Preparative, Structural, and Electrical Studies of the 1 : 1 and 2 : 3 Tetracyanoquinodimethane Salts of 4,4′-Bithiopyranylidene (BTP)

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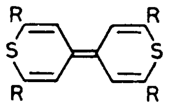
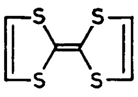
The preparation, single crystal growth, and single crystal conductivity of the 1 : 1 and 2 : 3 7,7,8,8-tetracyanoquinodimethane (TCNQ) salts of 4,4′-bithiopyranylidene are reported. The crystal structure of the 2 : 3 salt, the first structure of a 2 : 3 TCNQ salt from a neutral planar closed-shell donor, has been determined by *X*-ray diffraction at room temperature. $(BTP)_2(TCNQ)_3$ crystallizes in the triclinic space group $P\bar{1}$, a = 8.351(5), b = 17.445(4), c = 8.020(4), α = 97.35(3), β = 103.10(4), γ = 88.15(4), U = 1 128.6(8) Å^3, Z = 1, $D_{\text{calc.}}$ = 1.467 g cm^{-3}, $D_{\text{obs.}}$ = 1.46(1) g cm^{-3}. The structure was solved by Patterson and Fourier methods to a final R of 0.046 for 1 490 unique reflections with $F_0 > 3\sigma(F_0)$. $(BTP)_2(TCNQ)_3$ has a mixed stack crystal structure which alternates a pair of BTP cation-radicals and three TCNQ molecular species. There are two crystallographically distinct types of TCNQ: a centrosymmetric (c-TCNQ) and a non-centrosymmetric (n-TCNQ) form in the ratio 1 : 2. The bond lengths of centrosymmetric TCNQ closely resemble those of neutral TCNQ while those of non-centrosymmetric TCNQ are similar to those of TCNQ^{-1}, a situation found in other 2 : 3 TCNQ salts. The bridging double bond of the BTP cation-radical is quite long, 1.429(6) Å, *ca.* 0.05 Å longer than that of a neutral BTP derivative. As found in the 1 : 1 heterafulvalene–TCNQ segregated stack conductors, there are short contact distances between the sulphur atoms on the BTP cation and the cyano nitrogens on TCNQ. However, in the present structure this mode of interaction is qualitatively different in that each BTP sulphur atoms contacts (' plugs into ') two cyano groups, while in the heterafulvalene–TCNQ salts, each chalcogen contacts only one cyano nitrogen. While BTP is iso-π-electronic to tetrathiafulvalene (TTF), which interacts with TCNQ to give a metallic 1 : 1 salt, BTP–TCNQ is a semiconductor with a room temperature conductivity (σ) of 30 ohm^{-1} cm^{-1}. The temperature dependence of σ for BTP–TCNQ between room temperature and 80 K is well described by $\sigma(T) = AT^{-\alpha}\exp(-\Delta/T)$, an expression representing the product of an activated charge carrier concentration with a system specific activation energy, Δ and a temperature dependent mobility, with α 2.64 and Δ 1 480 K (0.13 eV). As expected from its mixed stack crystal structure, $(BTP)_2(TCNQ)_3$ is a semiconductor with a room temperature single crystal conductivity of 0.10, ohm^{-1} cm^{-1} and an activation energy of 0.16 and 0.18 eV measured from conductivity and thermoelectric power respectively.

THE molecular properties of the simple derivatives of 4,4′-bithiopyranylidene (BTP) (1a) ring system are analogous to those of the extensively studied π-donor tetrathiafulvalene (TTF) (2) in that both are 14π electron systems of D_{2h} symmetry, and both are highly polarizable in both neutral and cation-radical states.[1,2] While BTP (1a) fits numerous molecular ' design ' criteria for a metallic state in organic conductors,[3,4] the π-acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) (3) interacts with (1a and b) to give a series of ion-radical salts which exhibit a variety of stoicheiometries, topographical arrays, and electronic transport mechanisms not found in the analogous metallic TTF derivatives.[1,2] The role of specific non-bonded interactions in the formation of the uniform segregated stack structure of TTF–TCNQ and the quantitative relationships between crystal packing and its metallic state have been previously discussed.[5]

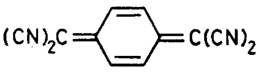


(1)



(2)

a; R = H
b; R = CH_3
c; R = $CO_2C_2H_5$
d; R = C_6H_5



(3)

This paper describes the preparation, crystal growth, and single crystal conductivity of the 1 : 1 and 2 : 3 TCNQ salts of BTP (1a). The crystal structure of the latter salt, the first structure of a 2 : 3 TCNQ salt of a neutral planar closed shell donor, is reported and several novel features are detailed. The crystal structure of the 1 : 1 TCNQ salt of TMBTP (1b), the first complete structure of a 1 : 1 ' mixed-stack ' TCNQ salt of a 14π-electron organochalcogen donor, has been previously reported.[6] The present conductivity and thermoelectric power studies of the 1 : 1 and 2 : 3 TCNQ salts of BTP demonstrate that both of these systems are semiconductors.

EXPERIMENTAL

BTP and TCNQ were purified by gradient sublimation as described earlier.[2,7] Acetonitrile (Burdick and Jackson) was distilled from anhydrous potassium carbonate under nitrogen before use. Dichloromethane (Eastman spectrophotometric grade), 1,2-dichloroethane (Eastman spectrophotometric grade), and chlorobenzene (Baker reagent) were distilled from calcium hydride under nitrogen before use. All crystal growth experiments were initiated in a glove box under nitrogen, and all glassware was baked dry before use. Elemental analyses were performed by

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Schwarzkopf Microanalytical Laboratory, Woodside, New York. The Debye–Scherrer patterns were obtained on a Phillips diffractometer (Cu-K_α radiation) by Mr. G. Fekete.

Four probe conductivity measurements were done at both 13 Hz and direct current. Typical currents used were 10^{-7} A. A Princeton Applied Research model 124A lock-in amplifier was used for the 13 Hz experiments. A Keithley model 225 current source and model 180 nanovoltmeter or model 616 electrometer were used for the direct current measurements. Temperature control was accomplished in a Janis Research Company ' supervaritemp ' Dewar and an Air Products closed cycle refrigerator. The single crystals used for the conductivity studies were typically <1 mm in length.

