

This expression is free from defect and the terms containing defects vanish. This is identical with the case for  $k = qn$  in Ray *et al.* (1980) as expected.

*Case II.* For  $h = nq_a$ ,  $k = n'q_b \pm 1$ , the situation is analogous to that of (16) of Ray *et al.* (1980) when  $k = nq \pm 1$ . Here too we get, under the above conditions,

$$I(\omega) = NF^2 \frac{\delta(2 - \delta)}{1 - 2(1 - \delta) \cos 2\pi\omega + (1 - \delta)^2}, \quad (17)$$

which is, as expected, identical with (19) of Ray *et al.* (1980). This shows that for this type of reflection, the intensity will be unaffected by a displacement in the  $a$  direction but will be affected by  $b$ -axis displacements.

*Case III.* When  $h = nq_a \pm 1$ ,  $k = n'q_b$ , the situation becomes almost similar to that of case II except that the intensity is now affected by  $a$  displacement and remains unaffected by  $b$ -axis disorder. Equation (15) reduces to

$$I(\omega) = NF^2 \frac{\gamma(2 - \gamma)}{1 - 2(1 - \gamma) \cos 2\pi\omega + (1 - \gamma)^2}. \quad (18)$$

Both (17) and (18) will on simplification reduce to equation (6) of Wilson (1962).

*Case IV.*  $h = nq_a \pm 1$  and  $k = nq_b \pm 1$ . This is the most general case when both the displacements will manifest themselves in the observed intensity which will be given by

$$I(\omega) = NF^2 \frac{(\gamma + \delta)(2 - \gamma + \delta)}{1 - 2(1 - \gamma + \delta) \cos 2\pi\omega + (1 - \gamma + \delta)^2}. \quad (19)$$

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## Intermolecular Energy, Structure and Stability of Regular Stacks of Tetrathiafulvalene (TTF) and Tetracyanoquinodimethane (TCNQ)

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### Abstract

The lattice energy of isolated, regular tetrathiafulvalene ( $C_6H_4S_4$ ) and tetracyanoquinodimethane ( $C_{12}H_4N_4$ ) segregated and mixed stacks was minimized for four structural parameters; a longitudinal and transverse slip of neighbouring molecules relative to each other, a rotation of a neighbouring molecule

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### Numerical computations and discussion

Numerical computations for different values of  $\alpha$ ,  $\beta$  and  $q_a$ ,  $q_b$  have been carried out for reflections  $h = nq_a \pm 1$  and  $k = n'q_b \pm 1$  which correspond to case IV. Hence, (19) was used for these calculations. The results of the calculation for different cases have been shown in Figs. 1 and 2. Fig. 1 shows that all the curves are symmetrical and have the same general features. Only the sharpnesses of the relative intensity peaks increase as the magnitudes of the displacements, *i.e.*  $a/q_a$  and  $b/q_b$ , both decrease—an observation similar to that of Ray *et al.* (1980). Similarly, Fig. 2 reveals that the peaks of the relative intensities corresponding to a fixed value of  $q_a$ ,  $q_b$  become broader and background more enhanced as the probabilities, *i.e.*  $\alpha$  and  $\beta$ , increase. These are expected results, as an increase in the values of  $\alpha$  and  $\beta$  and a decrease in the values of  $q_a$  and  $q_b$  obviously mean that the magnitude and probability of shift both increase and hence the crystal becomes more defective.

Thus the general conclusion is that the magnitude and the probabilities of the defect will not only broaden the peak but increase the general background as well.

### References

- RAY, B. K., DE, A. K. & BHATTACHERJEE, S. (1980). *Clay Miner.* **15**, 393.  
WILSON, A. J. C. (1962). *X-ray Optics*. London: Methuen.

perpendicular to the molecular planes and the perpendicular distance between two neighbouring molecules. The van der Waals and repulsive interactions only were calculated from atom–atom potentials. The absolute minima of the lattice energies were achieved at stack structures slipped longitudinally with all stack parameters deviating less than about 0.1 Å from their observed mid-range values. The mixed stack proved to

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be less stable than the segregated stack only by about some tenths of a  $\text{kJ mol}^{-1}$ . Additional local minima were found for the segregated tetrathiafulvalene stack and for the mixed stack, which are not (yet) observed experimentally. The eclipsed tetrathiafulvalene stack and the tetracyanoquinodimethane stack with transverse slip, both of these observed experimentally, could not be predicted within a one-dimensional isolated stack model.

### Introduction

A simple atom-atom approximation (Kitaigorodskii, 1973) has been shown useful in the calculation of the lattice energy and stability against dissociation into components of organic conductor crystals like TTF-TCNQ (Govers, 1978). Also, molecular libration and orientational disorder of related molecular compounds can be calculated (Shmueli & Goldberg, 1973) as can be substitutional disorder (Govers, 1979). It has been shown to be possible to derive atom-atom potential parameters for pure TTF, which predict unit-cell parameters within  $0.2 \text{ \AA}$  or about  $4^\circ$  from their observed values (Sandman, Epstein, Chickos, Ketchum, Fu & Scheraga, 1979). The electrostatic part of the atom-atom potential can be used to predict the stability of uniform charge distribution relative to a Wigner lattice (Metzger & Bloch, 1975). Recently it has been shown to be possible to predict the correct longitudinal slip of molecules relative to each other at constant values of the other stack parameters of isolated TTF stacks (Govers & de Kruif, 1980).

