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Preparation, X-ray crystal structures and electronic properties of *N*,*N*′-bis(2,6-dinitrophenyl)-1,3-phenylenediamine and a complex with tetracyano-*p*-quinodimethane

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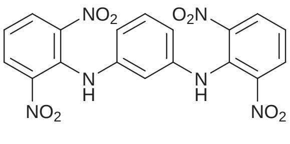
A novel dimer model for poly(*m*-aniline), two amino groups of which are effectively shielded by surrounding nitro groups, has been prepared in good yield and characterised by X-ray crystallographic, electrochemical and EPR studies. A 2 : 1 weak charge transfer complex with tetracyano-*p*-quinodimethane has been prepared and showed a moderate electrical conductivity ($\sigma_{rt} = 1.3 \times 10^{-3}$ S cm^{-1}) in the single crystalline form. The X-ray crystal structure of the complex has also been examined in connection with the electrical conductivity.

The search for high-spin organic molecules is an active research area.[1] Most of them so far synthesised have characteristic structures, in which spin sites are attached to *m*-phenylene.[1] On the other hand, many stable organic radicals contain hetero atoms.[2] In view of the above points, we have been interested in spin correlation among nitrogen radical centers connected through *m*-phenylene units.[3] In particular, the cationic and dehydrogenated forms of poly(*m*-aniline) are interesting candidates for polymer-based organic ferromagnets.[4] Furthermore, the corresponding cation radical crystals are interesting materials associated with the concept of a polaronic ferromagnet.[5] In the MO calculations of the dimer model, the ground state of the cationic diradical form is, with the configuration interaction (CI) method, predicted to be a triplet.[6]

On the other hand, in the 1970s, electrical properties of many donor–acceptor complexes containing several aromatic amine molecules[7] and several aromatic amine–iodine complexes[8] were investigated in connection with development of organic conductors and semiconductors. Some complexes showed relatively high electrical conductivity $\sigma \approx 10^0$ S cm^{-1}. Since then, the relationship between crystal structures in these complexes and their conductivity has been the subject of controversy. In this context, charge-transfer (CT) complexes containing new aromatic amine compounds may have novel conducting properties.



BDNP-PDA

We report here the synthesis, X-ray structural analysis, and electronic properties of *N*,*N*′-bis(2,6-dinitrophenyl)-1,3-phenylenediamine (BDNP-PDA) as a model dimer of poly(*m*-aniline). When BDNP-PDA is oxidised, the two radical centers are expected to be effectively shielded by the surrounding nitro groups. The conducting behaviour of the complex with tetracyanoquinodimethane (TCNQ) is also described.

Experimental

N,*N*′-Bis(2,6-dinitrophenyl)-1,3-phenylenediamine (BDNP–PDA)

To a stirred colourless, transparent solution of *m*-phenylenediamine (260 mg, 2.4 mmol) in EtOH (2.5 cm^3) under N_2 at 20 °C was added a light yellow solution of 1-chloro-2,6-dinitrobenzene[9] (1 g, 4.9 mmol) in EtOH–CH_2Cl_2 (2 : 1 v/v) mixed solvent (5 cm^3). The resultant solution rapidly turned orange whereupon 0.68 g (4.9 mmol) of K_2CO_3 was added and the solution was refluxed under N_2 for 24 h. The resultant deep-red solution was concentrated by partial evaporation of the solvent and the concentrated solution was chromatographed on silica gel using CH_2Cl_2 as eluent. The first fraction ($R_f = 0.76$) and the second fraction ($R_f = 0.46$) gave BDNP–PDA (400 mg, 38%) as a light orange powder and *N*-2,6-dinitrophenyl-1,3-phenylenediamine, DNP-PDA (400 mg, 61%) as a deep red purple powder, respectively.

BDNP-PDA. Mp 226–227 °C [from MeCN–EtOH (2 : 1 v/v)] (Calc. for $C_{18}H_{12}N_6O_8$; C, 49.09; H, 2.75; N, 19.09. Found: C, 49.27; H, 2.80; N, 19.34%); δ_H [400 MHz, $CDCl_3$–$(CD_3)_2CO$] 9.39 (2H, br s, NH), 8.30 (4H, d, *J* 8.0 Hz, H-3′ + H-5′), 7.21 (2H, t, *J* 8.0 Hz, H-4′), 7.14 (1H, t, *J* 8.1 Hz, H-5), 6.81 (1H, t, *J* 2.2 Hz, H-2), 6.72 (2H, dd, *J* 8.1 and 2.2 Hz, H-4 + H-6).