Preparation and Crystal Growth of BTP–TCNQ.—A solution of TCNQ (27.4 mg, 0.134 mmol) in acetonitrile (5 ml) was added at room temperature to a solution of BTP (28.3 mg, 0.147 mmol) in a mixture of acetonitrile (10 ml) and benzene (2 ml) prepared without heating. After 1 h in a refrigerator, a purple solid was isolated by filtration and vacuum dried to give product (45 mg, 85%), m.p. 199—201° (decomp.). The *X*-ray powder pattern exhibits the following *d* spacings greater than *d* 2.5 Å: 15, 9.7s (s = strong), 9.5, 7.8, 7.2s, 6.3s, 5.2, 5.0, 4.80, 4.60, 4.35, 3.95, 3.58, 3.40, 3.30s, 3.15s, 2.85, and 2.52 (Found: C, 66.75; H, 3.2; N, 13.95; S, 15.8. Calc. for $C_{22}H_{12}N_4S_2$: C, 66.65; H, 3.05; N, 14.15; S, 16.15%).

Single crystals of BTP–TCNQ were grown in several ways. To an acetonitrile (12 ml) solution of BTP (3.8 mg, 0.02 mmol) in a three-neck flask (25 ml) was added dropwise *via* a pipette an acetonitrile (5.25 ml) solution of TCNQ (3.5 mg, 0.017 mmol). The homogeneous solution was then removed from the glove box and was slowly evaporated using dry nitrogen. Within 1 h crystals had formed, and they were isolated by suction filtration to give purple crystals (2.7 mg). Single crystals of BTP–TCNQ may also be grown in chlorinated solvents by diffusion at room temperature. BTP (4.5 mg, 2.3 mmol) in dichloromethane (17 ml) and TCNQ (4.5 mg, 2.2 mmol) in dichloromethane (7 ml) were attached to a U-tube apparatus which was filled with dichloromethane to a total volume of 44 ml. After four days at room temperature purple crystals of BTP–TCNQ were isolated from the BTP flask and crystals of the 2 : 3 phase were isolated from the TCNQ flask. Occasionally, in such diffusion experiments, crystals which do not appear to be either of these phases are isolated.[8]

Preparation and Crystal Growth of $(BTP)_2(TCNQ)_3$.—This salt is prepared as a black polycrystalline powder as follows. A saturated dichloromethane solution of BTP (28 mg, 0.146 mmol) prepared without heating was added at room temperature to a dichloromethane solution of TCNQ (68 mg, 0.334 mmol). The black solid which precipitated immediately was filtered and vacuum dried to give the product (43 mg, 59%), m.p. 220—225° (decomp.). The *X*-ray powder pattern exhibits the following *d* spacings: 7.4, 6.8, 6.3s, 4.50, 4.25, 4.00, 3.82, 3.70, 3.45, 3.32, 3.15s, 3.05, 2.95, 2.82, 2.75, and 2.53. This pattern is consistent with that calculated for this phase from the crystal data (Found: C, 67.65; H, 2.65; N, 16.56; S, 12.6. Calc. for $C_{56}H_{28}N_{12}S_4$: C, 67.45; H, 2.85; N, 16.85; S, 12.85%).

Single crystals were grown in a U-tube apparatus. A flask (5 ml) containing BTP (2.2 mg, 0.012 mmol) dissolved in chlorobenzene and one (10 ml) containing TCNQ (6.9 mg, 0.034 mmol) were attached to a U-tube which was immersed in a constant temperature bath at 55°. Additional chlorobenzene to a total volume of 45 ml was added *via* a syringe through a stopcock. Nucleation occurred with 1 h, and black needles up to 1 mm in length were isolated after 12 h. Crystals of this quality were also grown from 1,2-dichloroethane at 45 °C.

Collection and Reduction of X-Ray Data for $(BTP)_2$-$(TCNQ)_3$.—A summary of the experimental details is given in Table 1. The crystal chosen for data collection had the approximate dimensions 0.10 mm between the (010) and $(0\bar{1}0)$ faces, 0.25 mm between the $(10\bar{1})$ and $(\bar{1}01)$ faces, and 0.30 mm between the $(1\bar{1}1)$ and $(\bar{1}1\bar{1})$ faces. The reflection width at half height from ω scans was 0.3°.

TABLE 1

Crystal data [a] and experimental conditions

a/Å	8.351(5)	α/°	97.35(3)
b/Å	17.445(4)	β/°	103.10(4)
c/Å	8.020(4)	γ/°	88.15(4)
U/Å^3	1 128.6(8)	D_c/g cm^{-3}	1.467
M/Dalton	997.2	D_m/g cm^{-3}	1.46(1)
Space group	$P\bar{1}$	Z	1
μ(Mo-K_α radiation)/cm^{-1}	2.66		

Scan rate/° min^{-1}	4–20 (depending on intensity)
Scan range/°	$2\theta(\text{Mo-}K_{\alpha_1}) - 0.9$ to $2\theta(\text{Mo-}K_{\alpha_2}) + 0.9$
Range of data/°	$0 < 2\theta(\text{Mo-}K_\alpha) < 45$
Total independent reflections	2 932
Reflections with $F_o > 3\sigma(F_o)$	1 490

$$I = S(C - rB)\,^{c} \qquad |F_o| = I^{\frac{1}{2}}(Lp)^{-\frac{1}{2}}$$

$$\sigma(F_o) = \frac{[S^2(C + r^2B) + (0.05I)^2]^{\frac{1}{2}}}{2|F_o|Lp}$$

S = scan rate, C = total integrated peak count, r = ratio of scan time to background time, B = total background time, L_p = Lorentz polarization factor.

$w = [\sigma(F_o)]^{-2}$

Function minimized $\Sigma w(|F_o| - |F_c|)^2$

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \qquad 0.046$$

$$R_w = \frac{\Sigma w||F_o| - |F_c||^2}{w|F_o|^2} \qquad 0.048$$

$$\text{Goodness of fit } \left(\frac{\Sigma w||F_o| - |F_c||^2}{N_{obs.} - N_{var.}}\right)^{\frac{1}{2}} \qquad 1.04$$

[a] From a least squares fit to the setting angles of 19 centred reflections. Crystallographic data were collected by Molecular Structure Corp., College Station, Texas 77840. [b] By flotation in CCl_4–cyclohexane mixtures. [c] Programs for the CDC Cyber 174 computer used in this work: FAMEB, Goldberg's modification of R. B. K. Dewar's Wilson plot and scaling routine, FORDAP, a local modification of Zalkin's Fourier program; LSTSQ, a local version of the Busing–Martin–Levy structure factor–least squares program (ORFLS); ORFFE, the Busing–Martin–Levy geometry and error function program; and ORTEP II, Johnson's thermal ellipsoid plotting program.

