Structural Studies of a Series of Organic Non-Linear Optical Materials

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Abstract

The crystal structures of {4-[bis(diethylamino)-methylium]phenyl}dicyanomethanide (I), {4-[cyano(4-methylpiperidyl)methylium]phenyl}dicyanomethanide (II), {4-[cyano(1-pyrrolidinyl)methylium]phenyl}dicyanomethanide (IV) and (Z)-{4-[1,3-dicyano-3-(diethylamino)-2-propenylium]phenyl}dicyanomethanide have been determined by X-ray crystallography. Together with (Z)-{4-[1-cyano-3-(diethylamino)-2-propenylium]phenyl}dicyanomethanide [(III): Cole, J. C., Howard, J. A. K., Cross, G. H. & Szablewski, M. (1995). *Acta Cryst.* C**51**, 715–718], these compounds exhibit varying degrees of quinoidal characteristics and yet have predominantly zwitterionic ground state character. The presence of high dipole moments in the crystal can thus be inferred and are substantiated by measurements of high solution-state dipole moments. Negative solvatochromism (hypsochromism on increasing solvent polarity) confirms the zwitterionic character in at least two of the series.

1. Introduction

The crystal structures of four novel TCNQ derivatives [(I), (II), (IV) and (V); Fig. 1] have been determined. Interest in these materials lies in the expectation that many will follow the pattern found for (III) [see Fig. 1; Szablewski (1994); Cole, Howard, Cross & Szablewski (1995)], in which the product of dipole moment and first hyperpolarizability, $\mu.\beta$, is exceptionally large. Of these two parameters characterizing the figure of merit for second-order non-linear optical molecules, the dipole moment μ is particularly important since generating a macroscopic second-order non-linearity ($\chi^{(2)}$) from an otherwise isotropic dispersion of molecules in a host often relies on a poling electric field coupling to the dipole moment.

These microscopic polarization components take on values which are characteristic of the effective polarizing field in the surrounding medium (Barzoukas, Runser, Fort & Blanchard-Desce, 1996). The simplest example is the classical reaction field of Onsager (1936), where an isotropic homogeneous and continuous dielectric medium surrounds the dipole. In the crystal state it is not appropriate to discuss the polarizing field in such simple terms, but rather the field is generated by the sum of the local dipole fields acting on the central dipole (Munn, 1988). Evidence for the strength of this field might be obtained from studies of the crystal structure and determination of the solid-state dipole moment compared with measured 'gas phase' values (Howard, Hursthouse, Lehmann, Mallinson & Frampton, 1992). The present study, whilst not determining these moments in absolute terms, demonstrates a trend in the expected crystal structure dipole moments and some correlation with experimental data (Table 1) on isolated molecules in solution is made.
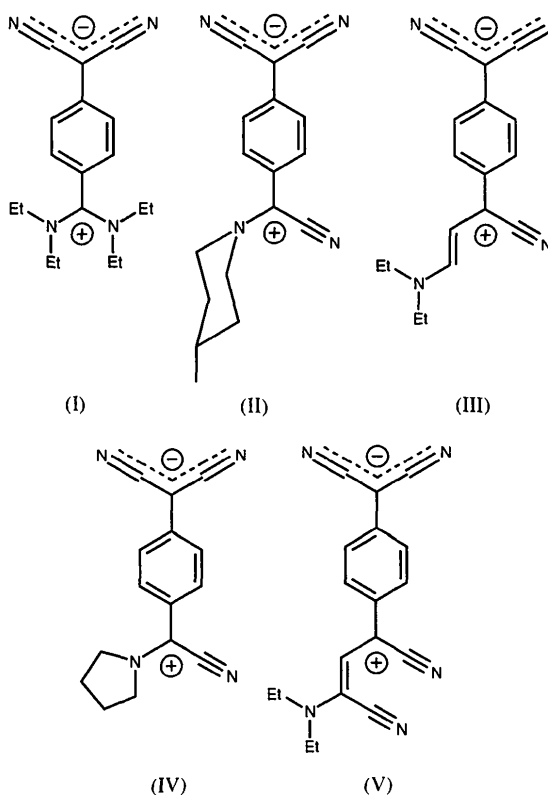

Fig. 1. A schematic diagram of the five molecules studied.

Table 1. *Solvatochromism (wavelength in units of nm) of the lowest energy excitation band of the series of molecules referred to in the text*

ε refers to the solvent dielectric constant at 298 K (Riddick & Bunger, 1986).

Solvent	ε	(I)	(II)	(III)	(IV)	(V)
CHCl$_3$	4.8	481	636	717		721
PhCl	5.6		636	722	617	727
DCM	8.9	459	639	720	611	723
C$_6$H$_{10}$=O	16.1		636	715	613	785
DMF	36.7	433	629	693	607	802
MeCN	37.5		628	698	604	785

2. Experimental

2.1. Synthesis

Compounds (I) and (II) were prepared by the reaction of TCNQ with 4-methylpiperidine and N,N-diethylamine, respectively, in THF, by methods analogous to those described by Hertler, Hartzler, Acker & Benson (1962). Compounds (III) and (V) were prepared by the action of a tertiary amine on TCNQ (Szablewski, 1994), while (IV) was the unexpected result of the reaction of TCNQ with 1-pyrrolidino-1-cyclopentene in 1,4-dioxane.

2.2. X-ray crystallography

All data for each molecule were collected using a standard four-circle diffractometer. As indicated in Table 2, two different types of diffractometers were employed across the series. Both types employed graphite monochromatized Mo $K\alpha$ X-radiation ($\lambda = 0.71073$ Å) and an Oxford Cryosystems Cryostream facilitated the low-temperature requirements (also stated in Table 2).

Standards were measured for all data, although the frequency and number of these were machine dependent: in the case of the AFC-6S Rigaku diffractometer, 3 standards were measured every 150 reflections; in the case of the Siemens $P4$ diffractometer, 3 standards were measured every 97 reflections. Data collection and refinement using the Rigaku AFC-6S diffractometer employed *AFC/MSC* software and data reduction utilized *TEXSAN* (Molecular Structure Corporation, 1989), whereas data collection, reduction and refinement were carried out on the Siemens $P4$ diffractometer *via* use of Siemens *XSCANS* (Siemens, 1994).

