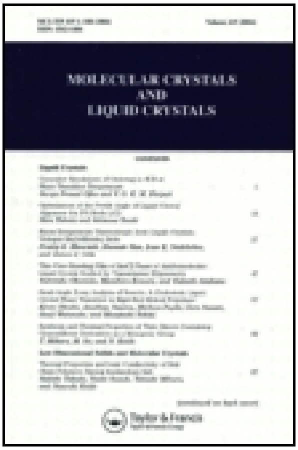

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Kinetic Models for the Formation of "Unconventional" TCNQ Ion-Radical Salts of 1 : 1 Stoichiometry

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Kinetic Models for the Formation of "Unconventional" TCNQ Ion-Radical Salts of 1 : 1 Stoichiometry

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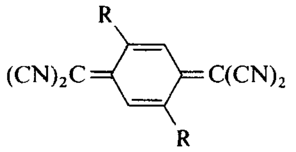
While there are many examples of salts of 7,7,8,8-tetracyanoquinodimethan (TCNQ) which form segregated stack crystal structures, in TCNQ salts of 1 : 1 stoichiometry, the only cations which always give stacked structures are the alkali metals. The TCNQ salts formed by reaction with tetrathiafulvalene (TTF) i.e., TTF-TCNQ-TCNQ, a quasi-one-dimensional metal with a uniform segregated stack crystal structure, is termed "unconventional" because, before its discovery, reactions of neutral closed-shell donor with a neutral closed-shell acceptor would have been expected to give an alternating cation–anion stacking arrangement. Prior to the discovery of (TTF-TCNQ), the best organic conductor was the 1 : 1 TCNQ salt of the N-methyl-phenazinium (NMP) cation which was found to have a uniform segregated stack crystal structure. This 1 : 1 salt is unusual because at least twenty-nine other 1 : 1 TCNQ salts of planar closed-shell nitrogen heterocyclic monocations are insulators with crystal structures that do not exhibit the "infinite chains" of the NMP-TCNQ structure in the three reported cases. The perspective adopted is that the twenty-nine insulating salts cited above constitute "normal" behavior for this subclass of 1 : 1 TCNQ salts and that an explanation for the formation of NMP-TCNQ would be desirable.

The formation of phases such as TTF-TCNQ, NMP-TCNQ, and all other 1 : 1 segregated stack structures in TCNQ salts may be accounted for by kinetic models involving van der Waals interactions, Mulliken donor–acceptor interactions, specific interatomic contacts, hydrogen bonding and molecular aggregation. The limitations of several of the models will be discussed. For example, the addition of bulky alkyl groups to the TTF ring system brings about a change in crystal structure from uniform segregated stacks to a conventional alternating cation–anion stacking arrangement. Additionally the difference in morphology of single crystal growth in supersaturated acetonitrile *vs.* the vapor phase for TTF-TCNQ is accounted for in terms of competing mechanisms for *b*- and *a*-axis growth.

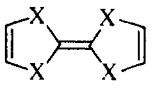
The implications of the model for formation of NMP-TCNQ, which invokes donor–acceptor interactions between several donor "impurities" and the acceptor NMP^+, for the low temperature heat capacity and magnetic susceptibility are discussed. The conductivity of the insulator *N*-ethylphenazinium-TCNQ is increased by more than 10^9 by the selective addition of phenazine and TCNQ in solution via formation of a new phase with a uniform segregated stack structure.

INTRODUCTION AND MOTIVATION

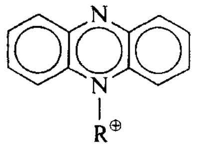
The π-acceptor 7,7,8,8-tetracyanoquinodimethan (**1a**, TCNQ) forms stable ion-radical salts having various stoichiometries with diverse types of cations which are of considerable interest for their novel electrical and magnetic properties.[1,2,3] While many of these salts have crystal structures which exhibit chains of anion-radicals of TCNQ, such segregated stack structures are *not* common in TCNQ salts of 1:1 stoichiometry *unless* the cation is an alkali metal. The considerable current interest in organic ion-radical salts was stimulated by the observation of metallic properties in the 1:1 TCNQ salts obtained by reaction of TCNQ with the π-donor tetrathiafulvalene (**2a**, TTF), i.e., TTF-TCNQ.[4,5] This salt exhibits[6] the uniform segregated stack crystal structure necessary for a metallic state,[7] and *not* the alternating cation–anion stacking arrangement found in previously reported 1:1 salts formed from neutral planar closed-shell donors and acceptors. Thus an inquity concerning physico-chemical reasons for the formation of a phase such as TTF-TCNQ is clearly of interest.



1a R = H
1b R = C_2H_5
1c R = CH_3
1d R = iC_3H_7



2a X = S
2b X = Se



3a R = CH_3
3b R = C_2H_5

The present work discusses the "unconventional" nature of 1:1 ion-radical salts such as TTF-TCNQ and *N*-methylphenazinium (3a, *R* = CH^3, NMP)TCNQ,[2] an anomalous conducting phase of a planar closed-shell nitrogen heterocyclic monocation, and proposes qualitative kinetic models involving various non-bonded interactions to account for their formation.

In addition to proposing answers to the question as to why these "unconventional" phases might form, the models proposed herein are expected to be of value in further systematic studies of ion-radical salts. Moreover, a model for the formation of a phase may provide insight into the physical properties of the phase. This is demonstrated for the low temperature magnetic susceptibility and heat capacity of NMP-TCNQ. Further, it may be anticipated that the perspective developed in the formulation of these models will stimulate innovative experimentation in novel molecular and polymeric systems.

NON-BONDED INTERACTIONS

Since crystallization occurs as a result of weak intermolecular forces,[8] these forces must be the basis of models for the formation of "unconventional" ion-radical salts. *A priori*, it is conceivable that examples of initiation of phase formation by all types of non-bonded interactions could be found. Van der Waals interactions (following Kauzmann,[9] this term is used to include weak interactions such as dispersion forces and electrostatic terms), Mulliken π-donor-acceptor interactions, hydrogen bonding and molecular self-aggregation are discussed below; specific intermolecular contacts between atoms are also considered. Table I lists these attractive intermolecular interactions along with examples of "unconventional" 1:1 ion-radical salts whose formation could be due to a given interaction.