Solution and Refinement of the Structure.—Sharpened and ordinary Patterson maps were calculated using the reduced data set of 1 490 unique reflections. The relative simplicity of the maps indicated that the BTP and TCNQ molecules must be nearly coplanar. Several attempts to phase the data by direct methods produced *E* maps with indistinct sheets of electron density, so the initial models were based on the Patterson maps. Since at the time of collection, we believed the data crystal to be of 1 : 1 stoicheiometry, a trial model containing one BTP and one TCNQ was used in a structure factor calculation assuming $P\bar{1}$ symmetry. This resulted in an *R* value of 0.58.

A Fourier map phased from this model gave a clear representation of the electron density in the unit cell, including that of another TCNQ molecule. This second TCNQ is required to be centrosymmetric in the $P\bar{1}$ space group; neither the BTP nor the first TCNQ have any crystallographic constraints on their symmetries. Least squares refinement of the model with all non-hydrogen atoms included reduced R to 0.28. A Fourier map calculated at this stage showed all the atoms clearly, and a difference Fourier showed only very small peaks, but further attempts at least squares refinement produced no real improvement in the R value.

A refinement using $P1$ symmetry also failed to produce any improvement. The false minimum in the least squares technique yielded some extremely short derived carbon–carbon distances for the BTP central double bond and the ring double bond of the centrosymmetric TCNQ (c-TCNQ). The parameters of the carbon atoms in these bonds were fixed so that the bond distances were held at 1.39 Å during the following cycles of refinement. These parameters were not varied again until the R value had dropped to 0.15. In subsequent calculations all positional parameters were refined, and anisotropic temperature factors were used to describe the thermal motions. A difference Fourier map calculated from input parameters at R 0.08 yielded the positions of the hydrogen atoms. These were included, with isotropic thermal parameters, in the final cycles of refinement. Because of limitations on computer memory, a maximum of 120 parameters could be refined in each cycle. The contents of each of the parameter groupings were changed after each complete refinement; no correlation coefficients greater than 0.5 were observed. Scattering factors for the hydrogen atoms were those of Stewart *et al.*;[9] the values of Cromer and Waber[10] were used for all other atoms. The factors for sulphur were corrected for anomalous dispersion.[11]

The refinement was considered complete when no positional parameter for a non-hydrogen atom shifted more than 0.01 times its estimated error and no thermal parameter shifted more than 0.15 times its error. A few of the hydrogen atom parameters shifted up to 0.45 of their errors in the final cycles. Some of the temperature factors for hydrogen atoms are quite unlikely ($B < 2$ Å^2), indicating that these atoms have not been located as accurately as the estimated errors would seem to indicate. The final R value was 0.046 and the final R_w was 0.048. The error in an observation of unit weight for the last cycle, in which the 109 positional parameters of the non-hydrogen atoms were refined, was 1.03. The weights w employed in the refinement were defined as $[\sigma^2(F_0)]^{-2}$. A final difference Fourier map showed two peaks of 0.3 eÅ^{-3} in the vicinity of the sulphur atoms; all other densities were at least 30% smaller than those observed for the hydrogen atoms. The final positional parameters are listed in Table 2. A listing of the final observed and calculated structure factor amplitudes, the thermal parameters, and best planes calculations are available as Supplementary Publication No. SUP 22826 (18 pp.).*

RESULTS AND DISCUSSION

Preparation and Crystal Growth.—When prepared as described in the Experimental section, BTP–TCNQ and $(BTP)_2(TCNQ)_3$ are homogeneous phases uncontaminated with other phases in the BTP system.[1,2] Under certain growth conditions, particularly room temperature diffusion in chlorinated solvents, both BTP–TCNQ and $(BTP)_2(TCNQ)_3$ simultaneously precipitate. The powder diffraction pattern of such materials reveals the presence of both phases. The simultaneous precipitation of more than one phase is not uncommon in organic ion-radical salts and powder diffraction is invaluable as a 'fingerprint' technique where the usual i.r. spectra are uninformative. When TCNQ is mixed with TMBTP (1b) in a 3 : 2 molar ratio, a mixture of the 1 : 1 and 1 : 2 phases is revealed by powder diffraction,[12] and studies of the N-methylphenazinium (NMP)–TCNQ system, which are often complicated not only by simultaneous precipitation of more than one phase but also by precipitation of 'anomalous' phases due to the reactivity

TABLE 2

Fractional co-ordinates ($\times 10^4$)[a,b]

	x	y	z
S(1)	2 053(2)	3 804(1)	2 324(2)
S(2)	5 628(2)	7 928(1)	5 396(2)
C(B1)	3 498(7)	4 265(3)	1 651(7)
C(B2)	1 720(6)	4 471(3)	3 972(7)
C(B3)	4 103(6)	4 972(3)	2 285(7)
C(B4)	2 430(6)	5 172(3)	4 417(7)
C(B5)	3 570(6)	5 469(3)	3 609(6)
C(B6)	4 193(6)	6 236(3)	4 148(6)
C(B7)	5 472(6)	6 531(3)	3 469(7)
C(B8)	3 625(7)	6 734(3)	5 396(7)
C(B9)	6 158(7)	7 241(3)	3 912(7)
C(B10)	4 116(6)	7 477(3)	6 008(7)
C(C1)	2 043(7)	1 917(3)	294(7)
C(C2)	888(7)	1 540(3)	989(7)
C(C3)	219(7)	2 033(3)	2 241(7)
C(C4)	1 166(6)	305(3)	−738(6)
C(C5)	472(6)	781(3)	498(7)
C(C6)	−726(6)	443(3)	1 217(6)
N(C1)	2 995(6)	2 228(3)	−201(6)
N(C2)	−351(6)	2 447(2)	3 189(6)
C(N1)	5 541(6)	9 723(3)	7 414(6)
C(N2)	6 695(6)	10 089(3)	6 707(6)
C(N3)	7 438(7)	9 615(3)	5 523(7)
C(N4)	6 410(6)	11 352(3)	8 424(7)
C(N5)	7 127(6)	10 872(3)	7 184(6)
C(N6)	8 327(6)	11 221(3)	6 492(6)
C(N7)	6 875(6)	12 099(3)	8 912(6)
C(N8)	8 085(6)	12 444(3)	8 240(6)
C(N9)	8 758(6)	11 964(3)	6 996(7)
C(N(10)	7 935(6)	13 701(3)	10 023(6)
C(N(11)	8 566(6)	13 224(3)	8 753(6)
C(N(12)	9 785(6)	13 557(3)	8 085(7)
N(N1)	4 627(6)	9 405(3)	7 934(6)
N(N2)	8 004(6)	9 211(3)	4 552(6)
N(N3)	7 418(6)	14 062(3)	11 076(6)
N(N4)	10 761(6)	13 833(3)	7 526(6)
H(B1)	3 890(53)	3 930(24)	845(56)
H(B2)	1 003(43)	4 280(19)	4 641(46)
H(B3)	5 028(50)	5 168(22)	1 850(51)
H(B4)	2 164(48)	5 508(22)	5 448(51)
H(B7)	5 795(49)	6 223(22)	2 630(50)
H(B8)	2 860(56)	6 620(27)	5 792(59)
H(B9)	6 987(58)	7 536(27)	3 386(61)
H(B10)	3 766(51)	7 839(24)	6 955(54)
H(C4)	2 031(45)	522(21)	−1 213(47)
H(C6)	−1 288(42)	756(19)	1 970(45)
H(N4)	5 615(48)	11 065(22)	8 923(50)
H(N6)	8 727(50)	10 837(23)	5 581(54)
H(N7)	6 526(49)	12 355(22)	9 738(52)
H(N9)	9 564(50)	12 101(23)	6 528(53)