Data were corrected for Lorentz and polarization effects. However, no absorption corrections were made as the absorption coefficient is <0.1 mm^{-1} in all cases.

All structures were elucidated by direct methods. Where necessary (see Table 2), an isotropic extinction correction was applied. Refinement on F^2 was performed *via* the full-matrix least squares algorithm of the *SHELXL93* package (Sheldrick, 1993) and molecular graphics were generated *via* *SHELXTL-Plus*

(Sheldrick, 1991). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The weighting scheme was defined by

$$w = q/[s^2(F_o^2) + (aP)^2 + bP + d + eSIN(t)],$$

where $P = [f(\text{max. of } 0 \text{ or } F_o^2) + (1 - f)F_c^2]$. Parameters c, d and e took the default value of 0 for molecules (I), (II), (IV) and (V).

The hydrogen positions were refined to varying extents: complete refinement of the hydrogens was performed for structures (I) and (V); in (II) the coordinates were refined, but the atomic displacement parameters were restrained to be 120% of their vicinal C atom; in (IV) the atomic displacement parameters were defined as in the latter case, but the coordinates were not refined – instead, their geometry was idealized and the C—H distances were set to 0.960 Å.

The final fractional coordinates and equivalent isotropic displacement factors for (I), (II), (IV) and (V) are given in Table 3. The corresponding bond distances and angles of the non-H atoms for all five molecules (I)–(V) are given in Tables 4 and 5. Thermal ellipsoid plots of (I)–(V) are shown in Figs. 2–6. Results for (III) are included here for comparison purposes and were generated from the X-ray structural data of Cole *et al.* (1995).†

2.3. Solvatochromism

The spectra in solution of the compounds exhibit a solvatochromic absorption band which is ascribed to the main intramolecular charge-transfer band. As an index of solvent polarity we prefer to use simply the solvent dielectric constant. In the description of the reaction field evolution of the gas-phase dipole moment (Böttcher, 1952) the only non-solute variable is the solvent dielectric constant. Thus, for molecules of similar type, *i.e.* similar gas-phase dipole moments and polarizabilities, the solvatochromism in the absence of bonding interactions should be similar. In this spirit we present the data in Table 1 as an aid to classifying the molecules of the present study.

Notable trends emerge for (I) and (III), wherein over the studied range of solvents the solvatochromism is negative. This implies that the ground-state dipole moment of the solute in these solutions contains more zwitterionic than quinoidal character (*vide infra*). There is no clear trend in the solvatochromism for (II) and (IV), whose solvatochromism is similar. These compounds are structurally similar in any case, but in the higher polarity solvents one might assign a negative

