20)	5025(3)	8001(2)	2849(1)	18(1)
C(21)	4467(3)	7233(2)	3410(1)	17(1)
C(22)	4369(3)	5970(2)	3197(1)	18(1)
C(23)	4730(3)	5475(2)	2427(1)	17(1)
C(24)	5202(3)	6259(2)	1869(1)	18(1)
C(25)	6017(3)	8411(2)	1554(1)	20(1)
C(26)	3999(3)	7670(2)	4221(1)	19(1)
C(27)	4602(3)	4167(2)	2152(1)	20(1)
C(28)	6281(3)	8284(2)	775(1)	21(1)
C(29)	3347(3)	8773(2)	4500(1)	19(1)
C(30)	4609(3)	3206(2)	2571(1)	21(1)
C(31)	5980(4)	7192(2)	247(1)	28(1)
C(32)	6966(3)	9336(2)	415(1)	26(1)
C(33)	2931(3)	9746(2)	4035(1)	22(1)
C(34)	2861(3)	9032(2)	5320(1)	23(1)
C(35)	4842(3)	3286(2)	3407(1)	23(1)
C(36)	4454(3)	1982(2)	2167(1)	27(1)
N(1)	5761(4)	6340(2)	−197(1)	45(1)
N(2)	7532(3)	10185(2)	151(1)	41(1)
N(3)	2537(3)	10540(2)	3690(1)	31(1)
N(4)	2463(3)	9264(2)	5966(1)	32(1)
N(5)	5068(3)	3355(2)	4072(1)	32(1)
N(6)	4326(3)	1023(2)	1836(1)	42(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

planes there are stacks of alternating molecules of the two kinds.

Charge-transfer. The bond lengths of triphenylene in compound **1** differ very little from those in pure triphenylene. Furthermore, the bond lengths of the triphenylene skeleton in compound **2** do not differ much from the pure triphenylene values. This suggests that the charge transfer is very small in these two compounds. It is also possible, however, that the molecular geometry depends on the molecular charge only to a very small extent. The latter often seems to be the case for various donors, although some success has been found in relating these quantities for, e.g., TTF (tetrathiafulvalene).[6] As for compound **2**, we do have the possibility of basing an

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**.

Atom	x/a	y/b	z/c	U_{eq}[a]
C(1)	−1595(3)	7757(3)	38(3)	19(1)
C(2)	−709(3)	8184(3)	−464(3)	23(1)
C(3)	70(3)	8328(3)	80(3)	25(1)
C(4)	11(3)	8034(3)	1169(3)	25(1)
C(5)	−839(3)	7631(3)	1663(3)	23(1)
C(6)	−1664(3)	7483(3)	1123(3)	21(1)
C(7)	−2574(3)	7076(3)	1681(3)	20(1)
C(8)	−2665(3)	6832(3)	2768(3)	23(1)
C(9)	−3525(3)	6489(3)	3298(3)	23(1)
C(10)	−4363(3)	6352(3)	2769(3)	20(1)
C(11)	−4291(3)	6569(3)	1717(3)	21(1)
C(12)	−3398(3)	6941(3)	1148(3)	19(1)
C(13)	−3302(3)	7171(3)	23(3)	19(1)
C(14)	−4088(3)	6987(3)	−531(3)	20(1)
C(15)	−4027(3)	7211(3)	−1582(3)	21(1)
C(16)	−3183(3)	7658(3)	−2141(3)	19(1)
C(17)	−2403(3)	7821(3)	−1609(3)	21(1)
C(18)	−2432(3)	7582(3)	−520(3)	19(1)
C(19)	1009(4)	9101(4)	−1418(3)	38(1)
C(20)	783(4)	7892(4)	2768(3)	34(1)
C(21)	−2861(4)	6420(4)	4905(3)	39(1)
C(22)	−6075(4)	5870(4)	2915(3)	28(1)
C(23)	−5672(4)	6694(4)	−1646(3)	31(1)
C(24)	−2448(4)	8376(4)	−3805(3)	35(1)
C(25)	3578(4)	9140(4)	2661(4)	36(1)
C(26)	4553(4)	9430(3)	2144(3)	31(1)
C(27)	5313(4)	9513(4)	2825(4)	35(1)
C(28)	4072(3)	9617(3)	338(3)	26(1)
C(29)	4767(4)	9681(3)	1093(3)	25(1)
C(30)	5710(3)	10074(3)	672(3)	25(1)
C(31)	−8626(4)	5046(3)	12254(4)	29(1)
C(32)	−8459(4)	5328(3)	11159(3)	26(1)
C(33)	−7519(4)	5758(3)	10808(3)	28(1)
C(34)	−10084(3)	4739(3)	11063(3)	22(1)
C(35)	−9197(3)	5181(3)	10562(3)	21(1)
C(36)	−9153(3)	5432(3)	9450(3)	22(1)
C(37)	1466(4)	8370(4)	−3996(3)	35(1)
C(38)	2268(4)	8880(4)	−4007(3)	39(1)
C(39)	3463(4)	8322(5)	−4239(3)	45(1)
C(40)	3829(4)	7259(5)	−4455(4)	47(1)
C(41)	3031(4)	6752(4)	−4447(3)	44(1)
C(42)	1841(4)	7306(4)	−4215(3)	39(1)
N(1)	2806(4)	8958(4)	3128(3)	48(1)
N(2)	5913(4)	9574(3)	3376(3)	53(1)
N(3)	−8789(3)	4822(3)	13130(3)	39(1)
N(4)	−6750(3)	6075(3)	10636(3)	35(1)
O(1)	931(3)	8748(2)	−326(2)	34(1)
O(2)	843(2)	8157(2)	1668(2)	33(1)
O(3)	−3667(2)	6253(2)	4345(2)	30(1)
O(4)	−5190(2)	6020(2)	3388(2)	27(1)
O(5)	−4733(2)	7041(2)	−2166(2)	28(1)
O(6)	−3240(2)	7883(2)	−3184(2)	28(1)
Cl(1)[b]	2953(1)	9060(1)	671(1)	26(1)
Cl(2)[b]	−8147(1)	5971(1)	8712(1)	24(1)
Cl(1A)[b]	6805(8)	10391(8)	1144(7)	64(3)
Cl(2A)[b]	−10647(11)	4114(11)	12305(10)	31(4)
Cl(3)	−23(1)	9098(1)	−3714(1)	45(1)
Cl(4)	850(1)	6641(1)	−4185(1)	60(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Site occupation factors for Cl(1), Cl(1A), Cl(2) and Cl(2A) are 0.829(3), 0.171(3), 0.919(3) and 0.081(3), repectively.