TABLE I

Intermolecular interactions that could cause formation of "unconventional" 1:1 ion-radical salts

Attractive interactions	Possible example
1. Hydrogen bonding	5,8-Dihydroxy-quinolinium TCNQ[1]
2. Donor–acceptor interaction	
a. NMPH-NMP$^+$; Phen-NMP$^+$	a. NMP-TCNQ[2]
b. TTF-TTF$^{\dot{+}}$ TCNQ$^{\dot{-}}$-TCNQ	b. TTF-TCNQ
3. Van der Waals interaction	
a. chain formation in a neutral crystal which persists in an ion-radical salt	a. TTF-TCNQ
b. Simple variant–one component is much larger than the other and self-stacks for packing reasons	b. Borderline-TTT salts[39] TCNQ salts of tetra-phenyl- BP and BTP[46]
4. Specific contacts between atoms	
a. between some type of atom	a. TCNQ salts of TMTTF, TMTSeF[23,24]
b. between different types of atoms	b. TTF-TCNQ-entire class of segregated stack structures including substituents, Se for S substitution; TTF-TNAP.[85]
Repulsive interactions	
1. "Localized" electrostatic repulsion	TTF-TCNQ

"CONVENTIONAL" AND "UNCONVENTIONAL" SALTS FROM NEUTRAL PLANAR CLOSED-SHELL DONORS AND ACCEPTORS

Figure 1 schematically summarizes the various situations which may arise when neutral planar closed-shell donors and acceptors interact, including covalent bond formation, which may arise via the intermediacy of a π-complex; situations involving weaker interactions, e.g., inclusion compounds, are ignored.

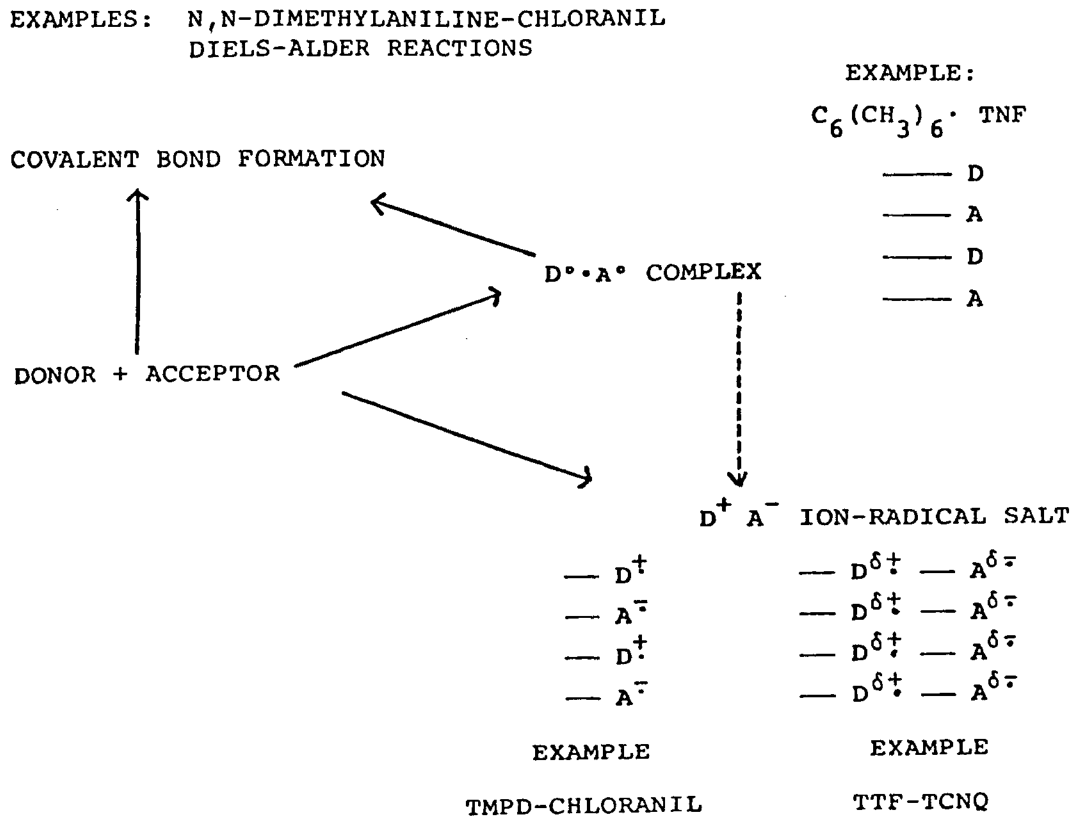
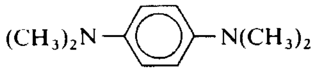


FIGURE 1 Range of interactions and topographical arrays arising from reactions between neutral planar closed-shell donors and acceptors.

The first reported crystal structures of 1:1 ion-radical salts of this class were the tetramethyl-*p*-phenylenediamine (TMPD, **4**) salts of TCNQ[10] and



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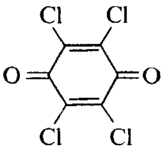

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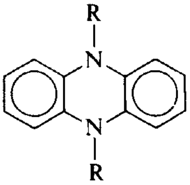
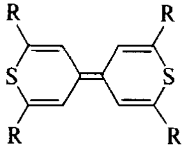


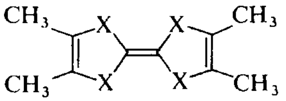
6a R = H, R′=CH$_3$
6b R = R′=CH$_3$
6c R = C$_2$H$_5$, R′=H



7a R = CH$_3$
7b R = H

p-chloranil (**5**).[11] Both of these structures exhibit chains with alternating cation-radicals and anion-radicals, analogous to the chain structures of numerous π-molecular complexes which alternate donor and acceptor molecules.[8] Other examples of 1 : 1 ion-radical salts with mixed stack crystal structures are the TCNQ salts of methyldihydrophenazine[12] (**6a**) and tetramethylbithiopyran[13] (TMBTP, **7a**). Such mixed stacks salts are termed "conventional" phases because historically they were discovered first and in a mixed stack topography, the presence of the cation over the anion should optimize electrostatic interactions.

The uniform segregated stack structure of TTF-TCNQ[6] contrasts sharply with the mixed stack structures cited above, and is termed "unconventional" because, prior to its observation, interaction of a neutral closed-shell donor with a neutral closed-shell acceptor would have been expected to give a mixed stack structure to optimize electrostatic interactions. Answers to the questions as to why a phase such as TTF-TCNQ might form are now presented, and it is apparent at the outset that there are subtleties involved. For example, tetramethyltetraselenofulvalene (TMTSeF. **8a**) reacts with TCNQ to give both a metallic form with a segregated stack structure and a semiconducting form.[14] Further, the formation of either a uniform segregated stack conducting phase or a semiconducting phase is dependent on the rate of cooling of acetonitrile solutions of **2b** (TSeF) and **1b** (DETCNQ).[15]



8a X = Se
8b X = S

The *a priori* knowledge that the crystal structure of neutral TTF consisted of chains was important in early work on TTF-TCNQ,[4,5] since it suggested a means to avert the "conventional" mixed stack structure if the TTF chain structure persisted after charge transfer.