Table 2. *Experimental details*

	(I)	(II)	(IV)	(V)
Crystal data				
Chemical formula	$C_{18}H_{24}N_4$	$C_{17}H_{16}N_4$	$C_{15}H_{12}N_4$	$C_{18}H_{15}N_5$
Chemical formula weight	296.41	276.34	248.29	301.35
Cell setting	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	Pn	$P2_1/n$	$P\bar{1}$
a (Å)	11.262 (2)	6.970 (1)	6.837 (1)	7.615 (4)
b (Å)	12.867 (3)	14.233 (3)	25.080 (5)	7.962 (4)
c (Å)	12.510 (3)	7.633 (2)	7.386 (1)	14.740 (4)
α (°)				91.45 (4)
β (°)	112.11 (3)	107.91 (3)	92.70 (3)	96.93 (4)
γ (°)				118.03 (4)
V (Å³)	1679.5 (6)	720.5 (3)	1265.1 (4)	779.7 (6)
Z	4	2	4	2
D_x (Mg m⁻³)	1.172	1.274	1.304	1.284
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	49	48	47	51
θ range (°)	6.9–10.8	10.8–12.6	10.1–13.0	10.3–13.1
μ (mm⁻¹)	0.072	0.079	0.082	0.081
Temperature (K)	150 (2)	150 (2)	150 (2)	150 (2)
Crystal form	Block	Needle	Rectangular plate	Square plate
Crystal size (mm)	$0.30 \times 0.22 \times 0.20$	$0.56 \times 0.44 \times 0.12$	$0.3 \times 0.2 \times 0.05$	$0.5 \times 0.5 \times 0.2$
Crystal colour	Brown	Purple	Very dark purple	Metallic green
Data collection				
Diffractometer	Siemens $P4$	Siemens $P4$	Rigaku AFC-6S	Rigaku AFC-6S
Data collection method	$2\theta/\omega$ scans	$2\theta/\omega$ scans	ω scans	ω scans
Absorption correction	None	None	None	None
No. of measured reflections	3758	1654	2233	3847
No. of independent reflections	2949	1526	2057	3590
No. of observed reflections	1550	1331	542	2641
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0370	0.0252	0.0945	0.0090
θ_{max} (°)	25.00	27.41	25.03	27.50
Range of h, k, l	$-1 \rightarrow h \rightarrow 13$	$-1 \rightarrow h \rightarrow 8$	$-8 \rightarrow h \rightarrow 8$	$-9 \rightarrow h \rightarrow 8$
	$-1 \rightarrow k \rightarrow 15$	$-1 \rightarrow k \rightarrow 16$	$-29 \rightarrow k \rightarrow 0$	$0 \rightarrow k \rightarrow 10$
	$-14 \rightarrow l \rightarrow 14$	$-9 \rightarrow l \rightarrow 8$	$-7 \rightarrow l \rightarrow 0$	$-19 \rightarrow l \rightarrow 19$
No. of standard reflections	3	3	3	3
Frequency of standard reflections	Every 97 reflections	Every 97 reflections	Every 147 reflections	Every 147 reflections
Intensity decay (%)	None	None	None	None
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0374	0.0352	0.0586	0.0381
$wR(F^2)$	0.0700	0.0991	0.1943	0.1158
S	0.764	1.037	0.920	1.031
No. of reflections used in refinement	2949	1525	2056	3589
No. of parameters used	295	238	173	254
H-atom treatment	All H-atom parameters refined	Only coordinates of H atoms refined, $U_{iso} = 1.2U_{eq}$ of vicinal C atom	H-atom parameters not refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.0152P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0460P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.1687P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	-0.041	-0.001	-0.014	-0.054
$\Delta\rho_{max}$ (e Å⁻³)	0.129	0.148	0.232	0.280
$\Delta\rho_{min}$ (e Å⁻³)	-0.208	-0.159	-0.216	-0.183
Extinction method	None	None	None	*SHELXL93* (Sheldrick, 1993)
Extinction coefficient	–	–	–	0.0265 (39)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)
Computer programs				
Data collection	*XSCANS* (Siemens, 1994)	*XSCANS* (Siemens, 1994)	*AFC/MSC* (MSC, 1989)	*AFC/MSC* (MSC, 1989)
Cell refinement	*XSCANS* (Siemens, 1994)	*XSCANS* (Siemens, 1994)	*AFC/MSC* (MSC, 1989)	*AFC/MSC* (MSC, 1989)
Data reduction	*XSCANS* (Siemens, 1994)	*XSCANS* (Siemens, 1994)	*TEXSAN* (MSC, 1989)	*TEXSAN* (MSC, 1989)
Structure solution	*SHELXS86* (Sheldrick, 1990)	*SHELXS86* (Sheldrick, 1990)	*SHELXS86* (Sheldrick, 1990)	*SHELXS86* (Sheldrick, 1990)
Structure refinement	*SHELXL93* (Sheldrick, 1993)	*SHELXL93* (Sheldrick, 1993)	*SHELXL93* (Sheldrick, 1993)	*SHELXL93* (Sheldrick, 1993)
Preparation of material for publication	*SHELXL93* (Sheldrick, 1993)	*SHELXL93* (Sheldrick, 1993)	*SHELXL93* (Sheldrick, 1993)	*SHELXL93* (Sheldrick, 1993)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\sum_i\sum_j U^{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Structure (I)				
N1	0.5222 (2)	1.22871 (14)	−0.35153 (14)	0.0412 (5)
N2	0.8684 (2)	1.04665 (15)	−0.33610 (14)	0.0427 (5)
N3	0.7624 (2)	0.99849 (12)	0.28181 (13)	0.0218 (4)
N4	0.7848 (2)	0.83460 (12)	0.21234 (12)	0.0238 (4)
C1	0.6077 (2)	1.1736 (2)	−0.3052 (2)	0.0297 (5)
C2	0.7953 (2)	1.0754 (2)	−0.2975 (2)	0.0310 (6)
C3	0.7097 (2)	1.1067 (2)	−0.2448 (2)	0.0263 (5)
C4	0.7250 (2)	1.06666 (15)	−0.1321 (2)	0.0232 (5)
C5	0.6415 (2)	1.0952 (2)	−0.0765 (2)	0.0266 (5)
C6	0.6567 (2)	1.0551 (2)	0.0303 (2)	0.0255 (5)
C7	0.7525 (2)	0.98252 (14)	0.08497 (15)	0.0211 (5)
C8	0.8362 (2)	0.9537 (2)	0.0312 (2)	0.0241 (5)
C9	0.8231 (2)	0.9955 (2)	−0.0742 (2)	0.0252 (5)
C10	0.7664 (2)	0.9375 (2)	0.1965 (2)	0.0224 (5)
C11	0.8019 (2)	1.1094 (2)	0.2897 (2)	0.0257 (5)
C12	0.9108 (2)	1.1318 (2)	0.4034 (2)	0.0330 (6)
C13	0.7144 (2)	0.9611 (2)	0.3705 (2)	0.0248 (5)
C14	0.6099 (2)	1.0323 (2)	0.3777 (2)	0.0337 (6)
C15	0.8628 (2)	0.7890 (2)	0.3261 (2)	0.0266 (5)
C16	0.9684 (2)	0.7198 (2)	0.3180 (2)	0.0306 (6)
C17	0.7286 (2)	0.7604 (2)	0.1155 (2)	0.0276 (5)
C18	0.6458 (2)	0.6798 (2)	0.1435 (2)	0.0323 (6)
Structure (II)				
N1	0.2839 (5)	0.2220 (2)	0.4240 (5)	0.0384 (7)
N2	0.3554 (5)	0.3441 (2)	−0.0842 (4)	0.0358 (7)
N3	0.2779 (5)	−0.1703 (2)	−0.5357 (4)	0.0291 (6)
N4	0.3309 (4)	−0.2524 (2)	−0.1035 (3)	0.0198 (6)
C1	0.2908 (5)	0.2131 (2)	0.2760 (5)	0.0258 (7)
C2	0.3320 (5)	0.2785 (2)	−0.0042 (4)	0.0251 (7)
C3	0.3044 (5)	0.1983 (2)	0.0966 (4)	0.0239 (7)
C4	0.2883 (5)	0.1061 (2)	0.0201 (4)	0.0212 (6)
C5	0.2506 (5)	0.0272 (2)	0.1184 (4)	0.0243 (7)
C6	0.2450 (5)	−0.0617 (2)	0.0512 (4)	0.0224 (7)
C7	0.2820 (5)	−0.0789 (2)	−0.1185 (4)	0.0203 (6)
C8	0.3057 (5)	0.0012 (2)	−0.2231 (4)	0.0220 (7)
C9	0.3099 (5)	0.0902 (2)	−0.1558 (4)	0.0215 (7)
C10	0.2983 (5)	−0.1705 (2)	−0.1889 (4)	0.0195 (7)
C11	0.2831 (5)	−0.1733 (2)	−0.3843 (4)	0.0221 (7)
C12	0.4167 (5)	−0.2657 (2)	0.0978 (4)	0.0236 (7)
C13	0.2802 (5)	−0.3285 (2)	0.1687 (4)	0.0250 (7)
C14	0.2518 (6)	−0.4242 (2)	0.0720 (4)	0.0271 (7)
C15	0.1820 (5)	−0.4101 (2)	−0.1374 (4)	0.0270 (7)
C16	0.3167 (6)	−0.3434 (2)	−0.2006 (4)	0.0236 (7)
C17	0.1063 (7)	−0.4859 (2)	0.1341 (5)	0.0408 (9)
Structure (IV)				
N1	1.0147 (10)	0.3833 (3)	0.4356 (9)	0.055 (2)
C1	0.8633 (12)	0.3901 (3)	0.3663 (12)	0.037 (2)
C3	0.6730 (10)	0.3984 (3)	0.2833 (11)	0.032 (2)
C2	0.5736 (12)	0.3526 (3)	0.2208 (11)	0.040 (2)
N2	0.4942 (9)	0.3145 (2)	0.1673 (10)	0.056 (2)
C4	0.5901 (10)	0.4496 (3)	0.2693 (11)	0.031 (2)
C9	0.3978 (10)	0.4579 (3)	0.1911 (11)	0.036 (2)
C8	0.3198 (10)	0.5073 (3)	0.1761 (12)	0.035 (2)
C7	0.4222 (9)	0.5541 (3)	0.2400 (10)	0.024 (2)
C6	0.6127 (10)	0.5452 (3)	0.3206 (10)	0.031 (2)
C5	0.6934 (10)	0.4956 (3)	0.3333 (11)	0.031 (2)
C10	0.3323 (9)	0.6040 (3)	0.2221 (12)	0.032 (2)
C11	0.1325 (12)	0.6052 (3)	0.1427 (11)	0.036 (2)
N3	−0.0240 (10)	0.6057 (3)	0.0777 (10)	0.052 (2)
N4	0.3992 (8)	0.6526 (2)	0.2637 (8)	0.035 (2)
C15	0.2767 (9)	0.7018 (2)	0.2504 (11)	0.046 (2)
C14	0.4148 (11)	0.7444 (4)	0.3423 (15)	0.039 (3)
C13	0.6153 (13)	0.7267 (3)	0.2732 (15)	0.039 (3)
C13′	0.5866 (45)	0.7253 (5)	0.3697 (43)	0.077 (12)
C14′	0.4293 (27)	0.7473 (8)	0.2311 (39)	0.043 (9)
C12	0.6046 (9)	0.6661 (3)	0.3130 (11)	0.042 (2)
Structure (V)				
N1	0.3662 (2)	1.0663 (2)	0.79419 (9)	0.0417 (4)
N2	0.3785 (2)	0.5993 (2)	0.63328 (9)	0.0358 (3)
N3	0.2021 (2)	−0.0096 (2)	1.07724 (9)	0.0310 (3)

