

## Lattice Energy, Structure and Stability of Three-Dimensional Tetrathiafulvalenium 7,7,8,8-Tetracyanoquinodimethanide (TTF–TCNQ) Models with Segregated and Mixed Stacks

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### Abstract

The lattice energy of tetrathiafulvalenium 7,7,8,8-tetracyanoquinodimethanide ( $C_6H_4S_4 \cdot C_{12}H_4N_4$ ) with space group  $P2_1/c$  and segregated stacks was minimized for four interstack parameters; the unit-cell parameters  $a$ ,  $c$  and  $\beta$ , and the angle,  $\phi$ , between the projection of the longitudinal molecular axis on the  $ac$  plane and  $a$ . The lattice energy of a model with space group  $C2/m$  and mixed stacks was minimized for the unit-cell parameters  $a$ ,  $b$  and  $\beta$  and the intrastack molecular distance,  $c$ . Van der Waals, repulsive and electrostatic interactions were calculated from two sets of atom–atom potentials and atomic charges. The minimum of the  $P2_1/c$  lattice was achieved at a structure with parameters deviating 0.2–2.5% from their observed values. The minimum of the  $C2/m$  lattice was achieved at a structure with parameters reasonably close to the observed values of related TCNQ compounds. The latter structure provided to be 9.2–16.8 kJ mol<sup>-1</sup> more stable than the  $P2_1/c$  modification, indicating the possibility of the preparation of mixed-stack structures.

### Introduction

The one-dimensional structures of TTF and TCNQ segregated and mixed stacks can be predicted partly, when the atom–atom approximation (Kitaigorodskii, 1973) is used for the calculation of stack energy and this energy is minimized for the relevant structural parameters (Govers & de Kruijff, 1980; Govers, 1981). This prediction can be considered the first step in a more complete three-dimensional calculation of stable lattice structures of organic conductors like TTF–TCNQ. The underlying idea is that a simultaneous minimization of lattice energy for intra- and interstack structural parameters would require too much computational time. Here we perform the second step of a separate minimization for (mainly) interstack parameters. TTF–TCNQ crystallizes in space group  $P2_1/c$  with segregated TTF (donor) and TCNQ

(acceptor) stacks (Kistenmacher, Phillips & Cowan, 1974). Our first objective was the prediction of this observed structure in order to test our method.

Several authors have argued the existence and stability of mixed stack lattices with partial charge transfer from donor to acceptor molecules within the stack (e.g. Goldberg & Shmueli, 1973; Soos, 1978; Torrance, 1979). Therefore we constructed a mixed-stack TTF–TCNQ lattice with space-group symmetry  $C2/m$  from structures observed for related TCNQ compounds. Then we attributed to it the charge transfer,  $\rho = 0.59 e$ , identical to the value observed for the  $P2_1/c$  lattice (Metzger, 1977) and we calculated its minimum energy in order to compare its stability to that of the latter one. The two models are depicted in Figs. 1 and 2, including the structure parameters varied.

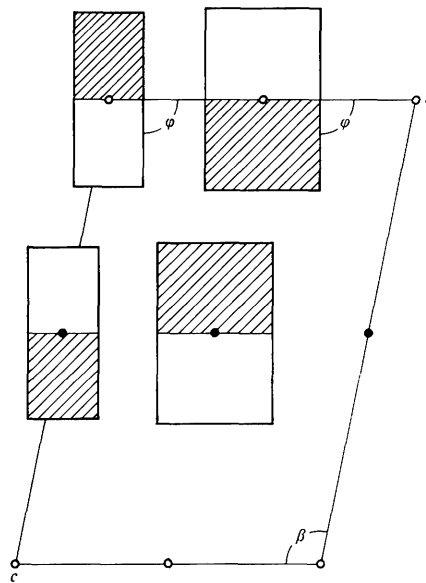


Fig. 1. A view along the stacking axis,  $b$ , of the  $P2_1/c$  model. Structural (interstack) parameters:  $a$ ,  $c$ ,  $\beta$  and  $\phi$ . Broad rectangles represent TCNQ molecules, narrow ones TTF molecules. Shaded parts are directed downwards. Shaded centroids are at  $\frac{1}{2}b$ .