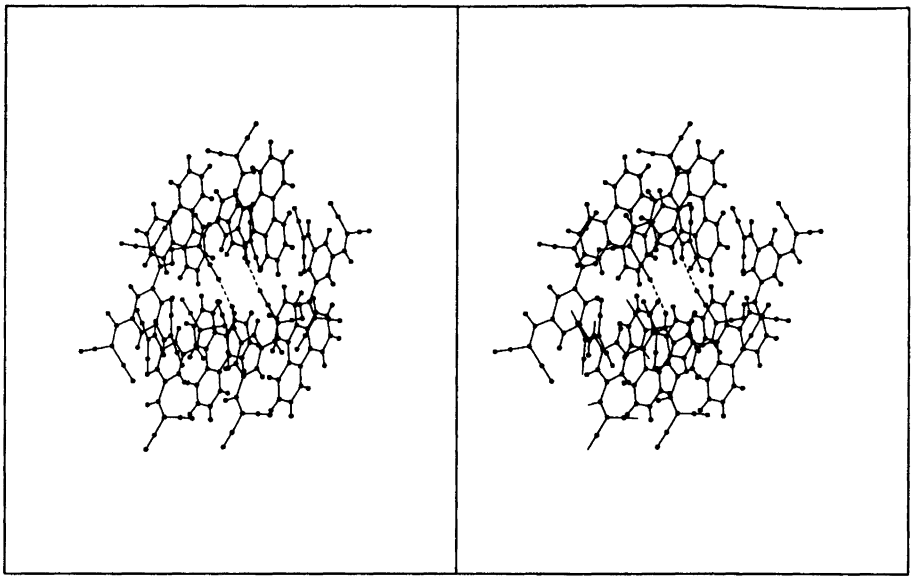

Fig. 3. Packing view of **1** showing mixed stacks and short N···H contacts.