The crystal structure of TTF-TCNQ is shown in Figure 2. It is known that TTF-TCNQ grows parallel to the metallic *b*-direction of the crystal in supersaturated acetonitrile solution, while in less concentrated acetonitrile or in the vapor phase, growth takes place along the *a*-axis of the crystal.[16] A model for phase formation of TTF-TCNQ should explain this difference in growth morphology. Additional interactions for chain formation are now discussed.

Figure 3 shows an energy level diagram appropriate for the weakly interacting components of a Mulliken π-donor-acceptor complex, such as anthracene-trinitrobenzene. Since such π-complexes have linear chain crystal structures,[8] they can initiate linear chain formation from solution. The redox pairs $TCNQ^- - TCNQ^\circ$ and $TTF^\circ - TTF^+$ are regarded as π-complexes which exist in acetonitrile solution and both conform to the energy level diagram in Figure 3, ignoring orbital occupancy. The TCNQ anion-radical has a relatively low solid state ionization energy, 5–6 eV depending on the cation,[17] clearly donor in character. The complex salts $Cs_2(TCNQ)_2$ TCNQ[1,18] may be regarded as a π-complex between $TCNQ^-$ and $TCNQ^\circ$ and the charge transfer exciton is believed to be important in the optical properties of this salt.[19] CNDO/S2 calculations for TTF and its cation-radical find the highest occupied molecular orbitals at 8.74 eV and 10.7 eV, respectively.[20]

Another mechanism for segregated stack formation would involve a specific interatomic contact between an atom in the resultant cation-radical and another atom in the resultant anion-radical. Additionally specific contacts in the structure of a neutral crystal may persist in the ion-radical salts derived from the neutral molecule. The dominant intermolecular features of the neutral TTF structure[21] are the chains of TTF molecules and sulfur–sulfur contacts as short as 3.41 Å.[22] While the intermolecular orientation of TTF in TTF-TCNQ[6] is similar to that found in neutral TTF, there are no short sulfur–sulfur contacts in TTF-TCNQ. However, the structures of the TCNQ salts of TMTTF[23] (**8b**) and TMTSeF[24] contain sulfur–sulfur[23] and selenium–selenium[24] contacts of 3.66 Å and 3.979 Å, respectively. The complete crystal structures of neutral TMTTF or TMTSeF have not been

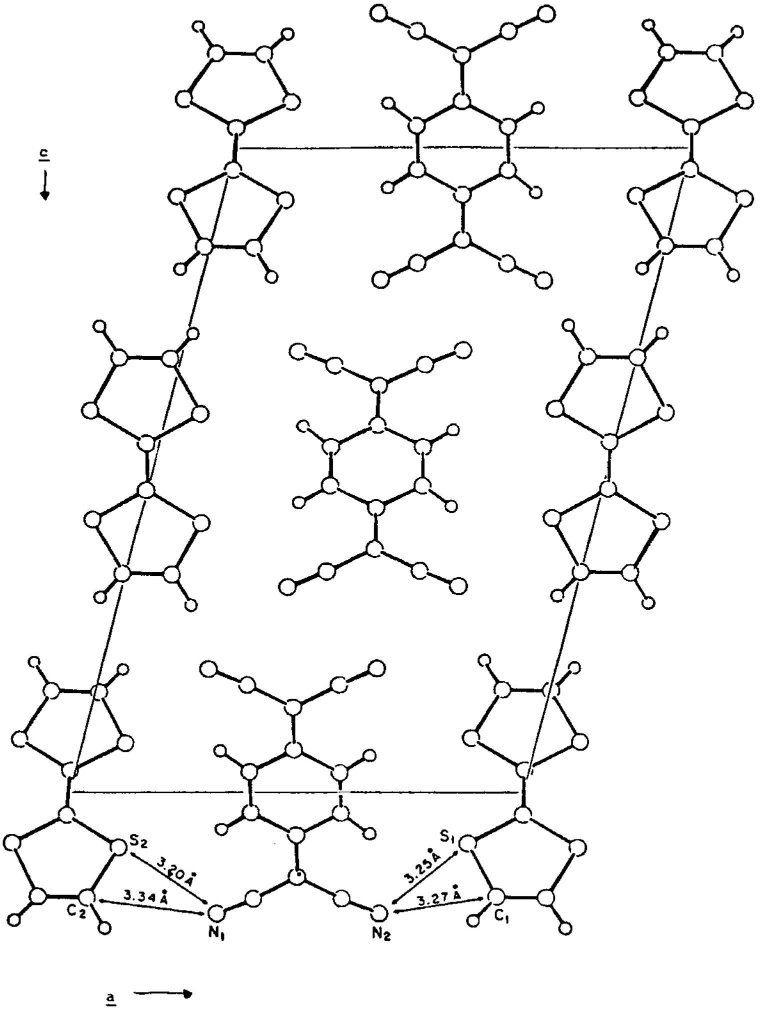


FIGURE 2 View of the *ac* plane in TTF-TCNQ looking down the *b*-axis. Short sulfur-nitrogen and carbon-nitrogen contacts are shown (from reference 6).

reported as yet. An important feature of the TTF-TCNQ structure is the two short nonequivalent sulfur–nitrogen contacts of 3.25 and 3.20 Å (see Figure 2).[6] Such short chalcogen–nitrogen contacts are a general feature of the heterofulvalene-TCNQ segregated stack crystal structures and have been discussed in connection with "interchain coupling" in these conductors.[23] It is now suggested that these contacts may be in part responsible for the formation of the segregated stack structures. Short sulfur–nitrogen contacts are also

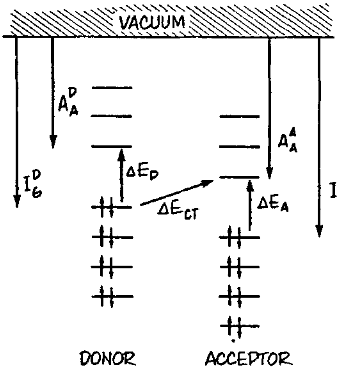


FIGURE 3. Energy level diagram for weakly interacting closed-shell components of a π-complex emphasizing energy levels of components.

observed[25] in the new mixed chain semiconducting salt $(BTP)_2(TCNQ)_3$[26] (BTP = 7b).