Throughout the calculation of intermolecular interaction the van der Waals, repulsive and classical electrostatic contributions were considered only. We are aware of some limitations of this method. It was shown (Metzger, 1981) that it can explain only 75 or 83% of the enthalpy of sublimation of TTF-TCNQ observed experimentally and not its complete value as has been stated before (Govers, 1978; de Kruijff & Govers, 1980). However, quantum-mechanical calculation, although more sophisticated and provided with the perspective of the prediction of the charge transfer, explains an even lower fraction of this enthalpy (Metzger, 1981). A second limitation had already appeared in our stack-structure predictions (Govers & de Kruijff, 1980; Govers, 1981). Only the observed structures of TTF and TCNQ segregated stacks with longitudinal molecular slip could be predicted and not the observed TTF stacks with eclipsed configuration and TCNQ stacks slipped transversally. Furthermore, recent correction of an error in these calculations (Govers, 1982) certainly does not improve this situation and one could doubt seriously of the separate minimization for intra- and interstack parameters. Therefore we decided to apply the observed TTF and TCNQ stack structures in our  $P2_1/c$  model and to vary simultaneously interstack parameters and the intrastack molecular distance in our  $C2/m$  model.

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 might well be within the limit of accuracy of the method. In both the segregated and the mixed-stack models calculation values of  $\rho = 0.0$  for uncharged molecules and of  $\rho = 0.59 e$  will be applied in order to study the influence of electrostatic interaction on the structures predicted.

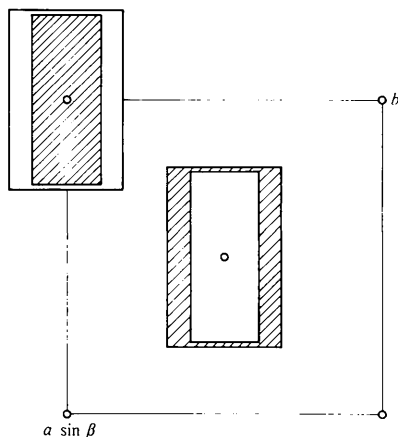


Fig. 2. A view along the stacking axis,  $c$ , of the  $C2/m$  model. Structural parameters:  $a$ ,  $b$ ,  $c$  and  $\beta$ . Broad rectangles represent TCNQ molecules, narrow ones TTF molecules. Shaded molecules are beneath unshaded ones.

Therefore four (MSR, MCR, SSR, SCR) out of eight Soos-type stack structures (Soos, 1974) are considered.

### Method

The lattice 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 lattice and the  $n'$  atoms,  $j$ , of the  $z$  surrounding molecules,  $k$  (Govers, 1978):

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

with

$$E_{kij}(r_{kij}) = -A_{tij} r_{kij}^{-6} + B_{tij} \exp(C_{tij} r_{kij}) + \frac{e_i e_j}{r_{kij}} \quad (2)$$

In (1) the factor  $\frac{1}{2}$  is introduced to avoid double counting of pair interactions.  $N$  is the number of molecules in the lattice, and  $r_{kij}$  are the interatomic distances. The parameters  $A_{tij}$ ,  $B_{tij}$  and  $C_{tij}$  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 with summation limits of about 5.5 Å, yielding 80% of the theoretical lattice energy for set 1, and with summation limits of 15 Å, yielding 100%, for set 2.  $E$  can be divided into a contribution  $E_{vdw+rep}$ , resulting from the van der Waals plus repulsive term in (2) and a contribution  $E_{electr}$ , resulting from the coulombic term in (2). The parameters  $e_i$  and  $e_j$  in (2) are the point charges on the atoms  $i$  and  $j$ . For the molecules charged  $\pm 1 e$  we used the CNDO/2 and CNDO-SCF charge distributions by Epstein, Lipari, Sandman & Nielsen (1976) (their sets 6 and 7 of Table II and sets 4 and 5 of Table III). The CNDO/2 distribution was applied in combination with the atom-atom potential set 1, the CNDO-SCF distribution with set 2 without special reason. The electrostatic contribution,  $E_{electr}$ , was calculated by the Ewald method with convergence acceleration (Williams, 1971). As convergence acceleration factor we applied the value  $K = 0.3$ . The value of the electrostatic contribution at  $\rho = 0.59 e$  (or 0.0) was calculated from its value at  $\rho = 1.0 e$  via (Epstein, Lipari, Sandman & Nielsen, 1976):