Here the latter calculation is extended to isolated stacks of TTF and TCNQ molecules with a four-parameter variation of the stack structure and the corresponding intermolecular stack energy. This effort can be considered as the first step of a complete three-dimensional structure prediction from atom-atom potentials, by which it could be possible to decide from given molecular geometry and composition whether stable conducting Soos-type structures (Soos, 1974) can be prepared. The second step should consist of positioning and orientation of stacks relative to each other by a search for absolute and local minima of the interstack interactions, whereas a simultaneous variation of intra- and inter-stack structural parameters would require too much computational time.

Within the eight Soos-type structures we will consider only regular stacks with uniform perpendicular distances between parallel and flat molecules for reasons of simplicity and because the non-uniformity in alternating stacks is small and might well be within the limit of accuracy of the method. In addition it is impossible to include the electrostatic part of the atom-atom potential in a charged isolated and segregated stack as interactions with neighbouring stacks

charged oppositely have to be considered (Govers & de Kruif, 1980). Therefore we will drop this electrostatic part, leaving only the van der Waals and repulsive contributions. As a consequence we cannot discern between complex and simple Soos stacks nor between Wigner stacks and stacks charged uniformly. Moreover, serious errors might be introduced in the predicted stack structures as the electrostatic contribution is not small. The four stack parameters  $R$ ,  $\delta$ ,  $\varepsilon$  and  $\chi$  are depicted in Fig. 1. These define completely the mutual position and orientation of two parallel molecular planes. A third, fourth, *etc.* molecule can be positioned forming either straight or zigzag or spiral stacks. Only if the summation limits of the atom-atom potentials exceed the doubled perpendicular distance will we be able to predict these variations of stack structure, and this will not be the case here.

Segregated stacks are built up from either identical TTF or TCNQ molecules. Mixed stacks contain alternate TTF and TCNQ molecules.

### Method

The stack energy,  $E$ , is considered to be a pairwise sum of interatomic interactions,  $E_{kij}$ , between the  $n$  atoms,  $i$ , of a central molecule in the stack and the  $n'$  atoms,  $j$ , of the  $z$  surrounding molecules,  $k$  (Govers & de Kruif, 1980):

$$E = \frac{1}{2}N \sum_k^z \sum_i^n \sum_j^{n'} E_{kij}(r_{kij}) \quad (1)$$

with

$$E_{kij}(r_{kij}) = -A_{ij} r_{kij}^{-6} + B_{ij} \exp(-C_{ij} r_{kij}). \quad (2)$$

In (1) the factor  $\frac{1}{2}$  is introduced to avoid double counting of pair interactions,  $N$  is the number of molecules in the stack and  $r_{kij}$  are the interatomic distances.

The parameters  $A_{ij}$ ,  $B_{ij}$  and  $C_{ij}$  in (2) depend only on the ten different types,  $tij$ , of interatomic pairs CC, CH, . . . , SS, which exist for the C, H, S and N atoms of TTF and TCNQ. We used the sets 1 and 2 of Table 1 of Govers (1978) throughout the calculations. These parameters were used as previously, *i.e.* in combination

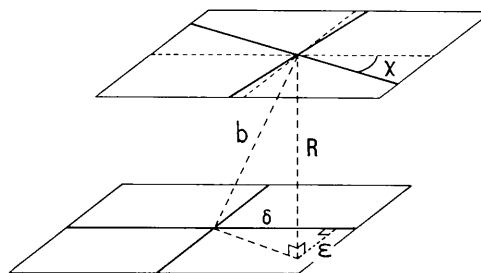


Fig. 1. The four stack parameters.

with summation limits of about 5.5 Å, yielding 80% of the stack energy for set 1, and with summation limits of 15 Å, yielding 100% of the stack energy for set 2 (Govers, 1978). As set 2 produced the expected and relatively low values for the stack energy and its

dependence on structure, we did not use it for the prediction of zigzag or spiral stack structures in spite of the fact that its summation limits are higher than the doubled perpendicular distance between two neighbouring molecules.