The tendency of alkali metal salts of anion-radicals to dimerize in polar solvents is well-known. It has been reported that $Li^+TCNQ^{\overline{\cdot}}$ dimerizes in water[27] and that alkali metal salts of tetracyanoethylene dimerize in 2-methyltetrahydrofuran.[28] Dimerization of the TTF cation-radical has been observed in aqueous solution.[29]

In dilute acetonitrile solution, only a relatively small fraction of TTF and TCNQ is ionized.[30,32] The following equilibria are relevant to the growth of TTF-TCNQ in solution:

$$\mathrm{TTF} + \mathrm{TCNQ} \xrightleftharpoons{K_1} \mathrm{TTF}^{\dot{+}} + \mathrm{TCNQ}^{\overline{\cdot}}$$

$$\left.\begin{array}{l} \mathrm{TTF} + \mathrm{TTF}^{\dot{+}} \xrightleftharpoons{K_2} (\mathrm{TTF}\cdot\mathrm{TTF}^{+}) \\ \mathrm{TCNQ}^{\overline{\cdot}} + \mathrm{TCNQ} \xrightleftharpoons{K_3} (\mathrm{TCNQ}^{\overline{\cdot}}\cdot\mathrm{TCNQ}) \end{array}\right\} b\text{-axis growth}$$

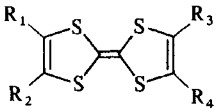
The concentrations of the complexes associated with K_2 and K_3, as well as the concentration of any dimerized ion-radicals possibly present, will clearly decrease as a solution is diluted. It is apparent that in the vapor phase, none of the solution interactions discussed above are operative and that the interatomic sulfur–nitrogen interactions will favor crystal growth in the *a* direction, as observed; this may also be the situation in dilute solution.

From the above discussions, it is apparent that in the solutions from which TTF-TCNQ grows a mixture of neutral and ionic species is present. At some stage between the initiation of chain formation and precipitation from solution of TTF-TCNQ, a charge reorganization from the neutral-ionic mixture to the uniformly charged observed species must occur.[33]

For (heterofulvalene) (TCNQ) systems in general, the constants for the equilibria analogous to those mentioned above may differ substantially from

TABLE II

Relationship between donor molecular volume and physical properties of 1:1 alkyl-TTF (TCNQ) derivative systems



Substituent	Calculated molecular volume	Nature of TCNQ salt	Ref.
$R_1{-}R_4{=}H$	202.14 Å^3[a]	Metal-to insulator system	6
$R_1, R_3{=}CH_3; R_2R_4{=}H$	245.14[b]	Metal-to insulator system	4, [c]
$R_1{-}R_4{=}CH_3$	288.14[b,d]	Metal-to insulator system	23
$R_1{-}R_2{=}R_3{-}R_4{=}(CH_2)_3$	296.74[b]	Metal-to insulator system	[e]
$R_1{-}R_2{=}R_3{-}R_4{=}(CH_2)_4$	330.96[b]	Mixed stack semiconductor	36
$R_1{-}R_4{=}nC_3H_7$	428.98[b]	Mixed stack semiconductor	37

[a] Ref. 21.

[b] Calculated by adding Kitaigorodsky's volume increments to molecular volume of TTF[6]: A. I. Kitaigorodsky, "Molecular Crystals and Molecules," Academic Press, 1973, p. 20.

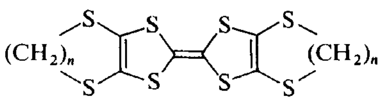
[c] J. C. Scott, A. F. Garito and A. J. Heeger, *Phys. Rev. B.*, **10**, 3131 (1974).

[d] Neutral TMTTF has a triclinic lattice. The crystal data, collected at Molecular Structure Corporation using MoK_α radiation, is as follows: $a = 6.086(5)$, $b = 6.877(10)$, $c = 7.916(6)$ Å, $\alpha = 108.90(11)$, $\beta = 105.29$, $\gamma = 95.25(11)$, $V = 296.6$ Å^3.

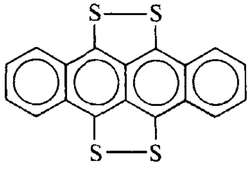
[e] R. L. Greene, J. J. Mayerle, R. Schumaker, G. Castro, P. M. Chaikin, S. Etemad and S. J. LaPlaca, *Solid State Comm.*, **20**, 943 (1976).

those for TTF-TCNQ. Thus, the relative contributions of the various interactions under discussion to formation of a given phase will vary from system to system.

The above discussions indicate that specific interactions, both within and between chains, are important for the formation of a phase such as TTF-TCNQ. Table II shows a relationship between donor molecular volume and the physical properties of some (alkyl-TTF) (TCNQ) derivative systems.[34] The mixed stack phases reported for the octamethylene[35] and tetra-*n*-propyl[36] derivatives of TTF are thus conventional phases which arise because the bulky alkyl substituents "break-up" the intermolecular interactions which would allow the "unconventional" segregated stack phases to form. Table 3 shows analogous data, some previously reported,[37] for TTF-(2,5-dialkyl-TCNQ) derivative systems. Structural data for the TTF salts of **1c** and **1d** has not been reported to date.



9a n = 2
9b n = 3



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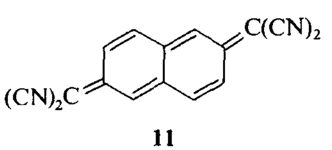
The thioalkyl TTF derivatives **9a** and **9b** from 1 : 1 TCNQ salts with sufficiently high polycrystalline conductivity[38] to expect uniform segregated stack structures. These observations are of interest because the molecular volumes of **9a** and **9b** are clearly as large or larger than the octamethylene TTF compound which gives a mixed-stack TCNQ salt. The structures of the TCNQ salts of **9a** and **9b** are clearly of interest as they may contain novel nonbonded interactions.

In the study of ion-radical salts from neutral planar closed-shell donors and acceptors, instead of relying on specific intermolecular interactions, as in TTF-TCNQ, it might be argued that the use of a large molecule with a small molecule might lead to uniform segregated stack structures, if electron transfer occurs. Tetrathiotetracene (TTT, **10**) with a molecular volume of 350 Å,[39] might be a molecule of this type, as it has long being known to form ion-radical salts with relatively low resistivities.[40] TTT forms a metallic salt of 1 : 2 stoichiometry with TCNQ with a uniform segregated stack structure,[41] and it also forms 1 : 1 conducting salts with TCNQ[42–44] and TNAP[44] (**11**).