$$E_{electr}(\rho) = \rho^2 E_{electr}(\rho = 1 e). \quad (3)$$

The interatomic distances  $r_{kij}$  were calculated from (Govers, 1979)

$$r_{kij} = |\mathbf{D}_s \mathbf{D}^{-1} (\tilde{\mathbf{R}}_k \mathbf{K}_{jk} + \mathbf{T}_k) + \mathbf{D} \mathbf{t}_k - (\tilde{\mathbf{R}}_o \mathbf{K}_{io} + \mathbf{T}_o)|. \quad (4)$$

In (4) the elements of matrix  $\mathbf{D}$  are a function of the unit-cell parameters  $a$ ,  $b$ ,  $c$  and  $\beta$  as defined in Figs. 1

and 2.  $s_k$  and  $t_k$  are the matrix and vector of the symmetry operation, which generates a certain surrounding molecule,  $k$ , from the asymmetric unit. Both of these are given by the space-group symmetry of the model and by the summation limits defining the surrounding molecules to be included.  $\mathbf{K}_{jk}$  and  $\mathbf{K}_{io}$  are the absolute atomic coordinates of the surrounding ( $k$ ) and central ( $o$ ) molecules, expressed in the axial system of the principal axes of inertia, of the observed TTF or TCNQ molecular geometry (Kistenmacher, Phillips & Cowan, 1974). The elements of the vectors  $\mathbf{T}_k$  and  $\mathbf{T}_o$  define the positions of the centres of gravity of surrounding and central molecules (see Figs. 1 and 2). The elements of the matrices  $\mathbf{R}_k$  and  $\mathbf{R}_o$  are a function of the Eulerian angles  $\varphi$ ,  $\theta$ ,  $\psi$ , which define the orientations of surrounding or central molecules with respect to a unit-cell fixed orthogonal axial system.

In the  $P2_1/c$  model  $\varphi$  denotes the angle between the projection of the longitudinal molecular axis on the  $ac$  plane and  $a$ , as shown in Fig. 1. The values of  $\varphi$  of TTF and TCNQ are assumed to be identical during the variation of  $a$ ,  $c$ ,  $\beta$  and  $\varphi$ .  $\theta$  denotes the angle between the longitudinal axis itself and its projection on the  $ac$  plane. The values of the  $\theta$ 's of TTF and TCNQ are constant, equal to those observed in TTF-TCNQ ( $+24.5$  and  $-34.0^\circ$ , respectively), and the transversal molecular axes remain in the  $ac$  plane during the variation, *i.e.*  $\psi = 90^\circ$  for TTF and TCNQ. The value of  $b$  is that observed in TTF-TCNQ (Kistenmacher, Phillips & Cowan, 1974).

In the  $C2/m$  model (see Fig. 2) the Eulerian angles  $\varphi$  and  $\psi$  are  $0^\circ$  for both TTF and TCNQ. The Eulerian angle  $\theta (= 90^\circ - \beta)$  denotes the angle between the normals on the molecular planes and the  $ab$  plane. As the TTF and TCNQ molecules are parallel in the mixed stack,  $\theta$  is identical for TTF and TCNQ. It should be noted that along with  $a$ ,  $b$  and  $\beta$  the unit-cell parameter  $c$  is varied as we vary the intermolecular intrastack distance (*i.e.* the elements of the vectors  $\mathbf{T}$  in the direction of the stacking axis) in this model.