DNP-PDA. Mp 139–140 °C (Calc. for $C_{12}H_{10}N_4O_4$; C, 52.56; H, 3.68; N, 20.43. Found: C, 52.60; H, 3.63; N, 20.27%); δ_H (400 MHz, $CDCl_3$) 9.50 (1H, br s, NH), 8.22 (2H, d, *J* 8.0 Hz, H-3′ + H-5′), 7.06 (1H, t, *J* 8.0 Hz, H-4′), 6.98 (1H, t, *J* 8.0 Hz, H5), 6.45 (1H, dd, *J* 8.0 and 3.4 Hz, H-6), 6.37 (1H, dd, *J* 8.0 and 3.4 Hz, H-4), 6.30 (1H, t, *J* 3.4 Hz, H-2), 3.71 (2H, br s, NH_2).

Preparation of the TCNQ complex

To a solution of BDNP-PDA (10 mg; 0.02 mmol) in MeCN (3 cm^3) was added a solution of TCNQ (4.7 mg; 0.02 mmol) in MeCN (3 cm^3); the resulting mixture was allowed to stand 3 days at 0 °C. During this time fine red crystals suitable for the study of X-ray crystallography had grown; these were collected by vacuum filtration (9.2 mg, 40%) (Calc. for $C_{48}H_{28}N_{16}O_{16}$; C, 53.14; H, 2.60; N, 20.66. Found: C, 53.15;

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H, 2.47; N, 21.01%); ν_{max}(KBr)/cm^{-1} 3352 (N—H), 3105, 3062, 2906, 2223 (C≡N), 1597, 1539, 1523, 1485, 1341, 1277, 1257.

X-Ray structure determination

Single crystal diffraction experiments were carried out at 20 K on a Rigaku AFC7R four-circle diffractometer equipped with graphite monochromated Mo-Kα radiation using the ω–2θ scan technique to a maximum 2θ of 60.0°. A total of unique 10 884(2764) reflections were measured and 4566(1235) were considered as observed [$I \geqslant 2.0\sigma(I)$] for BDNP-PDA [$I \geqslant 3.0\sigma(I)$ for (BDNP-PDA)$_2$TCNQ, values in parentheses]. The data were corrected for Lorentz and polarisation effects. In addition, a ψ-scan empirical absorption was applied for BDNP-PDA (several reflections; minimum, maximum transmission 0.94, 1.00). The structures were solved by direct methods using MITHRIL 90[10] (for BDNP-PDA) and SHELXS 86[11] [for (BDNP-PDA)$_2$TCNQ], expanded using DIRDIF92.[12] With the exception of the C atoms of the central benzene rings in the BDNP-PDA crystal, non-hydrogen atoms were refined by full-matrix least-squares analysis with anisotropic thermal parameters. After several cycles of refinements, the position of the H atoms were calculated and fixed. The final R and R_w values were 0.083(0.054) and 0.081(0.054) for 518(188) variables for BDNP-PDA [(BDNP-PDA)$_2$TCNQ]. There was a disorder of the O(11)—N(8)—O(12) nitro group in the BDNP-PDA crystal probably due to considerable thermal fluctuation. Although we investigated a disorder model, the problem was not solved. Hence, the geometrical parameters of the nitro group are unreliable. All the calculations were performed using teXsan crystallographic software package of the Molecular Structure Corporation.[13] Crystal data and experimental details are listed in Table 1.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CDCC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CDCC for this material should quote the full literature citation and reference number 1145/102.