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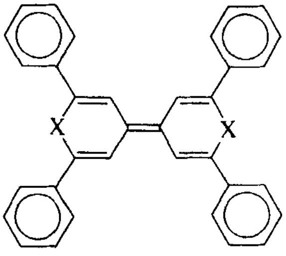
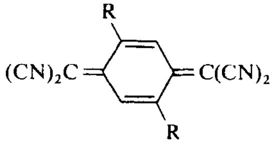


12a X = O
12b X = S

Since interest in ion-radical salts, with segregated stack structures, formed from neutral donors and acceptors was stimulated by the metallic properties of TTF-TCNQ and their possible elaboration, it is important in the selection of new molecules for this purpose to achieve maximum polarizability in a minimum molecular volume.[7] It is of interest to discuss the tetraphenylbipyrans (**12a**) and -bithiopyrans (**12b**) from this perspective. Both **12a** and **12b** are estimated to have molecular volumes of *ca.* 650–700 Å^3. However, the absorption spectra[46] of both the neutral and cation-radicals of **12a** and **12b** indicate that both of these molecules are less polarizable per unit volume than TTT, and on this basis, it would be expected that ion-radical salts from **12a** and **12b** would not be more metallic than previously reported systems. It has been reported that **12a** forms a conducting (σ_{RT} 40 (ohm-cm)$^{-1}$, single crystal) 1 : 1 TCNQ salt which is a semiconductor and that **12b** forms a 1 : 1 TCNQ salt within exhibits σ_{RT} 250–300 (ohm-cm)$^{-1}$ and a modest 10% enhancement down to 145°K.[46,47] The unit cell dimensions reported[46] for the latter salt are consistent with a uniform segregated stack structure.

TABLE III

Relationship between acceptor molecular volume and physical properties of 1:1 TTF (2,5-dialkyl-TCNQ) salts



1

Substituent	Calculated molecular volume	Resistivity[a] of TTF salt[37]	Crystal structure
R=H, *Ia*	256.25 Å^3 [b]	0.1 ohm-cm	Ref. 6
R=CH_3, *Ic*	299.25[c]	0.3 ohm-cm	—
R=C_2H_5, *Ib*	333.45[c]	0.1 ohm-cm	[b]
R—$CH(CH_3)_2$, *Id*	368.45[c]	2 × 10^5 ohm-cm	—

[a] Polycrystalline measurement.

[b] R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta Cryst.*, **18**, 932 (1965).

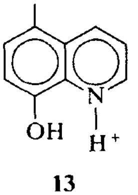
[c] Calculated as in Table II.

[d] A. J. Schultz, G. D. Stucky, R. Craven, M. J. Schaffman and M. B. Salamon, *J. Am. Chem. Soc.*, **98**, 5191 (1976).

The possibility that localized electrostatic repulsion in a "conventional" phase could lead to formation of an "unconventional" phase should at least be mentioned. While certain charge distribution for TTF^{+} and $TCNQ^{-}$ [48] might, in principle, lead to such repulsion, there is no strong reason at present to believe that such interactions are important.

1:1 TCNQ salts of planar closed-shell nitrogen heterocyclic monocations[49]

At least thirty-two salts in this class have been reported.[1,2,50,54] Of these twenty-nine are insulators and three cations, 5,8-dihydroxyquinolinium (**13**),[1] and *N*-methylquinoxalinium[2] (**14**), and *N*-methylphenazinium[2] (NMP, 3a) are reported to form 1:1 conducting salts with TCNQ. The latter exhibits



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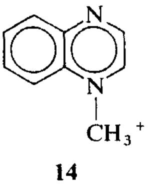
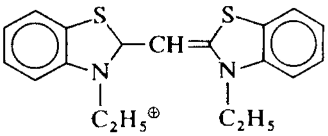


14

a uniform segregated stack crystal structure.[55,56] If the TCNQ salts of **13** and **14** have crystal structures analogous to NMP-TCNQ,[55,56] the formation of that of **13** might be attributed to hydrogen bonding both within and between cation chains and possibly between cation and anion chains, and the formation of that of **14** might be due to interactions such as those proposed in the present work for NMP-TCNQ. Solutions of the TCNQ salts of **14** were reported[2] to be unstable and reservations concerning the characterization of this salt were expressed in the original report.[2]

Of the twenty-nine insulating salts in this class, the crystal structures of three have been reported: 3,3-diethylthiocyanine[57] (**15**), trimethylbenzimidazolium[58] (**16**), and *N*-ethylphenazinium[59] (NEP, **3b**). None of these have infinite chain structures analogous to NMP-TCNQ. The perspective adopted herein is that the twenty-nine insulating salts cited above constitute "normal" behavior for this subclass of TCNQ salts and that an explanation for the formation of the conductor NMP-TCNQ would be desirable.



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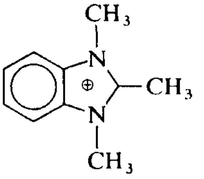

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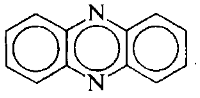

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After the report of the metal-insulator transition in TTF-TCNQ,[4,5] the remaining issues of major scientific interest with respect to NMP-TCNQ, the best organic conductor prior to the discovery of TTF-TCNQ, were:

1) the possibility of an antiferromagnetic ground state,[60]

2) the issue of its formation, since NEP-TCNQ has a room temperature conductivity lower than NMP-TCNQ by a factor of 10^{11}![2]; and

3) the speculation that the presence of diffuse streaks and weak reflections in Weissenberg and precession photographs of certain NMP-TCNQ crystals constitutes evidence for a phase in which the methyl groups on the NMP cation are ordered in the *a*-*b* layer.[56]

In the course of attempting to prepare "high purity" samples of NMP-TCNQ and related materials[61] for conductivity,[62] specific heat,[63] and other physical studies, the isolation of the crystalline phase expected from the reaction of methyldihydrophenazine (NMPH, (**6a**) and TCNQ)[64-66] the isolation of another phase with an x-ray powder diffraction pattern consistent with the reported[67] $(NMP)_2(TCNQ)_3$ structure, as well as variable elemental analyses,[63] gave the present author cause for alarm and wonder! Since many TCNQ salts are handled with no unusual difficulty, the isolation of the TCNQ salt of **6a** suggested that **3a** was reactive under conditions for formation and crystal growth of NMP-TCNQ. This point is well precedented in the literature,[68] and the relevant chemistry is shown in Figure 4. In the present work, **6a**