[a] Atoms are labelled as indicated in Figure 4. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter.

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index Issue.

of the NMP cation,[13] are facilitated by routine monitoring *via* powder diffraction.

We conclude that $(BTP)_2(TCNQ)_3$ is a more stable phase than BTP–TCNQ because it is preferentially formed in the presence of excess BTP under equilibrating conditions, it has a higher decomposition point, higher density, and tighter crystal packing. The single crystals of BTP–TCNQ we have obtained to date have not been suitable for *X*-ray crystallography because one of the dimensions is invariably <0.01 mm. From the density of BTP–TCNQ (1.37 g ml^{-1}), a volume for the ion-radical pair of 475 Å^3 may be calculated. Since the sum of the molecular volumes of neutral BTP and TCNQ is 480 Å^3, the ratio of the sum of the volumes of neutral BTP and TCNQ to the volume after charge transfer is a modest 1.01. The analogous ratio for the metallic TTF–TCNQ [5] is 1.10 and for $(BTP)_2(TCNQ)_3$ it is 1.08. Since the conductivity of BTP–TCNQ is several orders of magnitude higher than the representative 1 : 1 mixed stack ion-radical salts TMBTP–TCNQ,[2,6] methyldihydrophenazine (NMPH)–TCNQ,[14] and tetra-n-propyl-TTF (TPTTF)–TCNQ,[15] a simple mixed stack structure for BTP–TCNQ is unlikely.

Electrical Characterisation.—The polycrystalline conductivities of BTP–TCNQ and $(BTP)_2(TCNQ)_3$ are in the ranges 1—4 ohm^{-1} cm^{-1} and 0.05—0.10 ohm^{-1} cm^{-1}, respectively, both lower than the metallic TTF–TCNQ which has a polycrystalline conductivity >10 ohm^{-1} cm^{-1}.

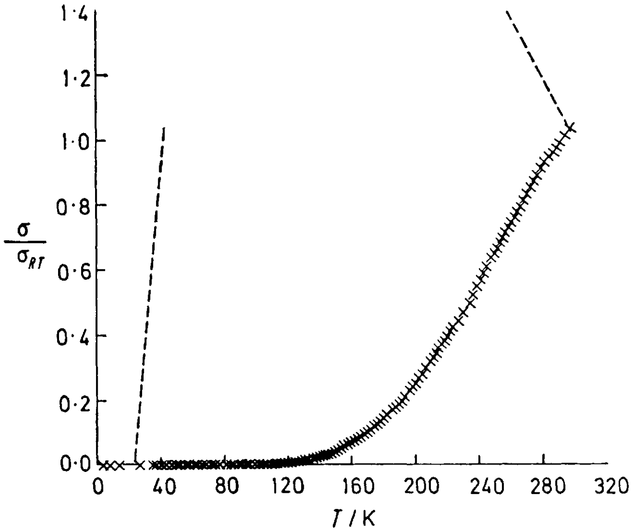


FIGURE 1 Plot of normalized direct current conductivity (σ/σ_{RT}) for BTP–TCNQ (×, experimental points), (σ_{RT} 30 ohm^{-1} cm^{-1}) and TTF–TCNQ (– – – –) (σ_{RT} 600—1 000 ohm^{-1} cm^{-1}) *versus* absolute temperature *T*. Low temperature TTF–TCNQ data from ref. 16

The normalized four probe direct current conductivity (σ) *versus* temperature (*T*) curve of Figure 1 is typical of the BTP–TCNQ crystals measured. Figure 1 also exhibits data for TTF–TCNQ over comparable temperature ranges.[16] The data for BTP–TCNQ are similar to those of many other ion-radical salts which exhibit semiconducting behaviour at low temperatures and often a broad weak maximum in their σ *versus* *T* curves at higher temperature. For such systems, the temperature dependent conductivity has been discussed [17] in terms of the product of an activated charge carrier concentration with a system-specific activation energy, $n(T) \propto \exp(-\Delta/T)$, and a temperature dependent mobility, $\mu(T) \propto T^{-\alpha}$ for $T > 65$ K with a constant $(2 < \alpha < 4.5)$

$$\sigma(T) = n(T)e\mu(T) = AT^{-\alpha}\exp(-\Delta/T) \qquad (1)$$

and μ(295 K) *ca.* 5 cm^2 V^{-1} s^{-1}, *i.e.* equation (1) obtains where the prefactor *A* is a constant.

The data in Figure 1 were fitted by least squares to (1) for $T > 80$ K. The prefactor *A* was fixed by utilizing the normalized σ, $\sigma_n(T) \equiv \sigma(T)/\sigma$ (295 K) and requiring the calculated $\sigma(T)$ to equal 1.0 at 295 K. The fit to the data of Figure 1 gave Δ 1 480 K (0.13 eV) and α 2.64; a plot of (1) with these parameters is indistinguishable from the experimental data. Data on other crystals of BTP–TCNQ gave values of Δ and α in good agreement with those derived from the data in Figure 1.