Table 1. *Observed regular TTF and TCNQ stack structures*

Stack	<i>R</i> (Å)	<i>ε</i> (Å)	<i>δ</i> (Å)	<i>b</i> (Å)	References
TTF <sup>0</sup>	3.62	0.25	1.79	4.05	(a)
TTF <sup>+e</sup> -TCNQ <sup>-e</sup>	3.47	0.02	1.65	3.84	(b)
TTF <sup>+e</sup> -DETCNQ <sup>-e</sup>	3.60	0.00	1.40	3.86	(c)
TTF <sup>+e</sup> -TNAP <sup>-e</sup>	3.4	0.0	1.61	3.76	(d)
TTF (tsl)	3.51 ± 0.11	0.12 ± 0.12	1.6 ± 0.2	3.90 ± 0.15	
TTF <sup>+0.77</sup> .Cl <sub>0.77</sub> <sup>-</sup>	3.56	0.0	0.0	3.56	(e)
TTF <sup>+0.68</sup> .Cl <sub>0.68</sub> <sup>-</sup>	3.60	0.0	0.0	3.60	(e)
TTF <sup>+0.92</sup> .Cl <sub>0.92</sub> <sup>-</sup>	3.59	0.0	0.0	3.59	(f)
TTF <sup>+0.76</sup> .Br <sub>0.76</sub> <sup>-</sup>	3.57	0.0	0.0	3.57	(e)
TTF <sup>+0.59</sup> .Br <sub>0.59</sub> <sup>-</sup>	3.56	0.0	0.0	3.56	(e)
TTF <sup>+0.72</sup> .I <sub>0.72</sub> <sup>-</sup>	3.56	0.0	0.0	3.56	(e)
TTF <sup>+0.69</sup> .I <sub>0.69</sub> <sup>-</sup>	3.77*	0.0	0.0	3.77	(e)
TTF <sup>+5/7</sup> .I <sub>5/7</sub> <sup>-</sup>	3.56	0.0	0.0	3.56	(g)
TTF <sup>+5/7</sup> .I <sub>5/7</sub> <sup>-</sup>	3.55	0.0	0.0	3.55	(h)
TTF <sup>+6/11</sup> .SCN <sub>6/11</sub> <sup>-</sup>	3.63	0.0	0.0	3.63	(i)
TTF <sup>+0.57</sup> .SCN <sub>0.57</sub> <sup>-</sup>	3.61	0.0	0.0	3.61	(j)
TTF <sup>+6/11</sup> .SeCN <sub>6/11</sub> <sup>-</sup>	3.61	0.0	0.0	3.61	(i)
TTF (ecl)	3.59 ± 0.04	0.0 ± 0.05	0.0 ± 0.05	3.59 ± 0.04	
TCNQ <sup>0</sup> (tsl)	3.45	2.29	3.91	5.69	(a)
TTF <sup>+e</sup> -TCNQ <sup>-e</sup>	3.17	0.07	2.10	3.80	(b)
TMTTF <sup>+e</sup> -TCNQ <sup>-e</sup>	3.20	0.03	2.03	3.79	(k)
TMTTF <sup>-e</sup> -TCNQ <sup>-e</sup>	3.27	0.04	2.10	3.89	(l)
TMTSF <sup>+e</sup> -TCNQ <sup>-e</sup>	3.26	0.05	2.07	3.86	(m)
TMTTF <sup>+e</sup> -TCNQ <sub>2</sub> <sup>-e,0</sup>	3.24	0.02	2.00	3.81	(n)
HMTTF <sup>+e</sup> -TCNQ <sup>-e</sup>	3.26	0.00	2.15	3.90	(o)
HMTSF <sup>+e</sup> -TCNQ <sup>-e</sup>	3.21	0.00	2.20	3.89	(p)
NMP <sup>+e</sup> -TCNQ <sup>-e</sup>	3.26	0.05	2.03	3.84	(q)
Quinolium <sup>+</sup> -TCNQ <sub>2</sub> <sup>-1/2</sup>	3.22	0.00	2.09	3.84	(r)
TMPD <sup>+</sup> -TCNQ <sub>2</sub> <sup>-1/2</sup>	3.24	0.00	2.00	3.81	(s)
Acridinium <sup>+</sup> -TCNQ <sub>2</sub> <sup>-1/2</sup>	3.25	0.04	2.09	3.86	(t)
TTT <sup>+</sup> -TCNQ <sub>2</sub> <sup>-1/2</sup>	3.18	0.0	2.06	3.79	(u)
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> Cr <sup>+</sup> .TCNQ <sub>2</sub> <sup>-0</sup>	3.29	0.00	2.05	3.88	(v)
TMA <sup>+</sup> (I <sub>3</sub> ) <sub>1/3</sub> -TCNQ <sup>-2/3</sup>	3.23	0.00	2.04	3.82	(w)
Rb <sup>+</sup> .TCNQ <sup>-</sup> (Tetragonal)	3.33	0.08	1.98	3.87	(x)
Rb <sup>+</sup> .TCNQ <sup>-</sup> (Triclinic)	3.43	0.03	1.85	3.90	(y)
NH <sub>4</sub> <sup>+</sup> .TCNQ <sup>-</sup>	3.31	0.05	1.83	3.78	(z)
TCNQ (tsl)	3.30 ± 0.13	0.04 ± 0.04	2.02 ± 0.2	3.84 ± 0.06	
Na <sup>+</sup> .TCNQ <sup>-</sup> (353 K)	3.39	0.91	0.27	3.52	(aa)
K <sup>+</sup> .TCNQ <sup>-</sup> (High temperature)	3.48	0.86	0.27	3.59	(bb)
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> Cr <sup>+</sup> .TCNQ <sup>-</sup>	3.42	1.15	0.04	3.61	(cc)
TCNQ (tsl)	3.44 ± 0.05	1.01 ± 0.15	0.16 ± 0.12	3.57 ± 0.05	
DMDBTTF-TCNQ (tsl)	3.55	0.24	2.82	3.54	(dd)