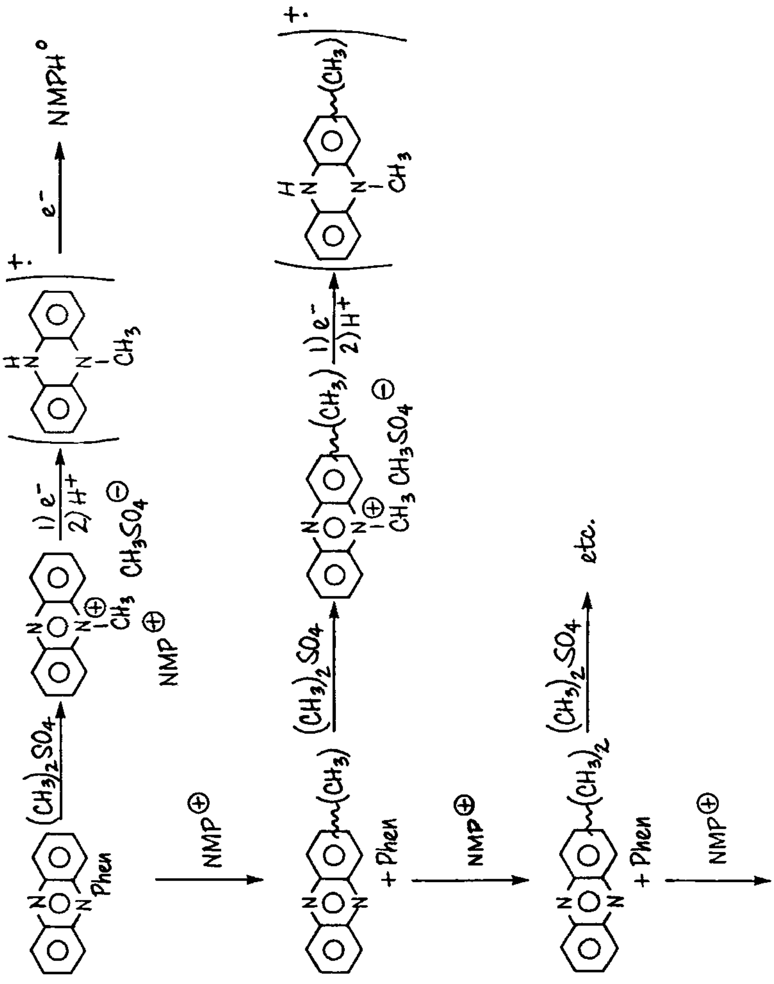
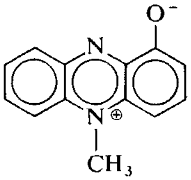


FIGURE 4 Chemistry of the *N*-Methylphenazinium system.

and phenazine (**17**), *inter alia*, were readily detected by chromatographic and mass spectral analyses. In marked contrast to salts of **3a**, the salts of **3b** are stable under more vigorous conditions. Thus the difference in *reactivity* between **3a** and **3b** may be part of the source of their different behavior with Li^+TCNQ^-.

Very recently, a report[69] appeared which confirms the detection[50] of **6a** by mass spectrometry in samples of NMP-TCNQ. This report[69] also noted a peak at *m/e* 210 in the mass spectrum of NMP-TCNQ which was assigned to the dimethyldihydrophenazine (**6b**) cation. Since the NMP-TCNQ samples were purposely exposed to light, the peak at *m/e* 210 may alternatively be due to pyocyanine (**18**), a known[68] photochemical reaction product of **3a**, or the C-methyl derivative of **6a**. In the present work, samples of NMP-TCNQ purposely doped with 2% of the C-methyl derivative of **6a** readily exhibit a peak at *m/e* 210 in mass spectral analysis.



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The presence of donors, such as **6a**, **17** and its 6-methyl derivatives in the presence of the acceptor **3a** suggests a model for the formation of NMP-TCNQ shown in Figure 5. It is proposed that the solution equilibrium for these donor–acceptor interactions[70] is sufficiently favorable to initiate formation of the linear cation chain which is then electrostatically compensated by TCNQ anion-radicals. Thus, the cation chain in NMP-TCNQ contains variable low levels of **17**, the cation radical of $\mathbf{6b}^{\dagger}$ and possibly their C-methyl derivatives and the *N*-methylphenazyl radical,[71] stabilized in a crystal,[72] ignoring for the present the possible presence of phenazine derivatives arising from reactions of **1a** initiated by visible light or with nucleophiles.[68] The presence of the dilute paramagnetic $\mathbf{6a}^{\dagger}$ adjacent to a one-dimensional electron gas in NMP-TCNQ invites analogy to the Kondo effect.[72]

It is natural to inquire whether the weak donor–acceptor interaction discussed above is capable for forming conducting phases with anion-radicals other than that of TCNQ. With TNAP (**11**) it has been reported[74] that **3a** forms both a conducting and an insulating form. With 2,3,5,6-tetrafluoro-TCNQ($TCNQF_4$), only an insulating salt with **3a** is reported.[75] Both TNAP and $TCNQF_4$ have reduction potentials higher than that of TCNQ.[44]

Evidence supportive of the suggestion that "impurities" can initiate formation of a conducting phase such as NMP-TCNQ might be obtained by removal of all impurities from a salt of **3a**, clearly an improbable task, or by

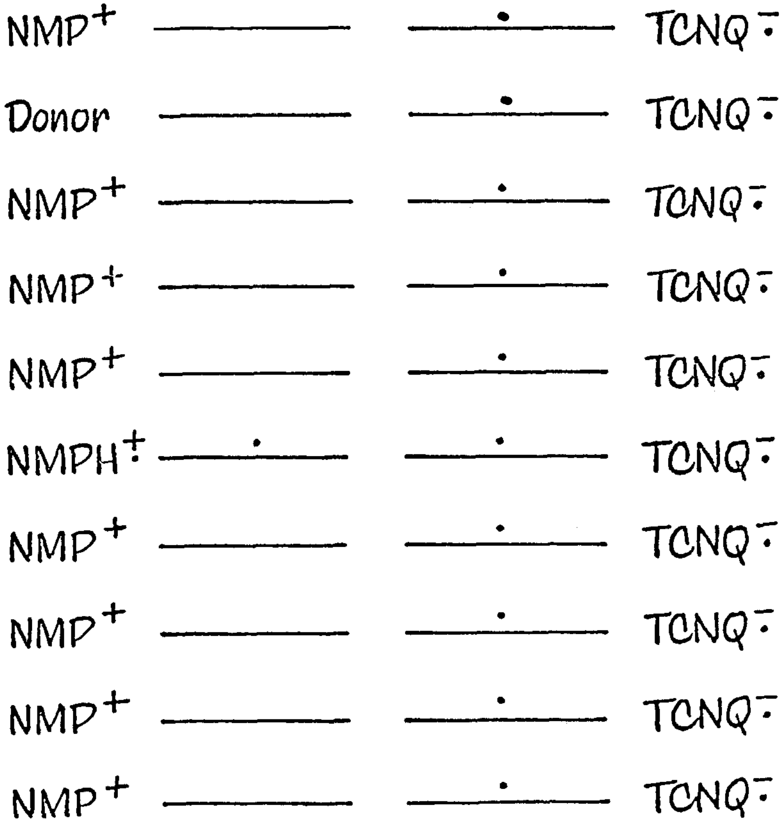


FIGURE 5 A simplified representation of NMP-TCNQ. The solid lines represent molecular planes and the dots represent unpaired electrons.