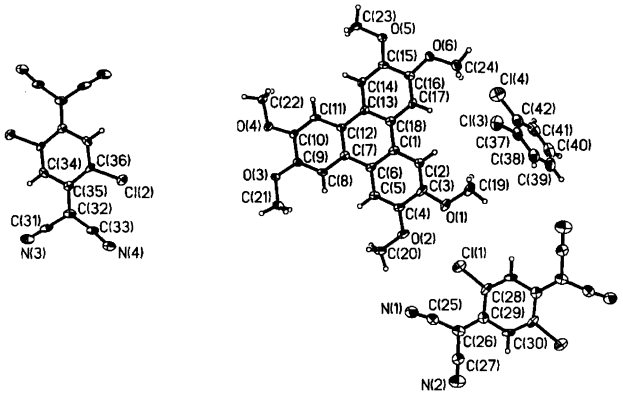

Fig. 4. View of constituent molecules in **2** including a 1,2-dichlorobenzene solvent molecule with atomic labels.

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3**.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
C(1)	17 943(5)	−4033(8)	−2735(4)	16(1)
C(2)	18 362(5)	−2345(8)	−2912(4)	14(1)
C(3)	17 863(5)	−848(9)	−2643(4)	18(2)
C(4)	19 831(5)	−3393(9)	−3512(4)	22(2)
C(5)	19 175(5)	−2096(8)	−3268(4)	17(2)
C(6)	19 506(5)	−345(9)	−3405(4)	20(2)
C(7)	12 913(5)	−5640(8)	−192(4)	18(2)
C(8)	13 339(6)	−7201(9)	−375(4)	23(2)
C(9)	12 923(5)	−8747(8)	−184(4)	20(2)
Cl(1)	18 443(1)	−5907(2)	−3047(1)	22(1)
Cl(2)	13 419(1)	−3710(2)	−473(1)	28(1)
N(1)	20 407(4)	−4278(7)	−3736(4)	26(1)
N(2)	19 755(5)	1027(7)	−3510(4)	26(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Bond lengths (Å) for **1**.

C(1)–C(6)	1.413(3)	C(19)–C(25)	1.466(3)
C(1)–C(2)	1.416(3)	C(20)–C(21)	1.406(3)
C(1)–C(18)	1.473(3)	C(21)–C(22)	1.397(3)
C(2)–C(3)	1.380(3)	C(21)–C(26)	1.467(3)
C(3)–C(4)	1.390(4)	C(22)–C(23)	1.402(3)
C(4)–C(5)	1.379(4)	C(23)–C(24)	1.400(3)
C(5)–C(6)	1.419(3)	C(23)–C(27)	1.465(3)
C(6)–C(7)	1.463(3)	C(25)–C(28)	1.347(3)
C(7)–C(8)	1.414(3)	C(26)–C(29)	1.349(3)
C(7)–C(12)	1.419(3)	C(27)–C(30)	1.349(3)
C(8)–C(9)	1.373(4)	C(28)–C(31)	1.433(3)
C(9)–C(10)	1.397(4)	C(28)–C(32)	1.448(3)
C(10)–C(11)	1.381(3)	C(29)–C(33)	1.446(3)
C(11)–C(12)	1.415(3)	C(29)–C(34)	1.452(3)
C(12)–C(13)	1.469(3)	C(30)–C(35)	1.440(3)
C(13)–C(18)	1.412(3)	C(30)–C(36)	1.446(3)
C(13)–C(14)	1.420(3)	C(31)–N(1)	1.148(3)
C(14)–C(15)	1.378(3)	C(32)–N(2)	1.150(3)
C(15)–C(16)	1.392(3)	C(33)–N(3)	1.153(3)
C(16)–C(17)	1.378(3)	C(34)–N(4)	1.151(3)
C(17)–C(18)	1.409(3)	C(35)–N(5)	1.148(3)
C(19)–C(20)	1.394(3)	C(36)–N(6)	1.144(3)
C(19)–C(24)	1.406(3)		

estimate of the charge transfer on the acceptor geometry, since compound **3** contains the very same acceptor. The presence of solvent molecules in both structures is a complication, but we may assume that the latter molecules are not significantly involved in charge transfer. We shall use the Kistenmacher approach and calculate the ratio $c/(b+d)$, where in compound **3** b is the average of the C(1)–C(2) and the C(2)–C(3) distances, c is the C(2)–C(5) distance, and d is the average of the C(5)–C(4) and the C(5)–C(6) distances. This ratio amounts to 0.466, whereas the corresponding calculation for the acceptor in compound **2** produces a value of 0.481. Very few other compounds with dichloro-TCNQ

Table 6. Selected bond lengths (Å) for **2**.