References: (a) Phillips, Kistenmacher, Ferraris & Cowan (1973); (b) Kistenmacher, Phillips & Cowan (1974); (c) Schultz, Stucky, Craven, Schaffman & Salamon (1976); (d) Berger, Dahm, Johnson, Miles & Wilson (1975); (e) Scott, La Placa, Torrance, Silverman & Welber (1977); (f) Dahm, Johnson, May, Miles & Wilson (1975); (g) Daly & Sanz (1975); (h) Johnson & Watson (1976); (i) Wudl, Schafer, Walsh, Rupp, DiSalvo, Waszczak, Kaplan & Thomas (1977); (j) Kobayashi & Kobayashi (1977); (k) Chasseau, Gaultier, Hauw, Fabre, Giral & Torreilles (1978); (l) Phillips, Kistenmacher, Bloch, Ferraris & Cowan (1977); (m) Bechgaard, Kistenmacher, Bloch & Cowan (1977); (n) Kistenmacher, Phillips, Cowan, Ferraris & Bloch (1976); (o) Chasseau, Comberton, Gaultier & Hauw (1978); (p) Phillips, Kistenmacher, Bloch & Cowan (1976); (q) Fritchie (1966); (r) Kobayashi, Fumiyuki & Yoshihiko (1971); (s) Hanson (1968); (t) Kobayashi (1974); (u) Shibaeva & Rozenberg (1976); (v) Shibaeva, Atovmyan & Orfonova (1969); (w) Filhol, Rovira, Hauw, Gaultier, Chasseau & Dupuis (1979); (x) van Bodegom, de Boer & Vos (1977); (y) Shirovani & Kobayashi (1973); (z) Kobayashi (1978); (aa) Konno & Saito (1975); (bb) Konno, Ishii & Saito (1977); (cc) Shibaeva, Atovmyan & Rozenberg (1969); (dd) Shibaeva & Yarochkina (1975).

\* Not included in the mid-range values.

The interatomic distances  $r_{kij}(\delta, \varepsilon, R, \chi)$  were calculated from

$$r_{kij} = |\mathbf{R}_k \mathbf{K}_{j0} + \mathbf{T}_k - \mathbf{K}_{i0}| \quad (3)$$

with

$$\mathbf{R}_k = \begin{pmatrix} \cos \chi & -\sin \chi & 0 \\ \sin \chi & \cos \chi & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{T}_k = \begin{pmatrix} k\delta \\ k\varepsilon \\ kR \end{pmatrix}. \quad (4)$$

In (3)  $\mathbf{K}_{i0}$  denote the vectors of the atomic coordinates of a molecule in the reference axial system of its principal axes of inertia. These were calculated from the fractional coordinates and cell parameters of TTF and TCNQ in TTF-TCNQ (Kistenmacher, Phillips & Cowan, 1974) and atomic masses.  $k$  denotes the  $k$ th neighbour of central molecule  $o$ .  $\mathbf{R}_k$  denotes the rotation matrix of neighbour  $k$ , in which  $\chi$  can be  $\neq 0$  only if  $k$  is odd.  $\mathbf{T}_k$  denotes its translation vector in the reference axial system.

Equations (1)–(4) were applied in a two-run gridpoint scan of  $E(R, \varepsilon, \delta, \chi)$  similar to other calculations of the lattice energy (e.g. Giglio, Liquori & Mazzarella, 1969). In the first run increments of 0.2, 0.2, 0.4 Å and 22.5° were used for  $R$ ,  $\varepsilon$ ,  $\delta$  and  $\chi$ , respectively. The ranges within which  $R$ ,  $\varepsilon$  and  $\delta$  were varied were inferred from experimental information (see *Experimental information*).  $\chi$  was varied from  $-90$  to  $+90^\circ$  in view of the symmetries of the TTF and TCNQ molecules. The coarse minima and new regions of variation found in the first run were refined in a second run with increments of 0.05, 0.1, 0.1 Å and 5°, respectively. In this way and by applying graphical interpolation we could find absolute and local minima with an accuracy of about  $\pm 0.02$  Å (for  $R$ ,  $\varepsilon$ ,  $\delta$ ),  $\pm 1^\circ$  (for  $\chi$ ) and  $\pm 0.04$  kJ mol $^{-1}$  (for  $E$ ). This accuracy is high enough in view of the accuracy of the experimental information on  $R$ ,  $\varepsilon$  and  $\delta$  and in view of the errors introduced by uncertainties of the atom-atom potential parameters. At the same time the total number of evaluations of the stack energy or grid points to be scanned in one run amounts to about one thousand, low enough for rapid calculations on a CDC-Cyber 173 computer.

### Experimental information

To find the ranges within which  $R$ ,  $\varepsilon$  and  $\delta$  have to be varied and for a comparison of calculated and experimental results we have collected all known experimental information on  $R$ ,  $\varepsilon$  and  $\delta$  of TTF and TCNQ compounds with regular stacks (Table 1). Two types of segregated TTF stacks are met; stacks in which the molecules are slipped longitudinally relative to each other (lsl) and eclipsed stacks (ecl). Segregated

TCNQ stacks are slipped either longitudinally (lsl) or transversely (tsl). Pure TCNQ displays a two-dimensional layer structure. Somewhat artificially one can discern interpenetrating stacks within a layer with molecules slipped longitudinally and transversely (ltsl). A mixed-stack TTF-TCNQ modification is not (yet) observed. However, the DMBTTF-TCNQ crystal displays mixed stacks with longitudinal slip (lsl).