Physical measurements

Cyclic voltammetry was performed with a Nikko NFG-3 generator, a Nikko NPGS-301 potentiostat and a Graphtec WX2400 X-Y recorder with a three-electrode cell using Pt wire as working and counter electrodes and SCE linked to an agar salt (KCl) bridge as reference electrode in a solution of 1 mM BDNP-PDA and 0.1 M NBu$^n{}_4$BF$_4$ in PhCN (25 °C, scan rate 200 mV s^{-1}). The electrochemically generated EPR spectrum was measured under nitrogen atmosphere using an electrochemical cell, consisting of an Au helical working electrode, a Pt wire counter electrode and an Ag wire quasi-reference electrode[14] in a JEOL JES-RE-2X X-band spectrometer. Electrical conductivity with four-probe technique was measured using a Huso Electro Chemical System HESS 994 multichannel four terminal conductometer. Electrical contacts were made with gold paste.

The magnetic susceptibility of the TCNQ complex was recorded on a Quantum Design MPMS-5S SQUID susceptometer under a constant magnetic field of 1 T in the temperature range 1.8–200 K. The magnetism of the sample holder and the diamagnetism of the sample estimated from high temperature extrapolation were subtracted to yield a paramagnetic component.

Table 1 Crystal data for BDNP-PDA and (BDNP-PDA)$_2$TCNQ

	BDNP-PDA	(BDNP-PDA)$_2$TCNQ
formula	$C_{18}H_{12}N_6O_8$	$[C_{18}H_{12}N_6O_8]_2[C_{12}H_4N_4]$
M	440.33	1084.85
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$C2/m$
a/Å	12.694(2)	15.752(5)
b/Å	14.921(1)	22.295(6)
c/Å	10.0749(8)	6.946(4)
α/°	94.609(7)	
β/°	99.883(10)	105.74(4)
γ/°	92.05(1)	
V/Å^3	1871.4(4)	1172.6(5)
Z	4	2
D_c/g cm^{-3}	1.563	1.534
crystal size/mm	0.20 × 0.20 × 0.30	0.45 × 0.15 × 0.12
no. of reflections used	4566 [$I \geqslant 2.0\sigma(I)$]	1235 [$I \geqslant 3.0\sigma(I)$]
R (R_w)	0.083(0.081)	0.054(0.054)

Results and Discussion

Synthesis

BDNP-PDA was prepared by refluxing a mixture of *m*-phenylenediamine with 1-chloro-2,6-dinitroaniline[9] in ethanol, in the presence of potassium carbonate for 24 h. This coupling reaction gave a 38% yield of BDNP-PDA and the by-product was monosubstituted phenylenediamine (61%). Extension of the reaction time did not improve the yield of BDNP-PDA. It was found that recrystallisation of BDNP-PDA from MeCN–EtOH (2∶1) gives deep red crystals suitable for study by X-ray crystallography.

Crystal structure of BDNP-PDA

As shown in Fig. 1, the crystal contains two crystallographically independent molecules **1a** and **1b**, which have different molecular conformations. Furthermore, molecules **1a** and **1b** form a dimer *via* weak intermolecular hydrogen bonds (N···O ≈ 3.0 Å[15]); the two dimers are correlated by an inversion centre. Molecule **1a** adopts a *syn* conformation, while **1b**, like the unsubstituted dimer, *N*,*N*′-diphenyl-1,3-phenylenediamine,[16] adopts an *anti* conformation with respect to the orientation of the two amino groups (Fig. 2). There are intramolecular hydrogen bonds between the O and N atoms of the nitro group and the H atom of the amino group. The formation of intramolecular hydrogen bonds is also reflected in the significant ^{1}H NMR chemical shifts of N—H to low field. Turning to the torsion angles of adjacent phenyl groups out of the C—N—C planes, for **1a**, the diphenylamine moieties formed by the central phenyl and the peripheral phenyl rings take a 'Morino'-like conformation, while those for **1b** a 'skewed' one.[17]

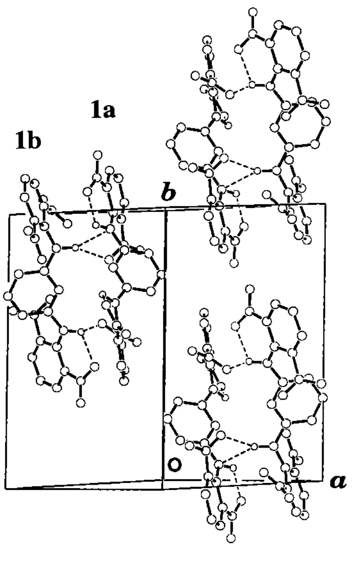

Fig. 1 Crystal structure of BDNP-PDA. Broken lines represent intra- and weak inter-molecular hydrogen bonds.