Table 3 (*cont.*)

	x	y	z	U_{eq}
N4	0.1201 (2)	−0.0436 (2)	1.28451 (9)	0.0407 (3)
N5	0.1535 (2)	0.3788 (2)	1.34754 (7)	0.0244 (3)
C1	0.3527 (2)	0.9159 (2)	0.78956 (9)	0.0289 (3)
C2	0.3573 (2)	0.6563 (2)	0.70120 (9)	0.0257 (3)
C3	0.3320 (2)	0.7286 (2)	0.78539 (9)	0.0236 (3)
C4	0.2958 (2)	0.6230 (2)	0.86225 (9)	0.0220 (3)
C5	0.2805 (2)	0.7036 (2)	0.94744 (9)	0.0236 (3)
C6	0.2512 (2)	0.6061 (2)	1.02313 (9)	0.0236 (3)
C7	0.2358 (2)	0.4199 (2)	1.02199 (8)	0.0207 (3)
C8	0.2497 (2)	0.3398 (2)	0.93657 (9)	0.0228 (3)
C9	0.2773 (2)	0.4359 (2)	0.86003 (9)	0.0230 (3)
C10	0.2091 (2)	0.3177 (2)	1.10098 (9)	0.0208 (3)
C11	0.2018 (2)	0.1333 (2)	1.08927 (9)	0.0231 (3)
C12	0.1979 (2)	0.3885 (2)	1.18762 (9)	0.0237 (3)
C13	0.1666 (2)	0.2991 (2)	1.26864 (9)	0.0223 (3)
C14	0.1412 (2)	0.1072 (2)	1.27456 (9)	0.0278 (3)
C15	0.1718 (2)	0.5711 (2)	1.35558 (9)	0.0264 (3)
C16	0.3879 (3)	0.7243 (2)	1.38586 (12)	0.0357 (3)
C17	0.1414 (2)	0.2874 (2)	1.43450 (9)	0.0283 (3)
C18	−0.0742 (3)	0.1658 (2)	1.45069 (11)	0.0344 (3)

Table 4. *Bond lengths (Å) for all five compounds (excluding those involving hydrogens)*

Data for (III) are from Cole *et al.* (1995).

	(I)	(II)	(III)	(IV)	(V)
N(1)—C(1)	1.159 (3)	1.153 (5)	1.155 (3)	1.146 (8)	1.152 (2)
N(2)—C(2)	1.162 (3)	1.154 (4)	1.157 (2)	1.159 (9)	1.148 (2)
N(3)—C(10)	1.339 (2)	—	—	—	—
N(3)—C(11)	1.487 (2)	1.145 (4)	1.150 (2)	1.153 (8)	1.148 (2)
N(3)—C(13)	1.486 (2)	—	—	—	—
N(4)—C(10)	1.343 (2)	1.321 (4)	—	1.333 (9)	—
N(4)—C(12)	—	1.479 (4)	—	1.474 (7)	—
N(4)—C(13)	—	—	1.316 (2)	—	—
N(4)—C(14)	—	—	1.478 (2)	—	1.150 (2)
N(4)—C(15)	1.483 (2)	—	—	1.491 (7)	—
N(4)—C(16)	—	1.479 (4)	1.476 (3)	—	—
N(4)—C(17)	1.484 (2)	—	—	—	—
N(5)—C(13)	—	—	—	—	1.347 (2)
N(5)—C(15)	—	—	—	—	1.471 (2)
N(5)—C(17)	—	—	—	—	1.481 (2)
C(1)—C(3)	1.407 (3)	1.417 (4)	1.418 (3)	1.43 (1)	1.423 (2)
C(2)—C(3)	1.415 (3)	1.423 (5)	1.421 (3)	1.40 (1)	1.427 (2)
C(3)—C(4)	1.450 (2)	1.427 (4)	1.420 (3)	1.405 (9)	1.404 (2)
C(4)—C(5)	1.412 (3)	1.419 (4)	1.425 (3)	1.421 (8)	1.438 (2)
C(4)—C(9)	1.408 (3)	1.415 (4)	1.417 (3)	1.426 (8)	1.428 (2)
C(5)—C(6)	1.382 (3)	1.361 (4)	1.363 (3)	1.363 (8)	1.356 (2)
C(6)—C(7)	1.396 (3)	1.418 (4)	1.417 (3)	1.424 (8)	1.431 (2)
C(7)—C(8)	1.398 (3)	1.430 (4)	1.421 (4)	1.435 (9)	1.435 (2)
C(7)—C(10)	1.464 (2)	1.428 (4)	1.427 (2)	1.397 (9)	1.418 (2)
C(8)—C(9)	1.379 (3)	1.363 (4)	1.367 (3)	1.351 (8)	1.361 (2)
C(10)—C(11)	—	1.463 (4)	1.453 (3)	1.46 (1)	1.448 (2)
C(10)—C(12)	—	—	1.388 (3)	—	1.411 (2)
C(11)—C(12)	1.516 (3)	—	—	—	—
C(12)—C(13)	—	1.522 (5)	1.399 (3)	1.551 (7)	1.393 (2)
C(12)—C(13′)	—	—	—	1.551 (9)	—
C(13)—C(14)	1.521 (3)	1.533 (4)	—	1.550 (9)	1.454 (2)
C(13′)—C(14′)	—	—	—	1.55 (1)	—
C(14)—C(15)	—	1.534 (4)	1.523 (3)	1.559 (9)	—
C(14)—C(17)	—	1.523 (5)	—	—	—
C(14′)—C(15)	—	—	—	1.56 (1)	—
C(15)—C(16)	1.519 (3)	1.515 (4)	—	—	1.518 (2)
C(16)—C(17)	—	—	1.516 (3)	—	—
C(17)—C(18)	1.521 (3)	—	—	—	1.517 (2)