In Table 1 the values of  $R$  are those reported in the literature.  $\varepsilon$  and  $\delta$  values were estimated from overlap projections as depicted in the literature comparing these with the dimensions of TTF and TCNQ molecules calculated from atomic coordinates in TTF-TCNQ (Kistenmacher *et al.*, 1974).

Also, symmetry considerations could be used in some cases. From the values of  $R$ ,  $\varepsilon$  and  $\delta$ , the stacking axis  $b$  was calculated:

$$b = (R^2 + \varepsilon^2 + \delta^2)^{1/2}. \quad (5)$$

Equation (5) is deduced easily from Fig. 1. The value of  $b$  calculated in this way corresponds within some hundredths of an Å with experimental values of  $b$  reported in the literature, showing the accuracy of our estimations.

The final results are the mid-range values and ranges per type of stack, which are also included in Table 1. These show clearly the potential of an isolated stack model per type of stack. *Interstack* and *intramolecular* interactions seem to influence intrastack structural parameters for each type of stack only to the extent of about 0.1 Å. These interactions seem to be more important for the establishment of the type of stack itself.

### Calculations and results

In the first run the TTF stack parameters  $R$ ,  $\varepsilon$  and  $\delta$  were varied from 3.3 to 3.9 Å, 0.0 to 1.0 Å and 0.0 to 2.4 Å, respectively, with increments and variations of  $\chi$  as mentioned under *Method*. These ranges were inferred from Table 1. For the TCNQ and mixed TTF-TCNQ stacks we used the ranges 3.0 to 3.8 Å, 0.0 to 1.0 Å and 0.0 to 2.4 Å.

The resulting coarse minima were always obtained at values of  $\varepsilon$  and/or  $\delta$  close to 0.0 Å. In these cases  $+\chi$  or  $-\chi$  produces about the same stack energy for reasons of molecular symmetry. Thus we used only positive values of  $\chi$  in the second run. The coarse minima were used for the definition of new ranges of variations and the small increments mentioned under *Method* were applied in the second run. As the mixed TTF-TCNQ stack did not show a minimum structure with longitudinal slip within  $\delta = 0.0$  to 2.4 Å, the variation of  $\delta$  was extended to 4.0 Å in the second run. As we wanted to compare with observed eclipsed TTF stacks and as no true eclipsed minimum was obtained,

an additional calculation was performed in this case, varying  $R$  at constant values of  $\delta = \epsilon = \chi = 0$ .

The final results are included in Table 2, which also contains (underlined> approximate values of the stack energy at the observed stack structures of Table 1. Overlap projections of neighbouring molecules in the stack showing  $\delta$  and  $\epsilon$  and obtained *via* set 1, are depicted in Figs. 2(a)–(e).

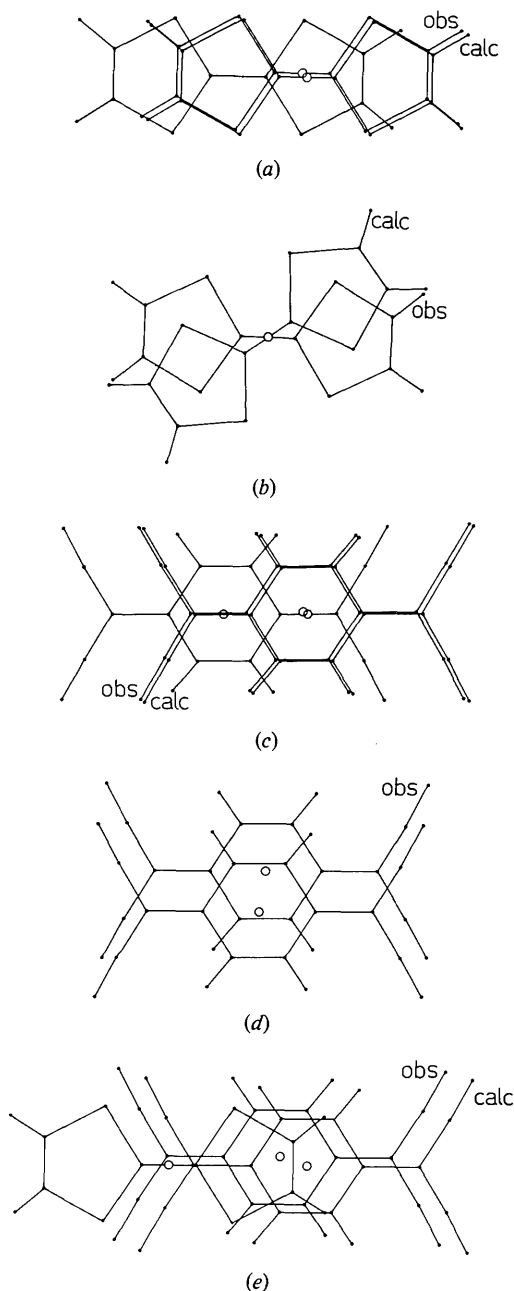


Fig. 2. Calculated (calc) and observed (obs) overlap projections of neighbouring molecules in a stack. (a) TTF (lsl), (b) TTF (ecl), (c) TCNQ (lsl), (d) TCNQ (tsl), (e) (DMDB)TTF-TCNQ (lsl).

## Conclusions

The following conclusions can be drawn from the results obtained from set 1 (Table 2).