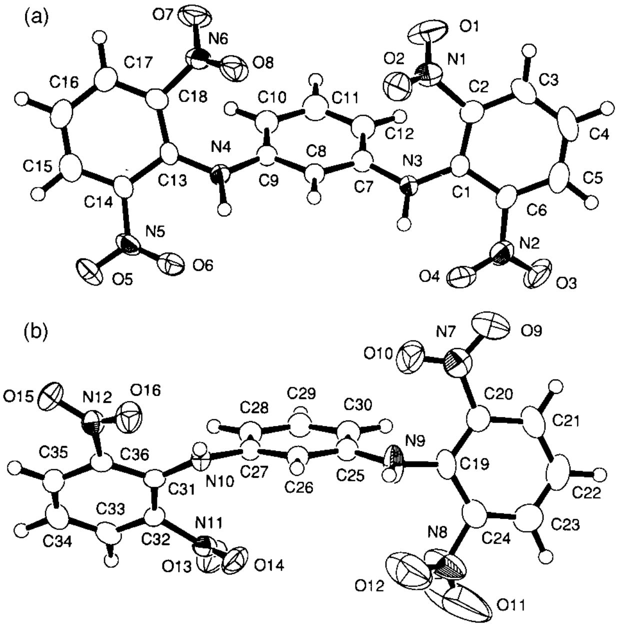

Fig. 2 Molecular structures of (a) **1a** and (b) **1b**. Selected bond lengths (Å), angles (°) and torsion angles (°): C1—N3 1.368(6), C7—N3 1.412(6), C9—N4 1.414(6), C13—N4 1.384(6), C19—N9 1.386(6), C25—N9 1.409(6), C27—N10 1.423(6), C31—N10 1.368(6), C1—N3—C7 127.4(4), C9—N4—C13 128.7(4), C19—N9—C25 125.3(4), C27—N10—C31 124.7(4), C1—N3—C7—C12 34.7(8), C2—C1—N3—C7 37.3(8), C10—C9—N4—C13 −23.1(8), C9—N4—C13—C18 −34.4(8), C19—N9—C25—C30 −1.3(8), C20—C19—N9—C25 73.7(8), C28—C27—N10—C31 34.8(7), C27—N10—C31—C32 32.4(7).

Cyclic voltammetry and electrochemical EPR

The cyclic voltammogram (CV) of BDNP-PDA in PhCN exhibited two pairs of redox waves at +1.02 V (reversible) and +1.58 V (quasi-reversible). Owing to the electron-withdrawing effect of the nitro groups, the donor ability decreases by *ca.* 0.2 V compared with the corresponding unsubstituted dimer ($E_1 = +0.79$ V and $E_2 = +1.20$ V, measured under the same conditions).[18]

Before the electrochemical EPR experiments, we checked that the MeCN solution of BDNP-PDA (10^{-3} M) containing $NBu^n_4BF_4$ showed no EPR signal. After the observation of a weak broad singlet ($g = 2.0031$) at +1.1 V, the spectrum began to reveal the influence of exchange coupling (J) between the two radical centers above +2.0 V [see Fig. 3(a)]. These results are consistent with the CV described above. Several chemical oxidations of BDNP-PDA were carried out. When treated with MCPBA in a THF or MeCN solution, no reaction occurred. On the other hand, oxidation with AgO in MeCN gave a dark brown solution and the EPR measurement showed a weak broad singlet ($g = 2.003$) similar to the EPR signal at +1.1 V. The observed signal above +2.0 V showed a rather resolved hyperfine structure as compared with the signal at *ca.* +1.0 V. However, we failed to detect the electron–nuclear double resonance (ENDOR) of this radical species. This hyperfine structure (hfs) is probably due to two N atoms [a(2N)] and two H atoms [$a(2H_{NH})$] of the two amino groups. In the corresponding monoradicals (*i.e.*, diarylaminiums), the coupling constants varied gradually according to the difference of the substituted groups, with a(N) 7.41–9.17 and $a(H_{NH})$ 9.15–11.14 [$a(H_{NH}) > a(N)$].[19] This seven-line EPR signal is equally separated by *ca.* 5 G. When $|J| \gg a(2N)$, $a(2H_{NH})$, the spectrum becomes a septet with half the splitting of the monoaminium radical.[20] The observed EPR spectrum could be simulated as shown in Fig. 3(b). From this simulation, the values of $a(2N)/2$, $a(2H_{NH})/2$ and $a(2H_{para})/2$ are estimated to be 5.6, 4.6 and 0.9 G, respectively. Therefore, the observed radical species can be interpreted as a magnetically coupled diradical.