C(1)–C(6)	1.411(5)	C(25)–C(26)	1.438(7)
C(1)–C(2)	1.423(5)	C(26)–C(29)	1.387(6)
C(1)–C(18)	1.469(5)	C(26)–C(27)	1.443(7)
C(2)–C(3)	1.375(6)	C(27)–N(2)	1.150(6)
C(3)–C(4)	1.414(6)	C(28)–C(30)^{i}	1.337(6)
C(4)–C(5)	1.366(5)	C(28)–C(29)	1.451(6)
C(5)–C(6)	1.420(5)	C(28)–Cl(1)	1.747(4)
C(6)–C(7)	1.459(5)	C(29)–C(30)	1.436(6)
C(7)–C(12)	1.403(5)	C(30)–C(28)^{i}	1.337(6)
C(7)–C(8)	1.419(5)	C(30)–Cl(1A)	1.787(10)
C(8)–C(9)	1.354(5)	C(31)–N(3)	1.153(5)
C(9)–C(10)	1.415(5)	C(31)–C(32)	1.435(6)
C(10)–C(11)	1.375(5)	C(32)–C(35)	1.385(5)
C(11)–C(12)	1.424(5)	C(32)–C(33)	1.445(6)
C(12)–C(13)	1.471(5)	C(33)–N(4)	1.146(5)
C(13)–C(18)	1.413(5)	C(34)–C(36)^{ii}	1.351(5)
C(13)–C(14)	1.423(5)	C(34)–C(35)	1.436(6)
C(14)–C(15)	1.371(5)	C(34)–Cl(2A)	1.821(13)
C(15)–C(16)	1.418(5)	C(35)–C(36)	1.450(6)
C(16)–C(17)	1.379(5)	C(36)–C(34)^{ii}	1.351(5)
C(17)–C(18)	1.420(5)	C(36)–Cl(2)	1.728(4)
C(25)–N(1)	1.143(6)		

Symmetry transformations used to generate equivalent atoms: $^{i}-x+1, -y+2, -z$; $^{ii}-x-2, -y+1, -z+2$

Table 7. Selected bond lengths (Å) for **3**.

C(1)–C(3)^{i}	1.356(10)	C(3)–C(1)^{i}	1.356(10)
C(1)–C(2)	1.471(9)	C(4)–N(1)	1.149(9)
C(1)–Cl(1)	1.715(6)	C(4)–C(5)	1.444(10)
C(2)–C(5)	1.354(10)	C(5)–C(6)	1.454(9)
C(2)–C(3)	1.447(9)	C(6)–N(2)	1.134(8)

Symmetry transformation used to generate equivalent atoms: $^{i}-x+7/2, -y-1/2, -z-1/2$.

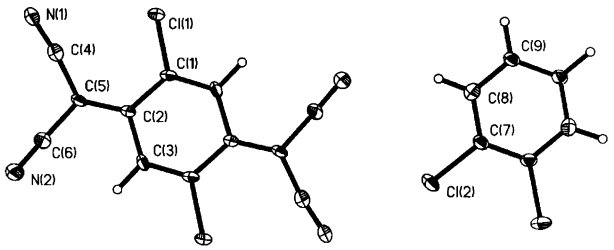

Fig. 6. View of 2,5-dichloro-TCNQ and solvent 1,2-dichlorobenzene in **3** with atomic labels.

have been studied. One of these is the 4,4-diethylmorpholinium salt,[19] which we assume to be fully ionized. Using the data stored for this compound in the Cambridge Structural Database we obtain a Kistenmacher ratio of 0.514. This structure determination is actually a room temperature study, but the ratio is probably not much dependent on temperature, unless the charge transfer changes. We made several attempts to produce single crystals of Cs^{+} and other salts of dichloro-TCNQ as a more direct reference, but only polycrystalline samples were obtained. Assuming a linear relationship the Kistenmacher ratio of 0.481 for **2** corresponds to an estimated charge transfer of about 0.3 *e*. Applying the same method to a previously studied complex of dibenzo-TTF with dichloro-TCNQ[22] produces a ratio of 0.485, corresponding to a charge transfer of about 0.4 *e*, which is in reasonable agreement with values of about 0.5 *e* as derived from studies of the charge-density wave superstructure in this organic conductor.[23]

Obviously, the Kistenmacher ratio is very sensitive to errors in bond lengths, values of which are not available for the morpholinium compound. The ratios given above probably have standard deviations of about 0.003, and therefore the charge transfers derived are only crude