C(*n*′) is the disordered atom related to C(*n*).

Table 5. *Bond angles (°) for all five compounds (excluding those involving hydrogens)*

Data for (III) are from Cole *et al.* (1995).

	(I)	(II)	(III)	(IV)	(V)
C(10)—N(3)—C(11)	121.1 (2)	—	—	—	—
C(10)—N(3)—C(13)	122.4 (2)	—	—	—	—
C(11)—N(3)—C(13)	116.4 (2)	—	—	—	—
C(10)—N(4)—C(12)	—	125.3 (2)	—	125.4 (6)	—
C(10)—N(4)—C(15)	122.3 (2)	—	—	123.8 (6)	—
C(10)—N(4)—C(16)	—	123.4 (2)	—	—	—
C(10)—N(4)—C(17)	121.3 (2)	—	—	—	—
C(12)—N(4)—C(15)	—	—	—	110.6 (5)	—
C(12)—N(4)—C(16)	—	110.6 (2)	—	—	—
C(13)—N(4)—C(14)	—	—	122.6 (2)	—	—
C(13)—N(4)—C(16)	—	—	119.9 (2)	—	—
C(14)—N(4)—C(16)	—	—	117.4 (2)	—	—
C(15)—N(4)—C(17)	116.4 (2)	—	—	—	—
C(13)—N(5)—C(15)	—	—	—	—	122.3 (1)
C(13)—N(5)—C(17)	—	—	—	—	122.1 (1)
C(15)—N(5)—C(17)	—	—	—	—	115.2 (1)
N(1)—C(1)—C(3)	177.5 (2)	177.3 (4)	178.8 (2)	178.9 (9)	178.5 (2)
N(2)—C(2)—C(3)	176.7 (2)	179.2 (3)	179.0 (2)	178.8 (9)	179.5 (1)
C(1)—C(3)—C(2)	119.1 (2)	117.6 (3)	116.7 (2)	116.1 (7)	117.2 (1)
C(1)—C(3)—C(4)	120.9 (2)	120.8 (3)	121.6 (2)	121.5 (7)	121.1 (1)
C(2)—C(3)—C(4)	120.0 (2)	121.6 (3)	121.7 (2)	122.4 (7)	121.6 (1)
C(3)—C(4)—C(5)	122.0 (2)	121.0 (3)	121.2 (2)	121.6 (6)	120.3 (1)
C(3)—C(4)—C(9)	121.0 (2)	121.2 (3)	121.6 (2)	121.6 (7)	122.1 (1)
C(5)—C(4)—C(9)	117.0 (2)	117.8 (3)	117.2 (2)	116.8 (6)	117.6 (1)
C(4)—C(5)—C(6)	121.1 (6)	121.7 (3)	121.6 (2)	121.6 (7)	121.2 (1)
C(5)—C(6)—C(7)	121.0 (2)	120.8 (3)	121.2 (2)	122.1 (7)	121.6 (1)
C(6)·C(7)—C(8)	118.6 (2)	117.2 (3)	117.2 (2)	115.5 (7)	116.9 (1)
C(6)—C(7)—C(10)	121.2 (2)	124.0 (3)	121.5 (2)	124.8 (7)	122.3 (1)
C(8)—C(7)—C(10)	120.3 (2)	118.8 (3)	121.4 (2)	119.7 (6)	120.8 (1)
C(7)—C(8)—C(9)	120.5 (2)	121.6 (3)	121.7 (2)	122.6 (7)	121.9 (1)
C(4)—C(9)—C(8)	121.7 (2)	120.6 (3)	121.0 (2)	121.3 (7)	120.8 (1)
N(3)—C(10)—N(4)	120.7 (2)	—	—	—	—
N(3)—C(10)—C(7)	120.3 (2)	—	—	—	—
N(4)—C(10)—C(7)	119.1 (2)	129.9 (2)	—	130.7 (6)	—
N(4)—C(10)—C(11)	—	115.2 (3)	—	112.2 (7)	—
C(7)—C(10)—C(11)	—	114.8 (2)	117.2 (2)	117.1 (7)	115.6 (1)
C(7)—C(10)—C(12)	—	—	126.3 (2)	—	124.0 (1)
C(11)—C(10)—C(12)	—	—	116.4 (2)	—	120.3 (1)
N(3)—C(11)—C(10)	—	175.6 (3)	176.9 (2)	178.9 (9)	176.9 (1)
N(3)—C(11)—C(12)	111.2 (2)	—	—	—	—
N(4)—C(12)—C(13)	—	110.3 (3)	—	103.3 (6)	—
N(4)—C(12)—C(13')	—	—	—	102 (1)	—
C(10)—C(12)—C(13)	—	—	121.5 (2)	—	128.8 (1)
N(3)—C(13)—C(14)	110.9 (2)	—	—	—	—
N(4)—C(13)—C(12)	—	—	126.4 (2)	—	—
N(5)—C(13)—C(12)	—	—	—	—	124.0 (1)
N(5)—C(13)—C(14)	—	—	—	—	113.8 (1)
C(12)—C(13)—C(14)	—	110.7 (3)	—	99.6 (6)	122.2 (1)
C(12)—C(13')—C(14')	—	—	—	103 (2)	—
N(4)—C(14)—C(13)	—	—	—	—	176.0 (2)
N(4)—C(14)—C(15)	—	—	112.0 (4)	—	—
C(13)—C(14)—C(15)	—	109.7 (2)	—	100.8 (7)	—
C(13)—C(14)—C(17)	—	111.2 (3)	—	—	—
C(15)—C(14)—C(17)	—	111.8 (3)	—	—	—
C(13')—C(14')—C(15)	—	—	—	97 (2)	—
N(4)—C(15)—C(14)	—	—	—	102.2 (5)	—
N(4)—C(15)—C(14')	—	—	—	104 (1)	—
N(4)—C(15)—C(16)	111.3 (2)	—	—	—	—
N(5)—C(15)—C(16)	—	—	—	—	111.9 (1)
C(14)—C(15)—C(16)	—	112.6 (3)	—	—	—
N(4)—C(16)—C(15)	—	109.9 (3)	—	—	—
N(4)—C(16)—C(17)	—	—	112.1 (2)	—	—
N(4)—C(17)—C(18)	111.2 (2)	—	—	—	—
N(5)—C(17)—C(18)	—	—	—	—	112.3 (1)