*Firstly*, the segregated stack structures predicted with longitudinal slip correspond with the experimental TTF and TCNQ stacks within the experimental range and even the slipped and mixed TTF-TCNQ stack predicted is close to the experimental DMBTTF-TCNQ structure in spite of the rather strong geometric difference between the TTF molecule and its derivative. Moreover, the structures predicted correspond to absolute minima of the stack energy with values from 3.8 to 6.5 kJ mol<sup>-1</sup> lower than those of local and other minima predicted. Finally, the  $\delta$  value predicted for TTF,  $\delta = 1.72 \pm 0.02$  Å at  $R = 3.50$  Å, is not too far from the value predicted previously,  $\delta = 1.54$  Å at  $R = 3.47$  Å (Govers & de Kruif, 1980).

However, the widths of the experimental ranges of  $R$ ,  $\epsilon$  and  $\delta$  vary from 0.04 to 0.2 Å and corresponding deviations from observed values, or uncertainties in predicted ones, can be expected in individual cases of TTF and TCNQ systems. These deviations and uncertainties can be caused by intra- and interstack effects and by uncertainties in the atom-atom potential method used. Intrastack interactions other than van der Waals and repulsive, *e.g.* electrostatic and metallic interactions, can be present (Govers, 1978; Govers & de Kruif, 1980) as can be geometric and electronic differences up to 0.05 Å and one-electron charge transfer in molecular species of TTF (Kobayashi & Kobayashi, 1977) or TCNQ (Flandrois & Chasseau, 1977). The latter, in turn, are caused by differences in counter(-ion) stacks and in the resulting interstack interaction.

Nevertheless, set 1 proves to be quite useful for the prediction of stack structures with longitudinal slip. In a three-dimensional structure calculation the variation of  $R$ ,  $\epsilon$ ,  $\delta$  and  $\chi$  can be largely excluded when dealing with this type of stack, stressing their one-dimensional character.

*Secondly*, interstack, electrostatic or metallic interactions seem to preserve the observed eclipsed stack structure in TTF compounds with spherical or rod-like anions (TTF<sup>+x</sup>X<sub>x</sub><sup>-</sup>, with  $X = \text{Cl, Br, I, SCN, SeCN}$ , Table 1) for changing into a slipped or a compact, but pseudo-eclipsed, structure with  $\chi = 36^\circ$ . The latter two structures have stack energies lower by 6.5 to 4.2 kJ mol<sup>-1</sup>, respectively, than the true eclipsed structure. The importance of electrostatic and metallic interactions in these systems has been pointed out by Scott, La Placa, Torrance, Silverman & Welber (1977). Although our isolated stack atom-atom potential method does not predict the true eclipsed minimum structure, yet it is successful in the prediction of  $R$  at constant  $\delta = \epsilon = \chi = 0$ . A value of  $R = 3.62 \pm 0.01$  Å is predicted, close to the experimental value of  $R =$

Table 2. Intermolecular van der Waals plus repulsive stack energies and structures of regular TTF and TCNQ stacks

Stack	Atom-atom potentials*	$E$ (kJ mol <sup>-1</sup> )†	$R$ (Å)	$\varepsilon$ (Å)	$\delta$ (Å)	$\chi$ (°)	$b$ (Å)‡
TTF lsl	Set 1	$-60.92 \pm 0.04$	$3.50 \pm 0.01$	0.0	$1.72 \pm 0.02$	0.0	$3.90 \pm 0.02$
		<u><math>-59.5</math></u>	<u><math>3.51 \pm 0.11</math></u>	<u><math>0.12 \pm 0.12</math></u>	<u><math>1.60 \pm 0.2</math></u>	<u>0.0</u>	<u><math>3.90 \pm 0.15</math></u>
ecl		$-54.39 \pm 0.04§$	$3.62 \pm 0.01§$	0.0	0.0	0.0	$3.62 \pm 0.01$
		<u><math>-54.5</math></u>	<u><math>3.59 \pm 0.04</math></u>	<u><math>0.0 \pm 0.05</math></u>	<u><math>0.0 \pm 0.05</math></u>	<u>0.0</u>	<u><math>3.59 \pm 0.04</math></u>
(ecl)		$-56.77 \pm 0.04$	$3.52 \pm 0.01$	0.0	0.0	$36 \pm 1$	$3.52 \pm 0.01$
lsl	Set 2	$-44.75 \pm 0.04$	$3.45 \pm 0.01$	0.0	$1.32 \pm 0.02$	0.0	$3.69 \pm 0.02$
ecl		$-42.78 \pm 0.04§$	$3.56 \pm 0.01§$	0.0	0.0	0.0	$3.56 \pm 0.01$
(ecl)		$-45.50 \pm 0.04$	$3.44 \pm 0.01$	0.0	0.0	$39 \pm 1$	$3.44 \pm 0.01$
TCNQ lsl	Set 1	$-65.74 \pm 0.04$	$3.39 \pm 0.01$	0.0	$2.10 \pm 0.05$	0.0	$3.99 \pm 0.05$
		<u><math>-63.7</math></u>	<u><math>3.30 \pm 0.13</math></u>	<u><math>0.04 \pm 0.04</math></u>	<u><math>2.02 \pm 0.20</math></u>	<u>0.0</u>	<u><math>3.84 \pm 0.06</math></u>
tsl		<u><math>-54.1</math></u>	<u><math>3.44 \pm 0.05</math></u>	<u><math>1.01 \pm 0.15</math></u>	<u><math>0.16 \pm 0.12</math></u>	<u>0.0</u>	<u><math>3.57 \pm 0.05</math></u>
lsl	Set 2	$-38.55 \pm 0.04$	$3.36 \pm 0.01$	0.0	$1.23 \pm 0.02$	0.0	$3.59 \pm 0.02$
(ecl)		$-38.72 \pm 0.04$	$3.36 \pm 0.01$	0.0	0.0	$24 \pm 1$	$3.36 \pm 0.01$
TTF-TCNQ lsl	Set 1	$-62.77 \pm 0.04$	$3.50 \pm 0.02$	0.0	$3.50 \pm 0.01$	0.0	$4.95 \pm 0.02$
		<u><math>-60.3¶</math></u>	<u><math>3.55¶</math></u>	<u><math>0.24¶</math></u>	<u><math>2.82¶</math></u>	<u><math>0.0¶</math></u>	<u><math>4.54¶</math></u>
ecl		$-59.04 \pm 0.04$	$3.50 \pm 0.01$	0.0	0.0	0.0	$3.50 \pm 0.01$
ecl	Set 2	$-43.62 \pm 0.04$	$3.39 \pm 0.01$	0.0	0.0	0.0	$3.39 \pm 0.01$