adding "impurities" to an insulating 1:1 salt to convert it to a conductor. The latter approach was successful for the case of NEP-TCNQ, an insulator.[2,59]

The donor "impurities" in salts of **3a** fall into two classes: planar phenazines and non-planar dihydrophenazines. It was found that the addition of 15 mole % **17** and at least 10 mole % TCNQ, or conveniently,[61] the TCNQ complex of **17**, leads to the formation of a new solid phase containing *ca.* 15 mol % **17′** and having a polycrystalline resistivity in the range 10–40 ohm-cm. The x-ray powder diffraction pattern of the new phase reveals no contamination from NEP-TCNQ or NEP(TCNQ)$_2$. Moreover, the role of **17** is *selective*; attempts to replace it in these experiments with **6b** or ethyldihydrophenazine (**6c**) have not led to the formation of new solid phases to date. While the amount of "impurities" needed to form the new phase are substantially larger than those for NMP-TCNQ and the need to add TCNQ suggests the importance of TCNQ'-TCNQ donor–acceptor equilibria, the result is clear. The conductivity of the insulator NEP-TCNQ has been enhanced by more than 10^9 by the addition of "impurities" in solution via formation of a new phase.

Equilibria involving the donor–acceptor pair TCNQ'.TCNQ may be important in the conversion of many 1:1 insulating TCNQ salts into 1:2 conductors.[1,2] As noted above for TTF-TCNQ, the neutral-ionic mixture must reorganize to the observed uniform $TCNQ^{-1/2}$ species on precipitation. If the presence of equimolar $TCNQ^{\overline{\cdot}}$ and $TCNQ^{\cdot}$ is required to convert a 1 : 1 salt to a 1 : 2 salt, it is clear that a 1 : 2 phase of TTF and TCNQ will not form in solution synthesis from the neutral components due to the predominance of neutral species.

While the role of cation-polarizability in reducing effective coulomb interactions in ion-radical salts such as NMP-TCNQ has been extensively discussed,[76] Bush[77] has pointed out the polarizability of **3a** alone is insufficient for the desired purpose.[76] However, in light of the donor–acceptor interactions discussed above and variable amounts of the highly polarizable $\mathbf{6a}^{\dot{+}}$;[78] it is apparent that the polarizability associated with the cation chain in NMP-TCNQ is somewhat larger than that due to **3a** alone.

The amount of paramagnetic species, such as $\mathbf{6a}^{\dot{+}}$ or possibly the *N*-methylphenazyl radical, presumably randomly distributed in the cation chain, will clearly vary from sample to sample of NMP-TCNQ depending on how a sample is handled. Consequently, a significant variation in the magnetic susceptibility of NMP-TCNQ is expected, as reported.[79] Moreover, the realization of the presence of random spins in the cation chain has allowed reinterpretation of the origin of the linear term of the specific heat of NMP-TCNQ;[63] the phase need not have an antiferromagnetic ground state.

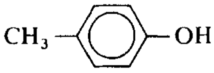
The description of NMP-TCNQ given herein is the most detailed to date, it is apparent that this phase,[80] in contrast to TTF-TCNQ, does not have a quantitatively described composition with respect to all reasonable impurities.[68] Depending on the nature and concentration of the impurities present, incomplete periodicity, hence diffuse streaks and new reflections, may result in any direction of the structure of NMP-TCNQ.

The tendencies of cyanine dyes to form aggregates both in solution and the solid state is well-known.[82] However, the strength of this interaction is not sufficient in the case of **15** to form an extended chain crystal structure with $TCNQ^{\overline{\cdot}}$, even though the crystal structure of the bromide salt of **15** exhibits chain structures.[82]

DISCUSSION

The existence of multiple crystal phases for a given cation with TCNQ has long been familiar to investigators in this area[1,2,7,49] and is taken to imply that different crystal structures are relatively close in energy.[7,49] While the models for the 1 : 1 salts discussed above cover a relatively small number of known ion-radical salts, they are the classes of major scientific interest, and their kinetic nature requires further comment. In a recent survey,[47] it was suggested that TTF-TCNQ and NMP-TCNQ may not be thermodynamically stable in the sense that their crystal structures may not be the most favored ones. The model discussed above for NMP-TCNQ is in accord with that view, since it invokes the presence of impurities to form that phase. However, the qualitative physico-chemical arguments given above for the formation of TTF-TCNQ are quite reasonable, and there is no reason to believe that the uniform segregated stack structures found for TTF-TCNQ and the other systems of that type discussed above are thermodynamically unstable. The only "instability" associated with the TTF-TCNQ lattice is that expected for a one-dimensional electron gas.[83]

With respect to ion-radical salts formed from neutral donors and acceptors where two different forms are reported to either crystalline simultaneously[14] or under slightly different conditions,[15] it is clear that there are kinetic pathways for both mixed and segregated stack structures to form, and that from a thermodynamic point of view, both structures should have different free energies of formation. It is also apparent that a mixed stack and a segregated stack structure cannot interconvert in the solid state and that even if two such solids had different free energies of formation, a statement that one structure is "more stable" than another is not necessarily meaningful. The situation is regarded as analogous to *p*-cresol (**19**) and anisole (**20**) which are not interconvertible and may be combusted to the same final products, yet a discussion of their relative stabilities is not productive because **19** is a phenol and **20** is an ether. It is apparent that if a given donor and acceptor gave the two different segregated stack structures with, e.g., different lattice constants, one of these structures would be "unstable" by the phase rule.



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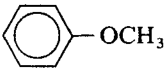

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The discussion of the previous paragraph serves to further emphasize the notion that the activation energies for competing kinetic pathways for ion-radical salts of different structure or stoichiometry may be very small. For example if **7a** and TCNQ are mixed in a 2:3 molar ratio,[84] a mixture of the 1:1[13] and 1:2[13] TCNQ salts precipitates simultaneously.