C(*n'*) is the disordered atom related to C(*n*).

solvatochromism. The solvatochromism of (V) is clearly positive, contrasting with (I) and (III) and demonstrating that the ground-state structure is predominantly quinoidal.

3. Discussion

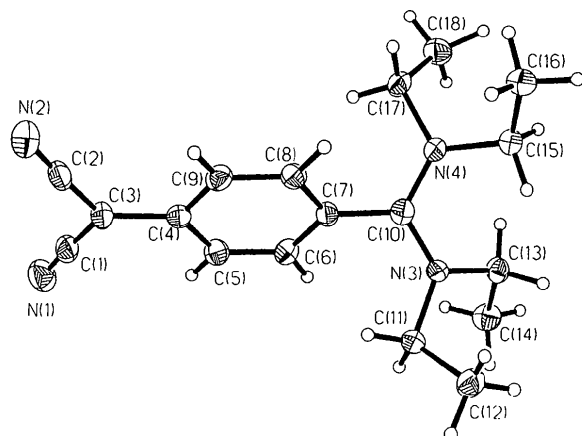The nature of time-averaged bond length alternation [BLA (Marder & Perry, 1993; Marder, Cheng, Tiemann,

Friedli, Blanchard-Desce, Perry & Skindhøj, 1994)] of all five molecules was analysed. In particular, the comparison between a TCNQ-like distribution of

Fig. 5. A 50% probability thermal ellipsoid plot of structure (IV).

Fig. 2. A 50% probability thermal ellipsoid plot of structure (I).

Fig. 6. A 50% probability thermal ellipsoid plot of structure (V).

Fig. 3. A 50% probability thermal ellipsoid plot of structure (II).
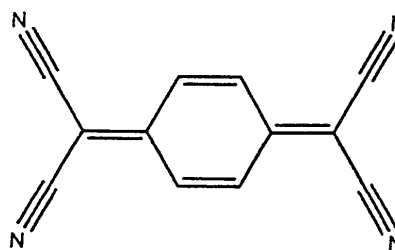
Fig. 7. Valence model representation of TCNQ.

Fig. 4. A 50% probability thermal ellipsoid plot of structure (III).
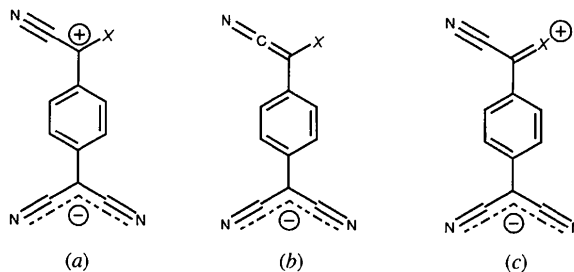
Fig. 8. Valence model resonances of monosubstituted TCNQ derivatives.

Table 6. *A comparison of quinoidal versus aromatic character for all five compounds*

	TCNQ type	Zwitterion	Bond (Å) (I)	(II)	(III)	(IV)	(V)
C3—C4	1.392	1.470	1.450 (2)	1.427 (4)	1.420 (3)	1.405 (9)	1.404 (2)
C4—C5	1.432	1.380	1.412 (3)	1.419 (4)	1.425 (3)	1.421 (8)	1.438 (2)
C5—C6	1.352	1.380	1.382 (3)	1.361 (4)	1.363 (4)	1.363 (8)	1.356 (2)
C6—C7	1.432	1.380	1.396 (3)	1.418 (4)	1.417 (3)	1.424 (8)	1.431 (2)
C7—C8	1.432	1.380	1.398 (3)	1.430 (4)	1.421 (3)	1.435 (9)	1.435 (2)
C8—C9	1.352	1.380	1.379 (3)	1.363 (4)	1.367 (3)	1.351 (8)	1.361 (2)
C4—C9	1.432	1.380	1.408 (3)	1.415 (4)	1.417 (3)	1.426 (8)	1.428 (2)
C7—C10	1.392	1.470	1.464 (2)	1.428 (4)	1.427 (3)	1.397 (9)	1.417 (2)
D^s_{TCNQ}	0.0	0.053	0.038 (1)	0.017 (2)	0.016 (1)	0.007 (3)	0.008 (1)
χ_s (%)	100	0	27 (2)	67 (4)	70 (2)	87 (6)	85 (2)

π-character (Fig. 7) and the more delocalized zwitterionic form(s) of the molecule (Fig. 8) was made.