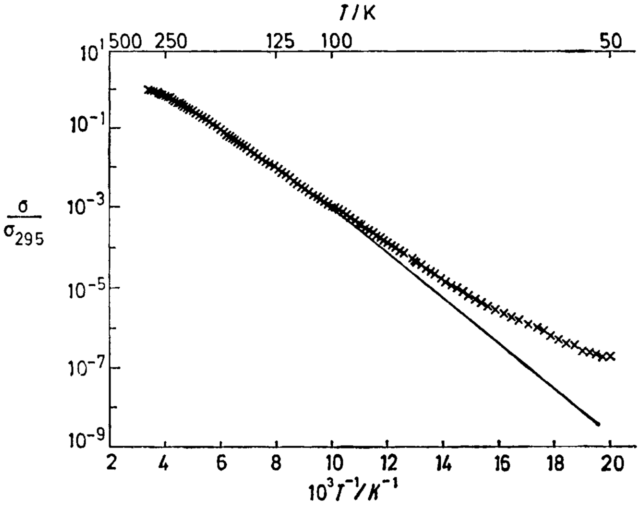


FIGURE 2 Experimental data of Figure 1 (×) plotted on a logarithmic scale as (σ/σ_{295}) *versus* the reciprical of the absolute temperature for BTP–TCNQ. The solid line is calculated using equation (1) with Δ 1 480 K and α 2.64

Figure 2 is a plot of the normalized conductivity (σ/σ_{295}) *versus* T^{-1} for the BTP–TCNQ data shown in Figure 1. The solid line is an excellent fit to the data using Δ 1 480 K (0.13 eV) and α 2.64 for $T < 80$ K. The low temperature Δ for TTF–TCNQ is 450 K (0.04 eV).[16] Below 80°, σ is higher than predicted by (1). This suggests the presence of a number of localized states ('impurities') in the gap. For $T < 80$ K, carriers excited from localized states to the extended band states would outnumber the intrinsic carrier population. At lower temperatures ($T < 50$ K), carrier hopping among localized states in the gap may be the dominant charge transport mechanism.

It is widely accepted [3,4] that high molecular polarizability is a necessary but not sufficient molecular criterion for the achievement of a metallic state in organic ion-radical salts. While BTP is more polarizable than

TTF in both neutral and cation-radical states,[2] the interactions which might arise from this enhanced molecular polarizability are not sufficient to dominate the weaker intermolecular forces which are largely responsible for phase formation and crystal packing in this class of materials,[5] and a metallic state is not achieved in BTP–TCNQ.

Subsequent to our initial reports [1,2] of the room temperature conductivity of BTP–TCNQ, on the basis of its room temperature conductivity and the electrochemical reduction potential of the cation-radical of BTP, BTP–TCNQ has been assigned membership in the class of conducting 1 : 1 TCNQ salts found to exhibit ' incomplete charge-transfer ', as opposed to the insulating 1 : 1 TCNQ salts where charge-transfer is thought to be complete.[18] While the importance of incomplete charge-transfer is well established in the TTF–TCNQ class of organic conductors by, *inter alia*, diffuse *X*-ray scattering studies, and by the report of an insulating state in the tetrafluoro-TCNQ salt of hexamethylenetetraselenafulvalene,[18] which certainly has a greater degree of charge-transfer than its isostructural TCNQ analogue, the critical distinction between conducting and insulating 1 : 1 TCNQ salts in those cases where the cation is not an alkali-metal must involve crystal structure.[5,13] The 1 : 1 conducting TCNQ salts always form a uniform segregated stack structure, while the 1 : 1 insulating salts of planar closed-shell nitrogen heteroaromatic monocations [5] and of quaternary ammonium cations, such as morpholinium,[19] tend to form either isolated dimers of $TCNQ^-$ or dimer stacks with large alternation in TCNQ spacings. It should further be noted that the formation of such dimers may be related simply to solution equilibria and not strongly dependent on the carrier population of a conduction band. In sum, crystallographic considerations may be sufficient to explain the absence of high conductivity in many 1 : 1 insulating ion-radical salts. The roles of complete charge-transfer and strong Coulomb interactions are more readily discussed for the 1 : 1 salts with uniform segregated stack structures.

The conductivity of $(BTP)_2(TCNQ)_3$ was measured by a two probe technique along the needle axis of the crystal, which corresponds to the (0 1 0) or stack direction of the crystal structure, for temperatures between 300 and 140 K. Representative data are plotted in Figure 3 as $\log_{10}\sigma$ *versus* T^{-1}, and the linearity of the plot reveals simple semiconducting behaviour over this temperature range as expected for an ion-radical salt with a mixed stack structure. The activation energy in $(BTP)_2(TCNQ)_3$ is 1 750—1 920 K or *ca.* 0.16 eV and the room temperature conductivity for the data in Figure 2 is 0.12 $\text{ohm}^{-1}\,\text{cm}^{-1}$. We note that the room temperature conductivity of this 2 : 3 mixed stack salt is two to three orders of magnitude higher than that reported for the 1 : 1 mixed stack TCNQ salts of TMBTP (1b),[2,6] NMPH,[14] and TPTTF.[1]

Also shown in Figure 3 is the negative of the thermoelectric power *S versus* T^{-1}. The negative values for *S* demonstrate that electrons are the principal charge carriers. The observed linear behaviour suggests a simplified semiconductor analysis for $S(T)$ [20] [equation (2)] where k_B is Boltzmann's constant, e is the electronic

$$S = -|k_B|/e(B/T + \varepsilon) \qquad (2)$$

charge, and B and ε are constants related to detailed band structure]. For an intrinsic three dimensional semiconductor, $B = \Delta(b - 1)/(b + 1)$, where b is the ratio of the electron to the hole mobilities ($b = \mu_e/\mu_h$). The $S(T)$ data in Figure **3** are consistent with this semiconductor model, although the B value obtained (0.18 eV) is slightly larger than Δ obtained from conductivity analysis.

Description of the Crystal Structure of $(BTP)_2(TCNQ)_3$.—The numbering system employed for the three independent molecules in the asymmetric unit is indicated in Figure 4. C in parentheses for an atom identifier refers to centrosymmetric TCNQ (c-TCNQ), N to non-centrosymmetric TCNQ (n-TCNQ), and B to BTP. Selected interatomic distances and angles are listed in Table 3.