There are several examples of ion-radical salts with uniform segregated stack structures where the cation and anion are of comparable size which are clearly not metallic or substantially less metallic than TTF-TCNQ.[85–87] These salts serve to bring out another important feature of the TTF-TCNQ structure, namely, that it is very tightly packed. It is frequently stated[7] that mean interplanar distances in ion-radical salts are significantly less than van der Waals distances. The issue of packing in ion-radical salts is dealt with in a three-dimensional sense in Table IV, where volume contractions[88] after charge transfer are shown as the ratio of the sum of volumes of the neutral donor (V_D) and acceptors (V_A) to the volume occupied by the same pair in a charge-transfer salt (V_{CT}).

With reference to Table IV, the volume contraction in TTF-TCNQ on charge transfer is about 10%. Since selenium has a larger van der Waals radius than sulfur, it is expected that the lattice constants of TSeF(**2b**)-TCNQ will expand when compared to those of TTF-TCNQ, as observed.[89] However, when the data are scaled, as in Table IV, the selenium salts are more tightly packed than their sulfur analogs, possibly reflecting the enhanced polarizability of the selenium compounds, or the greater compressibility of selenium as compared to sulfur.[90] The trend from metallic to semiconducting behavior as a function of crystal packing shown in Table IV is reminiscent of Mott's idea of a transition from metal-to-insulator as a function of interatomic separation.[91] The loosely packed structure of the metallic TTT(TCNQ)$_2$ is noteworthy and serves to emphasize the very high polarizability of the TTT system. The unit cell dimensions of the conducting salt **12b**-TCNQ suggest that system to be tightly packed, yet the cation is not particularly polarizable

TABLE IV

Crystal packing in ion-radical salts

Salt	$\frac{V_D + V_A}{V_{CT}}$	Interplanar spacings, Å Cation	Anion	Reference
TSeF-TCNQ	1.12	3.51	—	87
TTF-TCNQ	1.10	3.47	3.17	6
HMTSeF-TCNQ	1.10[a]	3.6	3.2	[b]
HMTTF-TCNQ	1.07[a]	3.57	3.23	[c]
TMTSeF-TCNQ	1.07[a]	3.60	3.26	24
TMTTF-TCNQ	1.04[a]	3.53	3.27	23
TSeF-DETCNQ	1.06[a]	—	—	[d]
TTF-DETCNQ	1.03[a]	3.60	3.26	[e]
TTF-TNAP	1.01[a]	3.4	3.1	85
BTP-TCNQ	1.01[f]	—	—	[g]
TTT(TCNQ)$_2$	0.96	3.52	3.18	41

[a] Calculated as in Table II, footnotes b, d.

[b] T. E. Phillips, T. J. Kistenmacher, A. N. Block and D. O. Cowan, *J. Chem. Soc. Chem. Comm.*, 334 (1976).

[c] Table II, footnote c.

[d] Ref. 15.

[e] Table III, footnote d.

[f] Calculated from the density of the crystal.

[g] Ref. 13a.

for its size. The metallic properties of TTF-TCNQ follow from a crystal structure formed by several types of non-bonded interactions which allow very tight packing, emphasizing the importance of maximum molecular polarizability with minimum molecular size.[7]

The present work approaches the problem of phase formation and stability in the ion-radical salts from a kinetic viewpoint by offering, at present, qualitative answers to the question: "What are the pathways by which 1:1 uniform segregated stack structures form?" This approach is clearly different from the traditional[92] approach to binding in the ion-radical salts which asks, for a given phase, "What is the relative contribution of various cohesive forces to the binding energy of the solid?"[48,93] While the two questions emphasize somewhat differing perspectives, the information gained from both is clearly complementary and useful.

Kitaigorodsky's geometric model of a molecular crystal[44] and the well-established[8] formation of linear chains in complexes derived from neutral, planar closed-shell donors and acceptors form major parts of the basis of the present models. Since it is apparent that the formation of any organic phase could be accounted for by some combination of the weak intermolecular forces discussed above, the examples discussed herein were chosen for the specificities they illustrate. In particular, it is to be nöted that the models were applied only to uniform segregated stack structures of TCNQ salts of 1:1 stoichiometry where the cation is effectively planar and molecular, and the conversion of certain 1:1 salts to salts of 1:2 stoichiometry. Further, the models discussed herein emphasize the intermolecular interactions which can *initiate* linear chain formation. It is conceivable that other weak interactions, as well as the stronger interactions which extend over the whole solid, may become important at stages between the initiation of phase formation and the precipitation of a macroscopic crystal. Such considerations may be important in the determination of crystal morphology. The obviously important role of the solvent has been ignored in the present discussions. Not enough can be said or written about the role of impurities in either the initiation of phase formation or in modification of the "intrinsic" physical properties of a resultant organic solid.[7] Tetrathiotetracene (**10**) is another example of a molecule which can carry along several "impurities" which are easily accommodated in a lattice.[95] While not appreciated by many current workers the non-stoichiometry of the 1:2 TCNQ salt of the quinolinium ion was established in the initial work on that phase.[96]

Finally, while there are several examples where mechanistic pathways have been proposed for chemical transformations, and hence phase formation, in the solid state,[94] the novel features of the "unconventional" 1:1 TCNQ salts discussed above afford the opportunity to propose models for the formation of solid phases precipitating from homogeneous solution.

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Notes added:

The lattice constants of the new conducting NEP-TCNQ are given in Table V, along with those of NMP-TCNQ and those of another phase which occasionally precipitates with the new conductor. The new conducting NEP-TCNQ has a structure generally similar to that of NMP-TCNQ with expansions in the *b* and *c* directions as expected for replacement of a methyl group by an ethyl group.

TABLE V

Lattice constants for NMP-TCNQ, conducting NEP-TCNQ and an unknown $(NEP)_x(TCNQ)_y$ phase

	NMP-TCNQ[a]	Conducting NEP-TCNQ[b]	$(NEP)_x(TCNQ)_y$[b]
a	3.8682 Å	3.817(3) Å	18.561(10) Å
b	7.7807	7.920(25)	34.222(19)
c	15.735	16.181(18)	8.117(2)
α	91.67°	93.65°(20)	93.70°(3)
β	92.67°	94.94°(8)	94.77°(3)
γ	95.38°	94.25°(17)	90.44°(4)
V	470.8 Å^3	484.8 Å^3	5127 Å^3

[a] Reference 55.

[b] Data taken at Molecular Structure Corporation using MoK_α radiation.

In acetonitrile solution, both **3a** (NMP) and **3b** (NEP) undergo two reversible one-electron reductions at −0.08 and −1.00, and −0.09 and −1.01 volts versus the saturated calomel electrode, (SCE), respectively. The iodide salt of **14** undergoes irreversible reduction at −0.39 volts versus SCE.