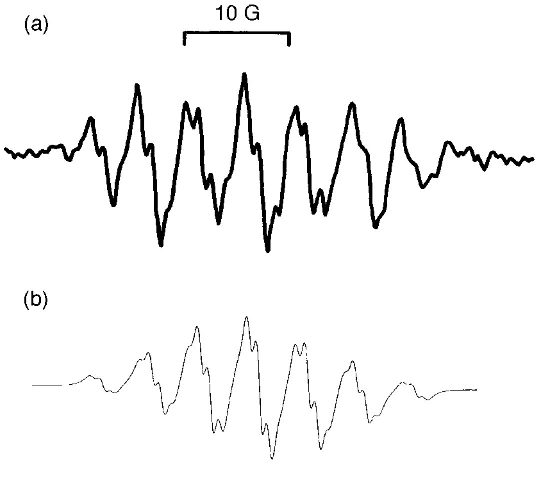

Fig. 3 (a) EPR spectrum of electrochemically generated BDNP-PDA radical species in MeCN solution at −35 °C and (b) its computer simulation

Crystal structures of a complex with TCNQ

TCNQ complex formation was examined by mixing equimolar amounts of BDNP-PDA and TCNQ in MeCN. BDNP-PDA provided fine red crystals whose composition was BDNP-PDA : TCNQ = 2 : 1.[21] Since the unit cell contains two complex units, while the space group $C2/m$ has eight positions, some symmetry elements must be common to the molecules and the crystal. The *a–c* mirror plane passing through the C1 and C4 atoms of the BDNP-PDA and the C12 and C13 atoms of the TCNQ is one of such symmetry elements. Furthermore, the twofold axis (1/2, y, 1/2) penetrates through the TCNQ molecule along the molecular plane. As a result, the BDNP-PDA and the TCNQ molecules belong to C_s and C_{2h} point groups, respectively. The molecular structure of BDNP-PDA

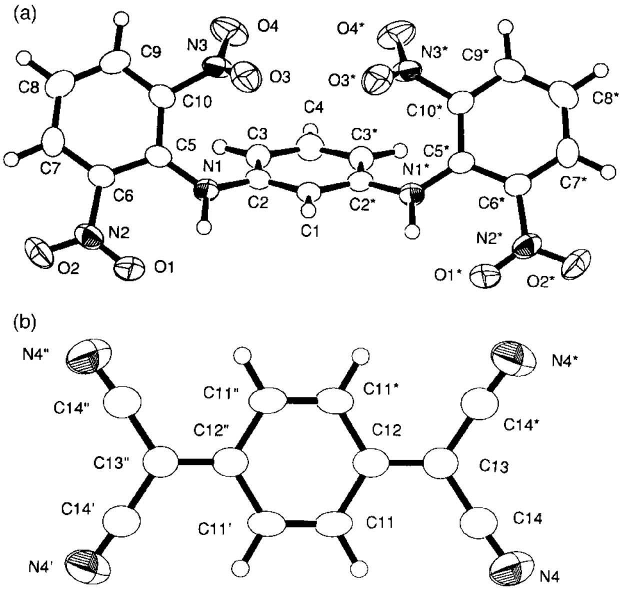

Fig. 4 Molecular structures of (a) BDNP-PDA and (b) TCNQ; symmetrically related atoms are starred. Selected bond lengths (Å), angles (°) and torsion angles (°): (a) BDNP-PDA; C2—N1 1.411(6), C5—N1 1.375(6), C1—N1—C7 125.8(4), C3—C2—N1—C5 −38.9(7), C2—N1—C5—C10 −29.9(7) [symmetry code: (*) x, $1-y$, z]. (b) TCNQ; C11—C12 1.449(6), C12—C13 1.377(10), C13—14 1.425(7), C11—C11′ 1.339(10), C14—N4 1.135(7), C11—C12—C11* 118.4(6), C14—C13—C14* 115.6(7), C13—C14—N4 176.5(7) [symmetry codes: (*) x, $1-y$, z; (′) $1-x$, y, $1-z$; (″) $1-x$, $1-y$, $1-z$].