Equations (1)–(4) were used in a one- or two-run gridpoint scan of  $E$  similar to other calculations of

lattice energies and structures (*e.g.* Giglio, Liquori & Mazzarella, 1969). For the  $P2_1/c$  model the increments 0.2, 0.2 Å, 10 and  $10^\circ$  were used for  $a$ ,  $c$ ,  $\beta$  and  $\varphi$ , respectively, in a single run. For the  $C2/m$  model we used the increments 0.5, 0.2, 0.2 Å and  $10^\circ$  for  $a$ ,  $b$ ,  $c$  and  $\beta$ , respectively, in the first run. In a final run we used the increments 0.2, 0.2, 0.2 Å and  $5^\circ$ . By applying graphical interpolation we were able to find absolute minima with an accuracy of about  $\pm 0.05$  Å (for  $a$ ,  $b$ ,  $c$ ),  $\pm 1^\circ$  (for  $\beta$  and  $\varphi$ ) and  $\pm 2.0$  kJ mol $^{-1}$  (for  $E$ ). This accuracy is high enough in view of the errors introduced by uncertainties of the atom-atom potential parameters, atomic charges, molecular geometries and by the assumptions made in the models. Moreover, errors in  $E$  introduced by summation limits amount to several percent, up to 4 kJ mol $^{-1}$ , of the lattice energy (Govers, 1978; Williams, 1971).

The total number of evaluations of the lattice energy was limited to about three hundred, low enough for rapid calculations on a CDC-Cyber 173 computer.

### Calculations and results

The results for the  $P2_1/c$  model with segregated stacks are included in Table 1, together with the observed lattice structure and unit-cell volume.  $a$ ,  $c$ ,  $\beta$  and  $\varphi$  were varied within ranges of  $\pm 0.4$ ,  $\pm 0.6$  Å,  $\pm 10$  and  $\pm 10^\circ$ , respectively, around their observed values. The increments used are given under *Method*.

The final results for the  $C2/m$  model with mixed stacks are included in Table 2 together with the observed lattice parameters of some related TCNQ compounds and the unit-cell volumes. In a first run  $a$ ,  $b$ ,  $c$  and  $\beta$  were varied within 10.0–14.0, 12.2–13.4, 6.8–7.2 or 6.6–7.0 Å, and  $90$ – $120^\circ$  respectively. The ranges for  $a$ ,  $b$  and  $\beta$  were inferred from the observed values for the related TCNQ compounds and from a comparison of the molecular dimensions of TTF, anthracene, benzidine and TMPD (see Table 3). The two different ranges for  $c$  stem from previous calculations of intrastack structures *via* different sets of

Table 1. Predicted and observed crystalline structure of TTF-TCNQ (segregated stacks)

$a$ (Å)	$c$ (Å)	$\beta$ ( $^\circ$ )	$\varphi$ ( $^\circ$ )	$V^{**}$ (Å $^3$ )	$E$ (kJ mol $^{-1}$ )	Contribution
12.56 $\pm$ 0.05	18.0 $\pm$ 0.1	102.5 $\pm$ 1	-92.2 $\pm$ 1	842.9	-103.9 $\pm$ 2.0	$E_{\text{vdw}}^* + E_{\text{rep}}^*$
12.35 $\pm$ 0.05	18.0 $\pm$ 0.1	102.5 $\pm$ 1	-92.4 $\pm$ 1	828.8 $\pm$ 6.3	-140.4 $\pm$ 2.0	$E_{\text{vdw}}^* + E_{\text{rep}}^* + E_{\text{electr}}^\dagger$
12.48 $\pm$ 0.04	18.3 $\pm$ 0.1	100.5 $\pm$ 1	-90.0 $\pm$ 1	857.6	-83.8 $\pm$ 2.0	$E_{\text{vdw}}^\ddagger + E_{\text{rep}}^\ddagger$
12.24 $\pm$ 0.05	18.44 $\pm$ 0.05	102.5 $\pm$ 1	-90.0 $\pm$ 1	841.5 $\pm$ 5.4	-124.4 $\pm$ 2.0	$E_{\text{vdw}}^\ddagger + E_{\text{rep}}^\ddagger + E_{\text{electr}}^\S$
12.298	18.468	104.46	-91.0 $\pm$ 1††	839.9	TTF-TCNQ¶	

\* Set 1 of Table 1 by Govers (1978).