Contributions from the valence model in Fig. 8(b) are considered very unlikely, because of the observation of clear triple-bond character in C11≡N3 as determined by analysis of the corresponding bond distance for each molecule (1.145–1.153 Å). Valence models Figs. 8(a) and 8(c), however, remain likely candidates for a zwitterionic model of the system and, with the exception of the C10—X bond, the bonding nature in these models is the same.

Thus, a ratio of the TCNQ-like bonding over that of the zwitterionic form can be determined for each bond in the common framework of the molecule. The reference bond-length values for each of the two types of bonding were obtained from the unweighted sample mean values (Allen, Brammer, Kennard, Orpen, Taylor & Watson, 1987). The unweighted rather than the weighted mean values were used in common with previous work (Taylor & Kennard, 1983, 1985, 1986) and in preference to the results from the single photographic study reported on TCNQ itself (Long, Sparks & Trueblood, 1965).

The bond-length ratios χ_s were obtained from the following analysis. First, the average bond deviation in the backbone of each structure was calculated from the ideal form of the TCNQ backbone that can be derived using published mean values (Allen *et al.*, 1987)

$$D^s_{TCNQ} = \sum_{i=1}^{N_b} |b^s_i - b^{TCNQ}_i|/N_b,$$

where b^s_i is the ith bond in structure S and b^{TCNQ}_i is the ith bond in the ideal TCNQ form. N_b is the number of bonds over which the average was derived.

A value for D^{ZWIT}_{TCNQ} can be derived by calculating the deviation of the ideal zwitterionic form from the TCNQ form. This value can be regarded as representing '0% TCNQ character', whereas a structure with a value of $D^s_{TCNQ} = 0$ can be regarded as having '100% TCNQ character'. Thus, we can define the ratio for structure S, χ_s, as

$$\chi_s = [(D^{ZWIT}_{TCNQ} - D^s_{TCNQ})/D^{ZWIT}_{TCNQ}] \times 100.$$

These calculations were deemed valid by the fact that the errors on the given experimental bond-distance values and the corresponding R factors obtained were, on average, significantly less than those used in determining the reference values (C—C bond of e.s.d. ≤ 0.010 Å and $R \leq 0.07$). Ratios χ_s are given in Table 6.

From Table 6 it can be seen that the molecules in order of increasing quinoidal nature are (I)–(V) [(IV) and (V) being equal within 3 e.s.d.'s]. The proposed rationale for this ordering is twofold: First, the presence of the C11≡N3 bond is important for retaining the extended conjugation needed to promote the quinoidal character in the molecule. Compound (I) is the only molecule in this series not to have this extra C—N group and, therein, the extent of conjugation supports only low quinoidal characteristics. Furthermore, (V) contains an extra nitrile group compared with (II), (III) and (IV), and this is sited such as to increase the conjugation further. The dramatic effect of this extra nitrile group can be seen by comparing (V) and (III), which are essentially isostructural except for this extra group and yet the quinoidal nature of (III) is much lower than for (V). The second factor affecting the quinoidal extent of the molecules is the presence of the heteroatom N vicinal to a C atom involved in conjugation.

In all five molecules, where a skeletal heteroatom N is present and vicinal to a C═C bond, the length of the C—N bond is more characteristic of a double bond than a single bond, the latter being expected from considerations of the overall bond order at the adjacent C site. This extra bonding electron density is due to donation from the amino lone pair, which reduces the formal positive charge on the adjacent C atom and in turn increases the formal positive charge on the amino nitrogen. The greater the localization of this positive charge around the N atom, the shorter the C—N bond. This counteracts the quinoidal nature of the system, which in the limit would cause the C—N bond to have no π character.

Compound (III) exhibits the shortest such C—N bond (1.316 Å), indicating a high degree of localization of the positive charge and concommitantly low quinoidal nature.

With regard to the predominantly negatively charged component of the zwitterion, the dicyanomethanide group, a perturbation of bonding characteristics also exists. The effect is spread essentially in a symmetrical manner between the two nitrile groups $C1\equiv N1$ and $C2\equiv N2$, seen by the general lengthening of these bonds compared with the corresponding $C\equiv N$ distance of $1.144\,Å$ in TCNQ; also, the consistent shortening of the $C(1)—C(3)$ and $C(2)—C(3)$ formally σ bonds in (I)-(V) compared with the corresponding distance in TCNQ $(1.427\,Å)$. A more extended, though smaller, effect is observed by noting the consistently shorter separations for C3—C4 compared with C7—C10 for each molecule.

3.1. Packing effects

All five molecules pack in primitive space groups [(III) is triclinic, space group $P\bar{1}$: Cole *et al.* (1995)] and all but (II) are centrosymmetric. The preponderance of centrosymmetry derives first from the planarity, which encourages plane-to-plane van der Waals contacts, and second from the compounds' dipolar character, which further favours anti-parallel alignment.

Compound (II) is interesting because it is non-centrosymmetric. Compound (II) adopts a head-to-tail arrangement in layers in the space group P_n; the non-centrosymmetric analogue of (IV). Powder SHG (second harmonic generation) studies of (II), measured using $1.907\,\mu m$ radiation, show a powder efficiency 13 times that of a urea standard sample, confirming the non-centrosymmetry and non-linearity simultaneously. Otherwise (II) is very similar to (IV), except for the nature of the hetero-atomic ring. Returning to the ordering in the quinoid/aromatic tendency of our series, at the molecular level we might expect (II) and (IV) to exhibit rather similar bond-length alternation. Indeed, in solution (II) and (IV) behave rather similarly in their solvatochromism (Table 1) and their calculated gas-phase dipole moments [using the *COSMIC* force field within '*NEMESIS*' (Oxford Molecular, 1994)] are also very similar (~ 8.4 and 9.4 debye, respectively). The observed marked differences in bond-length alternation are therefore presumably due to the differences in crystal packing. Molecules of (II) are arranged to give a polar crystal in which the local fields will act to promote zwitterionic character. Molecules in the crystal of (IV), by contrast, experience the reverse field of neighbouring dipoles acting to reduce the condensed phase equilibrium moments.

Molecules (III) and (V) each possess longer terminal chains (ethyl groups) linked to the common framework of this series of compounds. This reduces their ability to comply with high symmetry operations, consequent upon their non-planarity and the large number of similar low-energy conformations possible.

Table 7. *Secondary contacts in structures (III)–(IV) (only contacts $< 2.62\,Å$ are given)*

Data for (III) are from Cole *et al.* (1995).