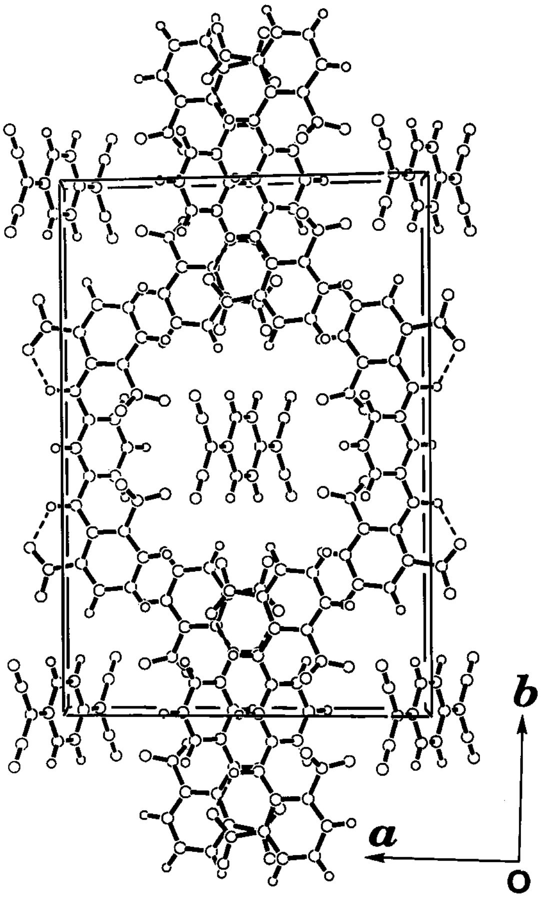

Fig. 5 Crystal structure of the TCNQ complex viewed along the *c*-axis

in the complex adopts a *syn* conformation like **1a**, as shown in Fig. 4(a): the peripheral π molecular plane consisting of unit **1** is coplanar with that of **2**; the dihedral angle between the central phenyl ring and the optimal plane is *ca.* 60°. The bond lengths and angles for the TCNQ molecule do not correspond to those for the neutral[22] and anionic[23] forms, as shown in Fig. 4(b). This suggests, to some extent, that charge transfer occurs in the complex.

As can be seen from the unit cell view (Fig. 5), the complex crystallises in segregated stacks of BDNP-PDA and TCNQ molecules along the *c* axis. The BDNP-PDA molecules form a dimer directing each central phenyl ring inwards, and the dimers are arranged in a parallel cross through π-stacking between the central phenyl rings as shown in Fig. 6: the interplanar distance in the dimer is 3.27 Å, the interdimer distance is 3.41 Å and the distance between the central phenyl rings is 3.31 Å. On the other hand, the TCNQ molecules form slipped stacks along the *c*-axis direction leading to a uniform interplanar distance of 3.44 Å. The intermolecular contact in the TCNQ column is due to overlapping $(CN)_2C\cdots C(CN)_2$ groups (Fig. 7) rather than the usual ring-over-ring[24] or ring-over-bond[23] types, often found in the segregated stack TCNQ complexes, so that the overlap integral between TCNQ molecules is estimated to be small.