† Set 6 of Table II and set 4 of Table III by Epstein, Lipari, Sandman & Nielsen (1976).

‡ Set 2 of Table 1 by Govers (1978).

§ Set 7 of Table II and set 5 of Table III by Epstein, Lipari, Sandman & Nielsen (1976).

¶ Kistenmacher, Phillips & Cowan (1974).

\*\* Calculated *via*  $V = abc \sin \beta$ .

†† Mean value of the observed values for TTF and TCNQ molecules.

Table 2. Predicted crystalline structure of TTF-TCNQ (mixed stacks) and observed structures of some related TCNQ compounds

$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)	$V^{**}$ (Å <sup>3</sup> )	$E$ (kJ mol <sup>-1</sup> )	Contribution
10.46 ± 0.04	12.37 ± 0.04	6.94 ± 0.04	104.5 ± 0.5	869.4 ± 5	-102.2 ± 2.0	$E_{vdw}^* + E_{rep}^*$
10.47 ± 0.04	12.37 ± 0.04	6.90 ± 0.05	105.0 ± 0.5	863.2 ± 5	-157.1 ± 2.0	$E_{vdw}^* + E_{rep}^* + E_{elect}^†$
10.81 ± 0.04	12.96 ± 0.04	6.61 ± 0.04	105.0 ± 0.5	894.5 ± 5	-75.0 ± 0.4	$E_{vdw}^† + E_{rep}^†$
10.97 ± 0.06	12.86 ± 0.04	6.63 ± 0.04	108.0 ± 0.5	889.5 ± 5	-133.7 ± 0.4	$E_{vdw}^† + E_{rep}^† + E_{elect}^§$
9.88	12.71	7.72	97.34	961.5		TMPD <sup>+</sup> -TCNQ <sup>-¶</sup>
12.231	12.679	6.477	94.84	1000.9		Benzidine-TCNQ <sup>††</sup>
11.476	12.947	7.004	105.4	1003.3		Anthracene-TCNQ <sup>‡‡</sup>

\* Set 1 of Table 1 by Govers (1978).

† Set 6 of Table II and set 4 of Table III by Epstein, Lipari, Sandman & Nielsen (1976).

‡ Set 2 of Table 1 by Govers (1978).

§ Set 7 of Table II and set 5 of Table III by Epstein, Lipari, Sandman & Nielsen (1976).

¶ Hanson (1965).

\*\* Calculated via  $V = abc \sin \beta$ .

†† Yakushi, Ikemoto & Kuroda (1974).

‡‡ Williams & Wallwork (1968).

Table 3. Crude molecular dimensions of TTF, TMPD, benzidine and anthracene

Molecule	Length (Å)*	Surface (Å <sup>2</sup> )*	Reference
TTF	7.8	23.4	(a)
TMPD	7.0	27.3	(b)
Benzidine	10.1	40.0	(c)
Anthracene	8.8	42.2	(d)

References: (a) Kistenmacher, Phillips & Cowan (1974); (b) Hanson (1965); (c) Yakushi, Ikemoto & Kuroda (1974); (d) Williams & Wallwork (1968).

\* Estimated via rectangles drawn around the exterior atoms of the molecular geometries depicted in the references cited.

atom-atom potentials (Govers, 1981, 1982). In this way we obtained a crude minimum with values of the structural parameters, around which we constructed smaller ranges for the final run. The increments used in both runs were mentioned under *Method*.

### Conclusions

The following conclusions may be drawn from the results in Table 1. The various atom-atom parameters and atomic charges all predict a segregated-stack crystalline structure close to the observed one. The minimum of the  $P2_1/c$  lattice was achieved at structures with parameters deviating 0.2-2.5% from their observed values. This result is a strong support for a further application of the atom-atom approximation. For the best calculation, which applies to set 2 of Table 1 by Govers (1978) in combination with CNDO-SCF atomic charges by Epstein, Lipari, Sandman & Nielsen (1976), even complete accordance is obtained between predicted and observed structural parameters. The results obtained by set 2 of Table 1 in combination with

CNDO/2 atomic charges are less good and imply too low values for  $a$ ,  $c$  and the unit-cell volume. The inclusion of electrostatic interaction causes a small contraction of the unit-cell volume of 1-2%. The four exterior nitrogen atoms of TCNQ and the four sulfur atoms of TTF, bearing the highest opposite charges, can be brought at smaller interstack distances by a small decrease of unit-cell edge  $a$  or an increase of  $\beta$  (see Fig. 1). This can be considered as the main reason for this contraction.