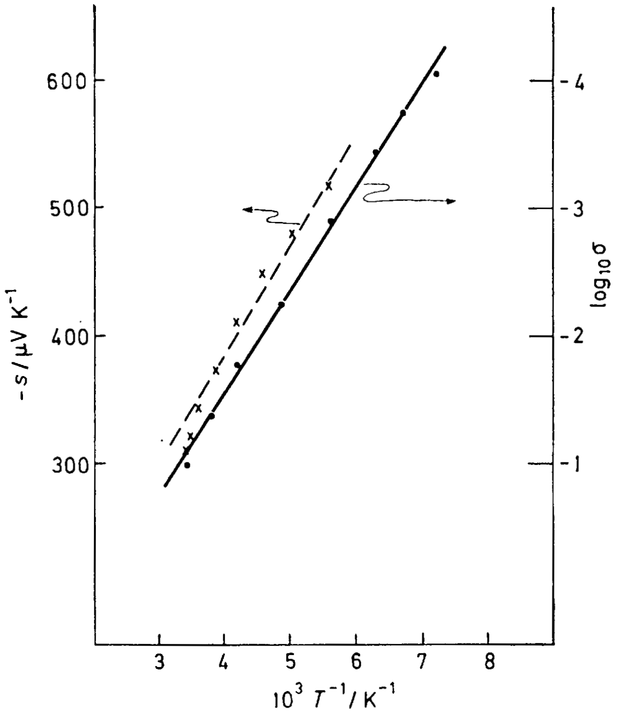


FIGURE 3 Negative of the thermoelectric power (S) (×) and logarithm of the direct current conductivity ($\log_{10}\sigma$) *versus* reciprocal of the absolute temperature for $(BTP)_2(TCNQ)_3$

The BTP moiety in this system is formally the cation-radical BTP^+. The bridging carbon–carbon bond, C(B5)–C(B6), is quite long for a double bond, 1.429(6) Å, and this can be at least partially attributed to the loss of an electron to TCNQ. Two compounds which contain the uncharged BTP species, 2,2′,6,6′-tetrakisethoxycarbonyl-4,4′-bithiopyranylidene (TLBTP) [21] (1c) and the 2,2′,6,6′-tetraphenyl derivative (1d), exhibit bridging bonds of 1.405(9) [22a] and 1.389(–) Å,[22b] respectively. Heptafulvalene, which is iso-π-electronic with neutral

BTP, has a corresponding bond distance of 1.373(5) Å.[23] In the charge transfer salt of 2,2′,6,6′-tetramethyl-4,4′-bithiopyranylidene with TCNQ, the bridging bond distance is 1.435(3) Å,[6] and in the biphenylide anion, which is iso-π-electronic with BTP⁺, it is 1.435(6) Å.[24] Neither of the latter values differs significantly from the value found for BTP⁺.

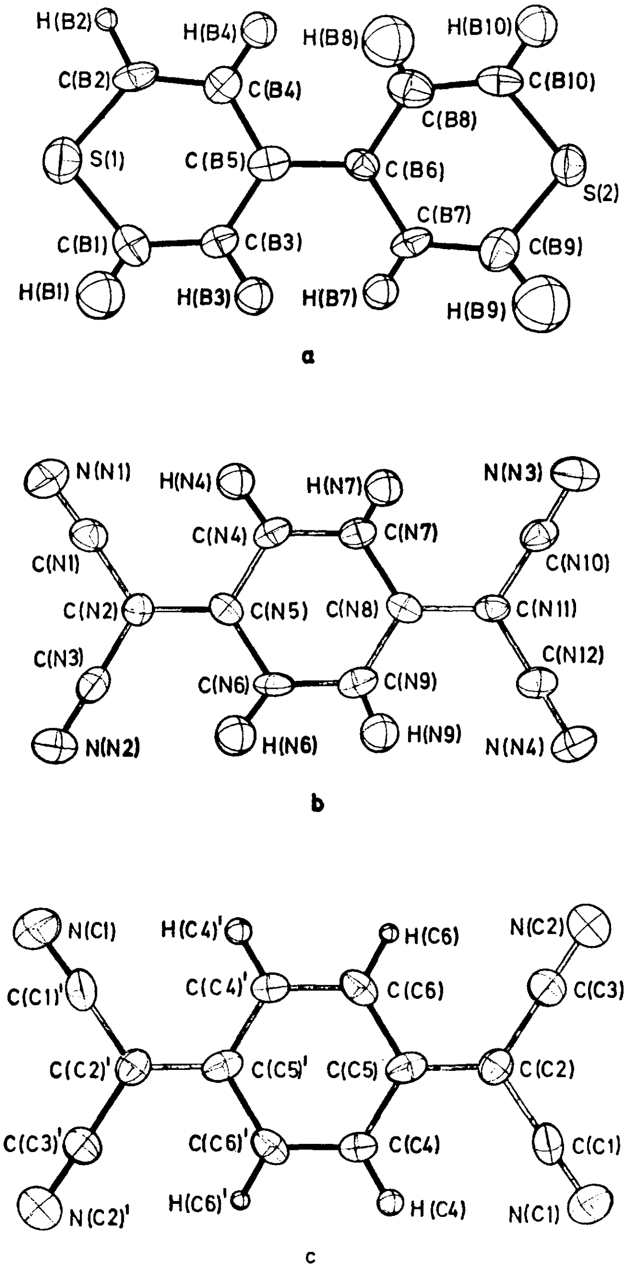


FIGURE 4 The labelling scheme employed for the three molecules. Primes refer to atoms related by a centre of symmetry. Ellipsoids are drawn at the 50% probability level

A comparison of the other bond distances of BTP⁺ with corresponding bonds in TCBTP[21] shows that in BTP⁺ the double bonds are longer and the single bonds are shorter.[22] This is consistent with a general delocalization of molecular orbitals resulting from the charge transfer. A similar delocalization occurs also in the formation of TCNQ⁻ from TCNQ.

Although the individual six-membered rings are nearly planar, the BTP⁺ molecule as a whole is not. The largest deviation from the least-squares plane for either ring is 0.042 Å for C(B5). The two rings are twisted by 5° with respect to each other around the S(1)–S(2) axis. Even if this twist were not present, the cation would lack ideal D_{2h} symmetry; there are several significant differences between bond lengths which should be identical in a D_{2h} molecule. This is explained at least in part by the different environments of the two rings, since the ring containing S(2) exhibits several short contacts with

TABLE 3

Interatomic distances (Å) and angles (°) [a]