Conducting and magnetic properties

The TCNQ complex showed a moderate conductivity of 1.3×10^{-3} S cm^{-1} for a single crystal at room temperature. The conductivity of the complex diminished on decreasing the temperature indicating a semiconductive property: the activation energy E_a is estimated to be 0.51 eV. A shift of the nitrile-stretching vibration (2223 cm^{-1}) in the complex was observed in the IR spectrum, as compared with that of neutral TCNQ (2232 cm^{-1}), suggesting that this complex is in a weak charge-transfer state (degree of charge transfer = 0.08).[25] These observations were also supported by the EPR measurement of the polycrystalline sample. The observed spectrum showed a very weak five-line hyperfine structure (A_{iso} = 5.96 G) due to two equivalent N atoms. This hfs constant is comparable with that obtained from the electrochemical EPR measurement. The *g*-value of 2.0024 also indicates that the generated radical spin is distributed over not only N atoms but also the other atoms. Furthermore, we measured the magnetic susceptibility of polycrystalline sample of the TCNQ complex on a SQUID susceptometer in the temperature range 1.8–200 K at constant field of 1 T. The temperature dependence of the magnetic susceptibility showed the TCNQ complex has weak paramagnetic behaviour. When $(BDNP\text{-}PDA)_2TCNQ$ is considered as a molecular unit, the effective magnetic moment μ_{eff} was estimated to be 0.1 μ_B. The μ_{eff} value is far below the theoretical value of 1.73 μ_B for the doublet monoradical species. It follows from what has been observed that the weak charge transfer leads to a moderate conductivity through the segregated columnar structure as described in the foregoing section. If complexes having a large overlapping TCNQ columnar structure can be constructed, we can expect high conductivity.

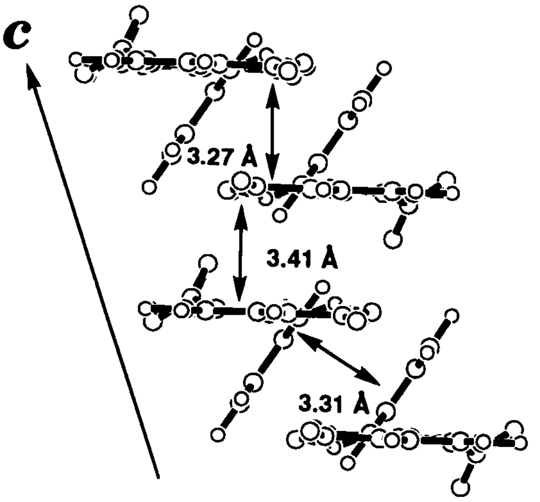

Fig. 6 Overlapping mode of BDNP-PDA molecules in the complex. The view direction is parallel to the molecular plane.

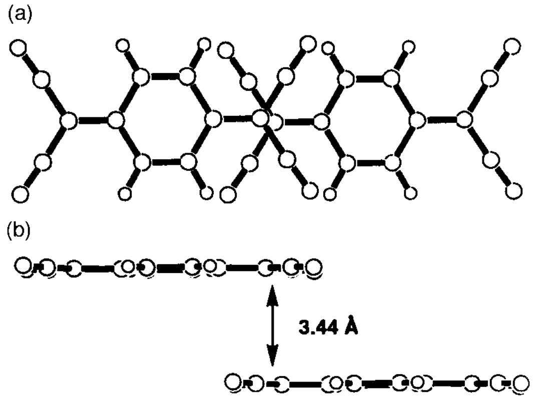

Fig. 7 Overlapping mode of TCNQ molecules in the complex. The view direction is (a) perpendicular and (b) parallel to the molecular plane.

Conclusions

In summary, we have carried out the preparation, X-ray crystallographical, electrochemical and EPR studies of a new poly(*m*-aniline) dimer, BDNP-PDA. As shown by the X-ray structural analysis of non-oxidised BDNP-PDA, the radical crystal of BDNP-PDA may afford new magnetic properties due to the 3-D hydrogen-bonded network. Owing to the presence of nitro groups, the donating ability of BDNP-PDA decreased to some extent as compared with that of the unsubstituted dimer. A TCNQ complex was formed with BDNP-PDA and showed a moderate conductivity indicating weak charge transfer between BDNP-PDA and TCNQ molecules. The crystal structure of the complex was of the segregated columnar type. In the donor column, BDNP-PDA molecules formed dimers which are arranged in a parallel cross. Such a crystal structure plays an important role in the conductivity of the weak CT complex. These results suggest that oligo(*m*-aniline) derivatives with stronger donor ability may give new CT complexes having electrically and magnetically intriguing properties.

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