From Table 2 we infer the following conclusions for the mixed-stack model. Each of the four calculations predict a minimum energy at values for the structural parameters, which are reasonably close to the observed values of three related TCNQ compounds. The unit-cell volume calculated for TTF-TCNQ and observed for TMPD-TCNQ, benzidine-TCNQ and anthracene-TCNQ showing a series of increasing values similar to that of the surfaces of the rectangles, which can be drawn around the exterior atoms of the flat donor molecules involved (see Table 3).

In the same way the series of values for the unit-cell parameter  $a$  is correlated to the series of the lengths of these donor rectangles (see Fig. 1 and Table 3). The mean values calculated for  $b$ ,  $c$  and  $\beta$  of TTF-TCNQ are close to the corresponding mean values of the observed structures. In this comparison the observed value for  $c$  of TMPD-TCNQ is exceptional as this structure has stacks slipped longitudinally, whereas the other structures have eclipsed stacks. From this comparison with observed structures we could not decide which calculation should be considered the better one. The inclusion of electrostatic interaction produces the expected small contractions of the structures. A comparison of the results of Table 1 and 2 shows that the energy of the mixed hypothetical  $C2/m$  structure is 9.2-16.8 kJ mol<sup>-1</sup> lower than that of the calculated and observed segregated stack,  $P2_1/c$ , structure. This is

mainly caused by the surplus value of the electrostatic contribution in the  $C2/m$  model. It suggests that a non-conducting mixed stack TTF–TCNQ structure can be prepared. At the same time it suggests the application of the atom–atom approximation for the prediction of conducting segregated stack structures, when only non-conducting mixed-stack structures are observed (e.g. for anthracene–TCNQ or benzidine–TCNQ). However, in the *Introduction* we have mentioned already some serious limitations of our method. In view of the apparent importance of electrostatic interaction for the relative stabilities of structures we would stress the uncertainties introduced by the assumption of a charge-transfer of  $\rho = 0.59 e$  for the  $C2/m$  model.

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## The Electrostatic Term in Lattice-Energy Calculations for Lithium Formate Monodeuterate: Determination from the Experimental Electron Density

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#### Abstract

The electrostatic energy of crystalline  $\text{LiCHO}_2 \cdot \text{D}_2\text{O}$  has been calculated with three sets of net atomic charges. These sets have been obtained from *ab initio* and extended Hückel calculations as well as by the method of Tsirel'son & Ozerov [*Sov. Phys. Crystallogr.* (1979), **24**, 662–666] from the X-ray electron density. It is shown that only the 'experimental' set of net atomic charges provides good agreement with the experimental evaluation of the lattice energy for  $\text{LiCHO}_2 \cdot \text{D}_2\text{O}$ .

been given by Tsirel'son & Ozerov (1981). These authors also proposed the determination of the idempotent charge–bond-order matrix from X-ray data (Tsirel'son & Ozerov, 1979). When the idempotent condition is taken into account an antisymmetric many-electron wave function is produced. This function describes the experimental electron density and, as a result, gives physically reliable net atomic charges.

The first application of the method above was realized on a lithium formate monodeuterate (LFD) crystal (Tsirel'son, Zavodnik, Fomitscheva, Ozerov, Kuznetsova & Rez, 1980). This crystal has an exceptional capacity for second harmonic generation. It has no center of symmetry (space group  $Pna2_1$ ) and is pyroelectric, piezoelectric and ferroelectric and also has nonlinear optical properties. In conjunction with its high dielectric strength, these properties are the basis of a wide use of LFD as a laser material. The deter-

Accurate diffraction data allows direct determination of the electron density to be made, leading to the understanding of the nature of the chemical bond. A complete survey of methods used for this purpose has