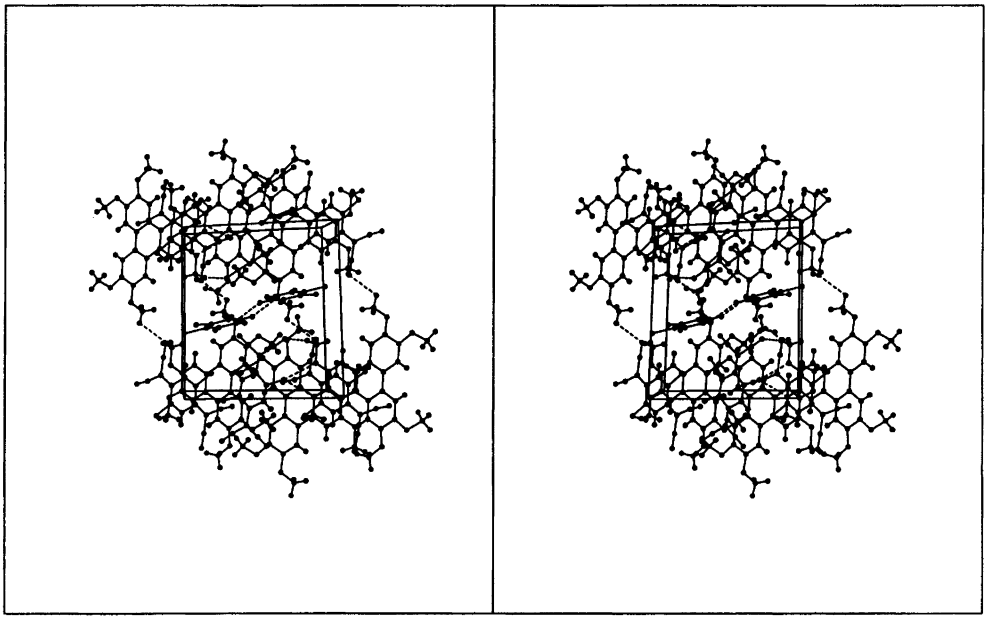

Fig. 5. Packing view of **2** showing mixed stacks and short N···H and O···H contacts.

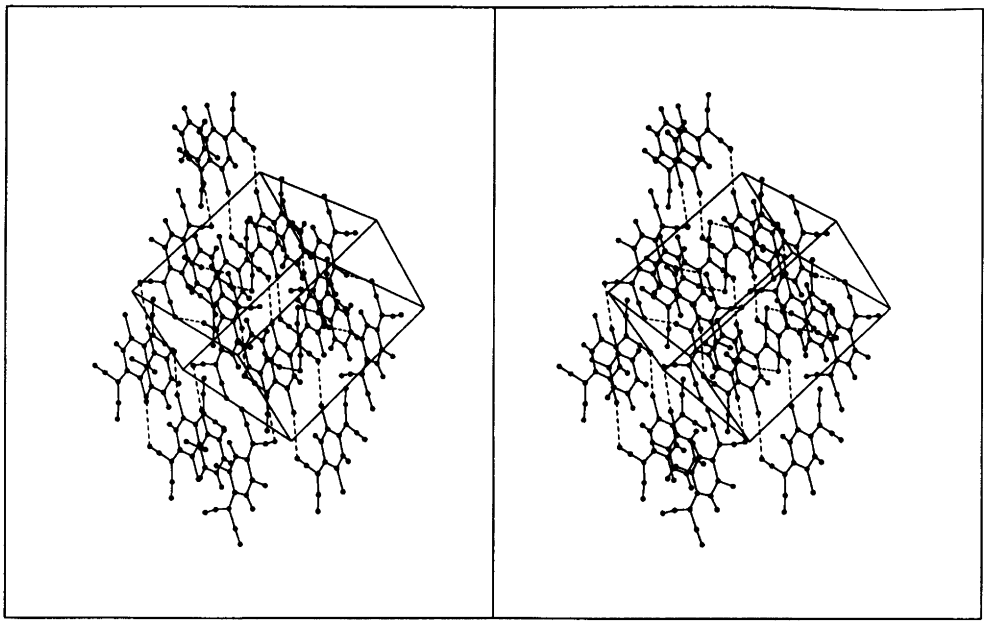

Fig. 7. Packing view of **3** showing short N···Cl contacts.

estimates. If a theoretical ratio of 0.500 (corresponding to *c*, *b* and *d* being of equal length) is used instead of 0.514 in the morpholinium case, the estimated charge transfer for **2** will increase to 0.4 *e* and in the dibenzo-TTF case to 0.5 *e*. In conclusion, we are rather confident that a partial transfer of charge has taken place in compound **2**, whereas no evidence for a charge transfer in compound **1** was produced in the present study.

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