\* Set 1 and 2 from Table 1 (Govers, 1978).

† Results obtained *via* kcal mol<sup>-1</sup> = 4.19 kJ mol<sup>-1</sup> using set 1 and set 2 (Govers, 1978).

‡ Calculated *via* (5), except for the experimental values (underlined).

§ No true minimum;  $E(R)$  minimized for an eclipsed stack ( $\delta = \varepsilon = \chi = 0.0$ ).

¶ Value for DMDBTTF-TCNQ stack structure.

$3.59 \pm 0.04$  Å. Thus, unless we are certain that a true eclipsed structure must be chosen for other reasons, a three-dimensional structure calculation demands variation of  $R$  and  $\chi$  and only  $\delta = \varepsilon = 0$  can be applied in this case. The situation is even worse for TCNQ stacks not slipped longitudinally as our method fails to predict the observed structure with transverse slip. These stacks are met only for TCNQ salts with spherical cations (Table 1). The importance of electrostatic interactions has been shown by Metzger (1975). In this case at least  $R$  and  $\varepsilon$ , but probably also  $\delta$  and  $\chi$ , must be varied in a three-dimensional structure calculation and the idea of an isolated stack has to be abandoned.

For the mixed TTF-TCNQ stack experimental information is lacking. A true eclipsed and local minimum is predicted with an energy only  $3.8$  kJ mol<sup>-1</sup> above the absolute minimum of the structure slipped longitudinally.

A three-dimensional structure prediction without variation of  $R$ ,  $\delta$ ,  $\varepsilon$  and  $\chi$  seems possible. Furthermore, the slipped and eclipsed structures of the mixed stack are only  $0.6$  to  $4.4$  kJ mol<sup>-1</sup> less stable than mean segregated stacks slipped longitudinally, indicating the possibility of a mixed-stack modification of TTF-TCNQ.

Finally, the conclusion drawn above only holds for atom-atom potential set 1. Set 2 has to be rejected for several reasons. It has already proven to be rather poor

for the calculation of the lattice energies of pure TCNQ and of TTF-TCNQ (Govers, 1978). Here it also produces stack energy values about  $20$  kJ mol<sup>-1</sup> higher than set 1 does. Moreover, it predicts much too low values for  $\delta$  of TTF and TCNQ and even no slipped structure for the mixed stack. It predicts values for the stacking axis,  $b$ , which are rather different for the slipped stack structures of TTF and TCNQ of  $3.69 \pm 0.02$  and  $3.59 \pm 0.02$  Å, respectively, and which are much too low in view of the experimental mid-range values of  $3.90 \pm 0.15$  and  $3.84 \pm 0.06$  Å, respectively. Set 1 is more correct with values of  $3.90 \pm 0.02$  and  $3.99 \pm 0.05$  Å, respectively. This criterion seems to be rather important for a three-dimensional structure calculation, in which two TTF and TCNQ stacks of equal length of say  $3.90$  Å have to be combined. The explanation of the poorer results of set 2 has to be sought in its method of derivation and the compounds on which it is based (Govers, 1978).

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#### References

- BECHGAARD, K., KISTENMACHER, T. J., BLOCH, A. N. & COWAN, D. O. (1977). *Acta Cryst.* B33, 417-422.  
 BERGER, P. A., DAHM, D. J., JOHNSON, G. R., MILES, M. G. & WILSON, J. D. (1975). *Phys. Rev. B*, 12, 4085-4089.