BTP

S(1)–C(B1)	1.692(6)	S(2)–C(B9)	1.700(6)
S(1)–C(B1)	1.712(5)	S(2)–C(B10)	1.702(5)
C(B1)–H(B1)	0.92(5)	C(B9)–H(B9)	1.06(6)
C(B1)–C(B3)	1.341(6)	C(B9)–C(B7)	1.351(6)
C(B2)–H(B2)	0.98(4)	C(B10)–H(B10)	1.01(5)
C(B2)–C(B4)	1.346(7)	C(B10)–C(B8)	1.367(7)
C(B3)–H(B3)	1.00(5)	C(B7)–H(B7)	0.89(4)
C(B3)–C(B5)	1.425(7)	C(B7)–C(B6)	1.440(7)
C(B4)–H(B4)	1.01(4)	C(B8)–H(B8)	0.82(6)
C(B4)–C(B5)	1.411(7)	C(B8)–C(B6)	1.396(7)
C(B5)–C(B6)	1.429(6)		
C(B1)–S(1)–C(B2)	100.5(3)	C(B9)–S(2)–C(B10)	101.9(3)
S(1)–C(B1)–C(B3)	126.3(4)	S(2)–C(B9)–C(B7)	124.3(4)
S(1)–C(B2)–C(B4)	125.1(4)	S(2)–C(B10)–C(B8)	123.9(4)
C(B1)–C(B3)–C(B5)	124.7(5)	C(B9)–C(B7)–C(B6)	126.4(5)
C(B2)–C(B4)–C(B5)	125.5(5)	C(B10)–C(B8)–C(B6)	127.2(5)
C(B3)–C(B5)–C(B4)	117.7(5)	C(B7)–C(B6)–C(B8)	116.2(5)
C(B3)–C(B5)–C(B6)	121.8(4)	C(B7)–C(B6)–C(B5)	122.0(4)
C(B4)–C(B5)–C(B6)	120.5(4)	C(B8)–C(B6)–C(B5)	121.8(4)

Non-centrosymmetric TCNQ

N(N1)–C(N1)	1.138(6)	N(N3)–C(N10)	1.144(6)
N(N2)–C(N3)	1.155(6)	N(N4)–C(N12)	1.159(6)
C(N1)–C(N2)	1.427(7)	C(N10)–C(N11)	1.418(7)
C(N3)–C(N2)	1.415(7)	C(N12)–C(N11)	1.424(7)
C(N2)–C(N5)	1.406(6)	C(N11)–C(N8)	1.413(6)
C(N5)–C(N4)	1.439(7)	C(N8)–C(N7)	1.429(7)
C(N5)–C(N6)	1.436(7)	C(N8)–C(N9)	1.423(7)
C(N4)–H(N4)	1.02(5)	C(N7)–H(N7)	0.85(5)
C(N6)–H(N6)	1.03(5)	C(N9)–H(N9)	0.89(5)
C(N4)–C(N7)	1.356(6)	C(N6)–C(N9)	1.343(6)
N(N1)–C(N1)–C(N2)	177.2(5)	N(N3)–C(N10)–C(N11)	177.4(6)
N(N2)–C(N3)–C(N2)	177.8(6)	N(N4)–C(N12)–C(N11)	179.1(5)
C(N1)–C(N2)–C(N3)	116.4(4)	C(N10)–C(N11)–C(N12)	116.4(4)
C(N1)–C(N2)–C(N5)	122.6(5)	C(N10)–C(N11)–C(N8)	122.1(5)
C(N3)–C(N2)–C(N5)	120.9(5)	C(N12)–C(N11)–C(N8)	121.4(5)
C(N2)–C(N5)–C(N4)	121.2(5)	C(N11)–C(N8)–C(N7)	122.1(5)
C(N2)–C(N5)–C(N6)	121.6(5)	C(N11)–C(N8)–C(N9)	121.6(5)
C(N4)–C(N5)–C(N6)	117.2(4)	C(N7)–C(N8)–C(N9)	116.3(4)
C(N5)–C(N4)–C(N7)	120.6(5)	C(N8)–C(N7)–C(N4)	122.2(5)
C(N5)–C(N6)–C(N9)	120.8(5)	C(N8)–C(N9)–C(N6)	122.8(5)

Centrosymmetric TCNQ

N(C1)–C(C1)	1.145(6)	N(C2)–C(C3)	1.152(6)
C(C1)–C(C2)	1.432(7)	C(C3)–C(C2)	1.436(7)
C(C2)–C(C5)	1.365(6)	C(C4)–C(C6)	1.351(6)
C(C5)–C(C4)	1.424(7)	C(C5)–C(C6)	1.437(7)
C(C4)–H(C4)	0.99(5)	C(C6)–H(C6)	0.95(4)
N(C1)–C(C1)–C(C2)	177.5(5)	N(C2)–C(C3)–C(C2)	177.0(6)
C(C1)–C(C2)–C(C3)	113.8(4)	C(C4)–C(C5)–C(C6)	118.0(4)
C(C1)–C(C2)–C(C5)	122.6(5)	C(C3)–C(C2)–C(C5)	123.6(6)
C(C2)–C(C5)–C(C4)	122.2(5)	C(C2)–C(C5)–C(C6)	119.8(5)
C(C5)–C(C4)–C(C6)	121.2(5)	C(C5)–C(C6)–C(C4)	120.8(5)

[a] See footnotes *a* and *b* of Table 2; primed atoms are related to the listed ones by the inversion centre at the origin. Values are not corrected for thermal motion.

n-TCNQ which are somewhat longer for the ring containing S(1).

The charges on the BTP^+ cations must be balanced by corresponding negative charges on the TCNQ molecules. The required negative charges might be equally distributed over three TCNQ molecules, or a situation with two $TCNQ^-$ anions and one neutral $TCNQ^0$ might develop. The latter situation holds for many TCNQ salts of 2 : 3 stoicheiometry.[25,26] A wide range of TCNQ salts have been structurally characterized, and there are consistent differences between the bond distances of $TCNQ^0$ and $TCNQ^-$.[27] On the basis of such differences it is widely accepted that in $Cs_2(TCNQ)_3$,[25] the centrosymmetric TCNQ is neutral while the non-centrosymmetric TCNQ acts as the anion. Independent evidence for the presence of $TCNQ^0$ in $Cs_2(TCNQ)_3$ was obtained in u.v. vacuum photoemission experiments.[28] In the present case, there is an indication that n-TCNQ is $TCNQ^-$ and c-TCNQ is $TCNQ^0$. Generally the greatest bond distance difference between $TCNQ^0$ and $TCNQ^-$ is found for the exocyclic carbon–carbon double bonds, which are 0.04—0.05 Å longer in the anionic species.[27] In n-TCNQ, C(N2)–C(N5) is 1.410(6) Å and C(N8)–C(N11) is 1.413(6) Å, while the corresponding bond in c-TCNQ, C(C2)–C(C5), is 1.365(6) Å.