Contact	Distance (Å)
Structure (III)	
$N(2)\cdots H(14A)$	2.56 (2)
$N(3)\cdots H(6)$	2.59 (2)
$N(1)\cdots H(14B)$	2.51 (2)
Structure (IV)	
$N(3)\cdots H(12A)$	2.542 (9)†
$N(2)\cdots H(13A)$	2.61 (1)†
Structure (V)	
$N(3)\cdots H(5)$	2.59 (2)
$N(2)\cdots H(17A)$	2.53 (2)

† The e.s.d. is smaller in this structure because the H atoms were placed at geometrically idealized positions.

Secondary interactions exist in (III) and (V) in the form of hydrogen bonds. The precision of the hydrogen positions in these structures gives confidence to the lengths of the $C\equiv N\cdots H$ contacts given in Table 7. Some marginal contacts were noted in structure (IV), but the H atoms were added at idealized positions and the disordering in this compound means that little confidence can be ascribed to the distances observed.

The distances given in Table 7 are all considerably shorter than the sum of the associated van der Waals radii [$1.2\,Å$ for H, $1.55\,Å$ for N (Bondi, 1964)]. Structures (III), (IV) and (V) all pack in layers, as seen in Fig. 9, maximizing these interactions. The third interaction given for structure (III) (between N1 and H14B) is not shown in Fig. 9(a). This acts between the layers of molecules rather than within the layers.

The intermolecular interactions noted for structures (III), (IV) and (V) are classical examples of $C\equiv N\cdots H$ hydrogen bonds. Systems with $C\equiv N\cdots X$ intermolecular contacts in the Cambridge Structural Database, CSD [(Allen, Davies, Galloy, Johnson, Kennard, Macrae, Mitchell, Mitchell, Smith & Watson, 1991), where $X = Cl$, Br or I], have been studied by Desiraju & Harlow (1989). The contacts in structures (III), (IV) and (V) could be considered to be structure determining.

Some positional disorder exists within the pyrolidyl ring in (IV). This disorder is confined to the atoms C13 and C14, which show site occupancies of 0.733 (for unprimed atoms) and 0.267 (for primed atoms), an approximate ratio of 3:1. Disorder arises from the potential for the hetero-atomic ring to invert about the vector C12—C15. Furthermore, as a result of the disorder there is a lowering of both the local accuracy and, to a lesser extent, the general accuracy of refinement, because of the limits in modelling the occupancy of the disorder. This effect, in conjunction with the poor quality of the crystals, compared with those of the other crystals in the series, is the cause of the high final R values.

4. Conclusions

The crystal structure determination of a series of dipolar TCNQ derivatives allows the indexing of molecules according to their neutral or zwitterionic character in the crystal. Molecules retaining nitrile moieties (*e.g.* —C11≡N3) as side groups on the link connecting the dicyanomethanide and amino functionalities exhibit higher quinoidal character in the tricyanoquinodimethanide ring. Moreover, the presence of extra nitrile groups in the substituted part of the molecule increases the quinoidal character further. The degree of planarity of these substituted components also seems important, as does the relative localization of the positive charge

(a)

(b)

(c)

Fig. 9. Packing of layers of structures (III)–(IV), respectively, showing secondary contacts in each case.

around the N atoms, resulting from the lone-pair donation. The crystal field effect can override these molecular constraints, providing the polarizing field required to evolve the ground-state structure towards the zwitterionic form. In two crystal structures comprising molecules of nearly identical molecular structure, but where one is non-centrosymmetric, the consequent macroscopic polarity polarizes the molecules and produces quite distinct differences in the bond-length alternation compared with its non-polar homologue. Second harmonic generation from powder samples of the non-centrosymmetric material confirms the macroscopic optical non-linearity. This study suggests that further work correlating crystal state molecular polarization with free-state or solution-state polarization could provide valuable evidence to confirm the theoretical predictions that non-linear optical susceptibilities can be optimized by tuning the local field effects.

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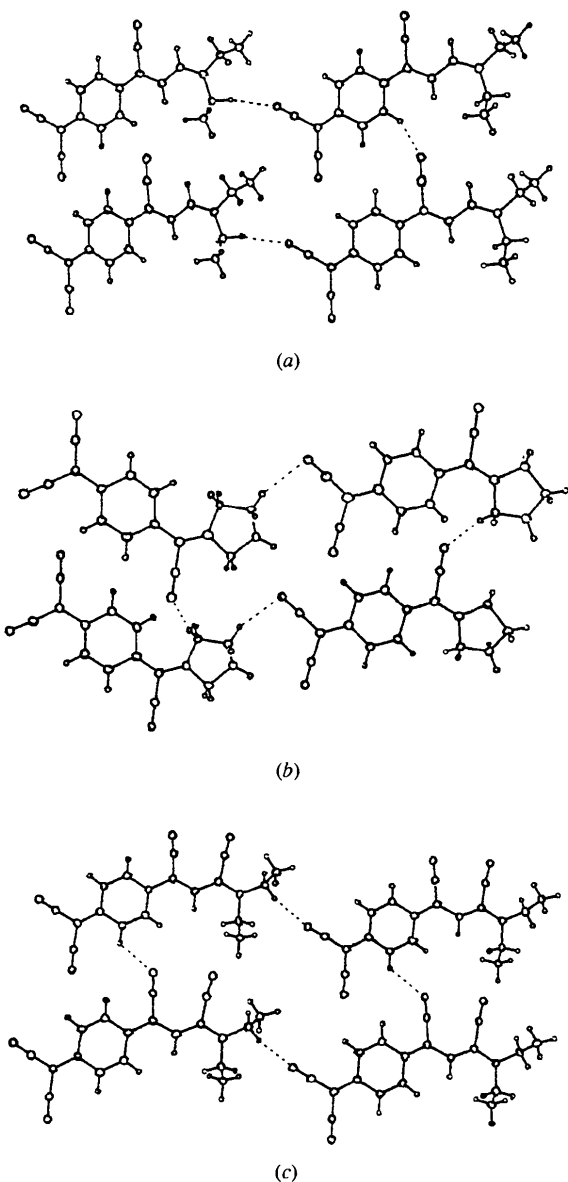
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