- BODEGOM, B. VAN, DE BOER, J. L. & VOS, A. (1977). *Acta Cryst.* **B33**, 602–604.
- CHASSEAU, D., COMBERTON, G., GAULTIER, J. & HAUW, C. (1978). *Acta Cryst.* **B34**, 689–691.
- CHASSEAU, D., GAULTIER, J., HAUW, C., FABRE, J. M., GIRAL, L. & TORREILLES, E. (1978). *Acta Cryst.* **B34**, 2811–2818.
- DAHM, D. J., JOHNSON, G. R., MAY, F. L., MILES, M. G. & WILSON, J. D. (1975). *Cryst. Struct. Commun.* **4**, 673–676.
- DALY, J. J. & SANZ, F. (1975). *Acta Cryst.* **B31**, 620–621.
- FILHOL, A., ROVIRA, M., HAUW, C., GAULTIER, J., CHASSEAU, D. & DUPUIS, P. (1979). *Acta Cryst.* **B35**, 1652–1660.
- FLANDROIS, S. & CHASSEAU, D. (1977). *Acta Cryst.* **B33**, 2744–2750.
- FRITCHIE, C. J. (1966). *Acta Cryst.* **20**, 892–898.
- GIGLIO, D., LIQUORI, A. M. & MAZZARELLA, L. (1969). *Lett. Nuovo Cimento Ser. I*, **1**, 135–139.
- GOVERS, H. A. J. (1978). *Acta Cryst.* **A34**, 960–965.
- GOVERS, H. A. J. (1979). *Lect. Notes Phys.* **96**, 303–308.
- GOVERS, H. A. J. & DE KRUIF, C. G. (1980). *Acta Cryst.* **A36**, 428–432.
- HANSON, A. W. (1968). *Acta Cryst.* **B24**, 768–778.
- JOHNSON, C. K. & WATSON, C. R. (1976). *J. Chem. Phys.* **64**, 2271–2286.
- KISTENMACHER, T. J., PHILLIPS, T. E. & COWAN, D. O. (1974). *Acta Cryst.* **B30**, 763–768.
- KISTENMACHER, T. J., PHILLIPS, T. E., COWAN, D. O., FERRARIS, J. P. & BLOCH, A. N. (1976). *Acta Cryst.* **B32**, 539–547.
- KITAIGORODSKII, A. I. (1973). *Molecular Crystals and Molecules*. New York: Academic Press.
- KOBAYASHI, H. (1974). *Bull. Chem. Soc. Jpn*, **47**, 1346–1352.
- KOBAYASHI, H. (1978). *Acta Cryst.* **B34**, 2818–2825.
- KOBAYASHI, H., FUMIYUKI, M. & YOSHIHIKO, S. (1971). *Acta Cryst.* **B27**, 373–378.
- KOBAYASHI, H. & KOBAYASHI, K. (1977). *Bull. Chem. Soc. Jpn*, **50**, 3127–3130.
- KONNO, M., ISHII, T. & SAITO, Y. (1977). *Acta Cryst.* **B33**, 763–770.
- KONNO, M. & SAITO, Y. (1975). *Acta Cryst.* **B31**, 2007–2012.
- METZGER, R. M. (1975). *J. Chem. Phys.* **63**, 5090–5097.
- METZGER, R. M. & BLOCH, A. N. (1975). *J. Chem. Phys.* **63**, 5098–5107.
- PHILLIPS, T. E., KISTENMACHER, T. J., BLOCH, A. N. & COWAN, D. O. (1976). *J. Chem. Soc. Chem. Commun.* pp. 334–335.
- PHILLIPS, T. E., KISTENMACHER, T. J., BLOCH, A. N., FERRARIS, J. P. & COWAN, D. O. (1977). *Acta Cryst.* **B33**, 422–428.
- PHILLIPS, T. E., KISTENMACHER, T. J., FERRARIS, J. P. & COWAN, D. O. (1973). *J. Chem. Soc. Chem. Commun.* pp. 471–472.
- SANDMAN, D. J., EPSTEIN, A. J., CHICKOS, J. S., KETCHUM, J., FU, J. S. & SCHERAGA, H. A. (1979). *J. Chem. Phys.* **70**, 305–313.
- SCHULTZ, A. J., STUCKY, G. D., CRAVEN, R., SCHAFFMAN, M. J. & SALAMON, M. B. (1976). *J. Am. Chem. Soc.* **98**, 5191–5197.
- SCOTT, B. A., LA PLACA, S. J., TORRANCE, J. B., SILVERMAN, B. D. & WELBER, B. (1977). *J. Am. Chem. Soc.* **99**, 6631–6639.
- SHIBAEVA, R. P., ATOVMIAN, L. O. & ORFONOVA, M. N. (1969). *Chem. Commun.* p. 1494.
- SHIBAEVA, R. P., ATOVMIAN, L. O. & ROZENBERG, L. P. (1969). *Chem. Commun.* pp. 649–650.
- SHIBAEVA, R. P. & ROZENBERG, L. P. (1976). *Sov. Phys. Crystallogr.* **20**, 581–584.
- SHIBAEVA, R. P. & YAROCKINA, O. V. (1975). *Sov. Phys. Dokl.* **20**, 304–305.
- SHIROTANI, I. & KOBAYASHI, H. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2595–2596.
- SHMUELI, V. & GOLDBERG, I. (1973). *Acta Cryst.* **B29**, 2466–2471.
- SOOS, Z. G. (1974). *Ann. Rev. Phys. Chem.* **25**, 121–153.
- WUDL, F., SCHAFFER, D. E., WALSH, W. M., RUPP, L. W., DISALVO, F. J., WASZCZAK, J. V., KAPLAN, M. L. & THOMAS, G. A. (1977). *J. Chem. Phys.* **66**, 377–385.