The c-TCNQ is nearly planar, with the greatest deviation from the least squares plane being 0.024 Å for C(C3); the n-TCNQ is considerably less planar with eight atoms deviating >0.04 Å from the plane. In n-TCNQ the $C(CN)_2$ groups and the quinonoid ring are individually planar, with the two $C(CN)_2$ planes bent 3° out of the quinonoid plane toward the adjacent c-TCNQ in the stack. The stacking of the triad of n-TCNQ, c-TCNQ, n-TCNQ in the present structure is remarkably similar to that found in $Cs_2(TCNQ)_3$.[25]

The molecules in $(BTP)_2(TCNQ)_3$ form indeterminate sheets parallel to the $(10\bar{1})$ plane. Figure 5 depicts a portion of such a sheet and its orientation with respect to the unit cell axes. There are short intermolecular contacts between molecules stacked along the $[1\bar{1}1]$ direction (upper right to lower left in Figure 5) and between the roughly coplanar molecules which form chains along the $[23\bar{2}]$ direction (left to right in Figure 5). Most of the interatomic distances between atoms in adjacent sheets are relatively long, the shortest of these being C(N6)–N(N2) $(2 - x, 2 - y, 1 - z)$ at 3.392(7) Å; all other such distances are >3.4 Å.

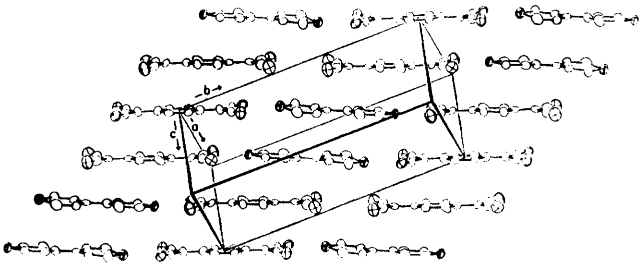
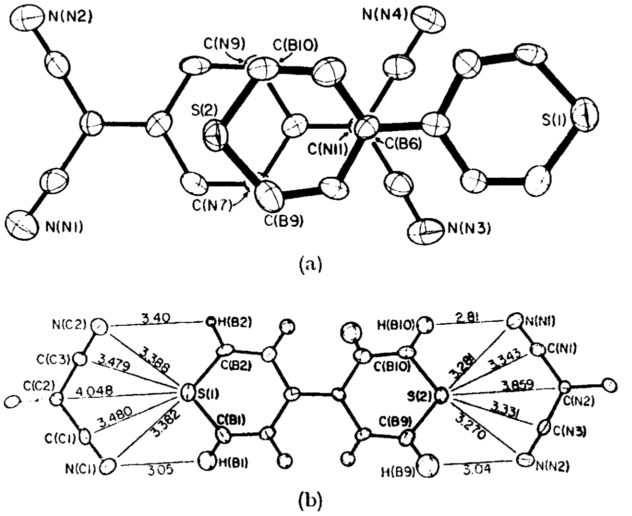


FIGURE 5 The orientation of one of the molecular sheets with respect to the unit cell axes. The view is perpendicular to the chain axis $[23\bar{2}]$, 8° above the mean molecular plane. Ellipsoids are drawn at the 50% probability level

The shortest interplanar distances occur between BTP^+ and n-TCNQ at $1 - x, 2 - y, 1 - z$: C(B6)–C(N11) 3.099(7) Å, C(B10)–C(N9) 3.216(7) Å, and C(B9)–C(N7) 3.278(7) Å. Figure 6(a) shows the overlap of these two molecules, viewed normal to the mean molecular plane. Although the shortest interatomic distances between molecules in the 'stack' are observed for the BTP–n-TCNQ pair, the average distance of the atoms of BTP to the least squares plane of n-TCNQ is 3.37 Å while the corresponding average is only 3.23 for atoms of c-TCNQ to the n-TCNQ plane. The latter stacking distance for TCNQ compares well with the 3.22 Å value reported for $Cs_2(TCNQ)_3$ [23] and the 3.25 Å value reported for $(morpholinium)_2(TCNQ)_3$.[28a] The average distance of the atoms of one BTP^+ to the least squares plane of the other is 3.44 Å. The analogous distance in neutral TCBTP is 3.39 Å but in that case the molecules are strictly planar and staggered by nearly 90°.



(a)

(b)

FIGURE 6 (a) Overlap of the BTP^+ with the non-centrosymmetric TCNQ; view is perpendicular to the mean molecular plane. Ellipsoids are drawn at the 40% level. (b) Intermolecular contacts of BTP^+ within a chain; view is perpendicular to the mean BTP^+ plane. Ellipsoids are drawn at the 30% level

As indicated in Figure 6(b), there are also several short contacts along the chains c-TCNQ, BTP, n-TCNQ, BTP, c-TCNQ, the shortest of which again occur between BTP^+ and n-TCNQ. In effect, some of these contacts are shorter than those previously mentioned along the stack; even though the distances are comparable, the sulphur atom, with a van der Waals radius 0.1—0.2 Å larger than that of carbon, is involved in these interactions. The shorter contacts of BTP^+ with n-TCNQ as compared to c-TCNQ indicates that the c-TCNQ is less involved in the charge-transfer process. As Figure 6(b) shows BTP^+ conforms quite well to the TCNQ geometry. The chains found in this compound may well be a result of the BTP 'plugging into' the TCNQ, yielding a linear array of molecules.

Figure 6(b) further reveals that the BTP sulphur atoms each interact with *two* nitrogen atoms on a TCNQ molecule. This mode of interaction is qualitatively different from that observed in the heterofulvalene–TCNQ salts,[29,30] where each chalcogen interacts with only *one* nitrogen on a TCNQ molecule. The distances between S(2) and the nitrogen N(N1) and N(N2) of n-TCNQ given in Figure 6(b) (3.281 and 3.270 Å, respectively) are comparable with those observed in TTF–TCNQ (3.20 and 3.25 Å), while the distance between S(1) and the nitrogens of c-TCNQ [N(C1) and N(C2)] are longer (3.382 and 3.388 Å, respectively), implying at least a weaker electrostatic interaction between BTP^+ and c-TCNQ than between BTP^+ and n-TCNQ.

Conclusions.—While the present study revealed that the behaviour of BTP with TCNQ is more complex in terms of stoicheiometries, crystal structure, and the electronic transport properties than its iso-π-electronic counterpart TTF, the observation of short sulphur-nitrogen contacts in $(BTP)_2(TCNQ)_3$ in a qualitatively new manner compared with TTF–TCNQ and its derivatives suggests a novel, perhaps general, crystal-chemical role for the chalcogen atom in these ion-radical salts.

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