Acta Cryst. (1978). A**34**, 960–965

The Atom–Atom Approximation and the Lattice Energies of 2,2'-Bis-1,3-dithiole (TTF), 7,7,8,8-Tetracyanoquinodimethane (TCNQ) and their 1 : 1 Complex (TTF–TCNQ)

By H. A. J. Govers

General Chemistry Laboratory, Chemical Thermodynamics Group, Rijksuniversiteit Utrecht, Padualaan 8, *Utrecht* 2506, *The Netherlands*

(*Received* 4 *May* 1978; *accepted* 2 *June* 1978)

The van der Waals and repulsive contributions to the lattice energies of TTF ($C_6H_4S_4$), TCNQ ($C_{12}H_4N_4$) and TTF–TCNQ ($C_6H_4S_4.C_{12}H_4N_4$) at room temperature were calculated by the atom–atom approximation. In addition the Madelung electrostatic contributions were calculated by Ewald's method for TTF and TCNQ. The combined atom–atom and electrostatic contributions produced lattice energies in accordance with the experimental enthalpies of sublimation and dissociation within 0–5 kcal mol^{-1}.

Introduction

Interest in the calculation of the lattice energies of organic donor–acceptor crystals with high electrical conductivity is growing (Metzger & Block, 1975; Epstein, Lipari, Sandman & Nielsen, 1976; Klimenko, Krivnov, Ovchinnikov, Ukrainskii & Shvets, 1976; Scott, La Placa, Torrance, Silverman & Welber, 1977; Torrance & Silverman, 1977). In addition, enthalpies of formation and sublimation have been determined experimentally (Metzger, 1977). The main purpose of these studies is to obtain a better understanding of the degree of ionicity and charge transfer, and hence of the unusual electrical and magnetic properties of these crystals, of which TTF–TCNQ is the most prominent example. Meanwhile a better understanding of the formation of multiple crystal phases, including disordered ones, and/or multiple stoichiometries is aimed at.

Several energies contribute to the crystal stability against transition into nonconducting phases or against dissociation into separate donor and acceptor lattices. Among these are the classical electrostatic (Madelung) energy, the van der Waals energy, the core repulsion energy, the exchange energy caused by intermolecular electron wave-function overlap along chains, the configuration interaction energy and the energy of delocalization of electrons and holes in bands. The electrostatic energy is the only one which could be calculated rather easily by the Ewald or Evjen method (Epstein *et al.*, 1976). The other contributions demand extensive quantum-mechanical calculations, which still have to be developed (Smit, 1978; André & Ladik, 1975; Rae, 1969). Therefore, we are studying here the substitution of these other contributions by the simple attractive and repulsive terms of the atom–atom approximation (Kitaigorodskii, 1973). The latter approximation is rather well established, for single-component systems at least, and offers possibilities for the calculation of molecular substitutional and orientational disorder in multicomponent systems (Govers, 1977). For the sake of simplicity and in accordance with the derivation of the interatomic interaction parameters available (Govers, 1975; Williams, 1967; Nauchitel' & Mirskaya, 1972; Mirskaya & Nauchitel', 1972), we opt for a static atom–atom approximation, in which lattice dynamics are either ignored completely or estimated by rough statistical considerations.

As TTF–TCNQ shows the considerable charge transfer of $\rho = 0{\cdot}59$ e* (Metzger, 1977) from a TTF molecule to a TCNQ molecule, we also wish to examine the atom–atom approximation in pure TTF and pure TCNQ. Similar atom–atom potential calculations were performed previously for neutral TCNQ complexes (Shmueli & Goldberg, 1973). In these crystals intermolecular charge transfer will be less or even zero as will the electrostatic contribution to the lattice energy. In contrast to the case TTF–TCNQ, the latter contribution has not yet been calculated for TTF and TCNQ and therefore we shall estimate it from molecular charge distributions, which were used previously for TTF–TCNQ. Moreover, by the combined calculation of the lattice energies of the complex and its components the stability of the complex against dissociation into its components can be estimated.

Method

The relevant thermodynamic quantities are shown in Fig. 1. In this scheme ΔH_f is the heat of formation at standard temperature and pressure. $\Delta H_{\rm diss}$ is the

---

* Hereafter we shall use the notation TTF$^{\rho+}$–TCNQ$^{\rho-}$.

standard heat of dissociation of $TTF^{\varrho+}$–$TCNQ^{\varrho-}$, ΔH_{subl} denotes the room-temperature heat of sublimation, $I(g)$ the ionization potential of gaseous TTF and $A(g)$ the electron affinity of gaseous TCNQ (c and g denote crystalline and gaseous phases respectively). The lattice (binding) energy of $TTF^{\varrho+}$–$TCNQ^{\varrho-}$, $U(TTF^{\varrho+}$–$TCNQ^{\varrho-})$, is defined as the negative enthalpy difference between crystalline $TTF^{\varrho+}$–$TCNQ^{\varrho-}$ and a gaseous mixture of ρ moles of univalent $TTF^+ + TCNQ^-$ molecules and $(1-\rho)$ moles of neutral $TTF^0 + TCNQ^0$ molecules. The lattice energies U(TTF) and U(TCNQ) are simply the negative enthalpy differences between a mole of crystalline and a mole of gaseous neutral molecules of TTF and TCNQ, respectively. All quantities, including those of TTF–TCNQ, are defined per mole of *monomer* molecules.

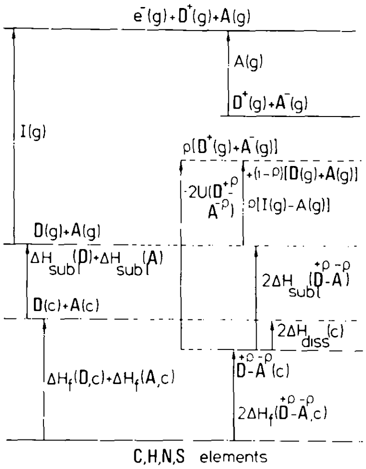

Fig. 1. Enthalpy scheme of TTF, TCNQ and $TTF^{\varrho+}$–$TCNQ^{\varrho}$ (A = TCNQ, D = TTF).

We use the following expressions for the calculations of the lattice energies

$$U = -\Delta H_{subl} \quad (1)$$

$$U(TTF^{\varrho+}\text{–}TCNQ^{\varrho-}) = -\Delta H_{subl}(TTF^{\varrho+}\text{–}TCNQ^{\varrho-}) - \tfrac{1}{2}\rho[I(g) - A(g)] \quad (2)$$

$$-\Delta H_{subl}^{calc} = E_{vdw} + E_{rep} + E_{electr}(+E_{dyn}). \quad (3)$$

(1) and (2) follow directly from Fig. 1. In (3), E_{vdw} is the attractive contribution of the intermolecular van der Waals interactions, E_{rep} is the repulsive energy and E_{electr} is the classical (Madelung) electrostatic energy. The lattice sum of these three contributions is considered to be a sum of interatomic interactions E_{kij} between the n atoms i of a central molecule and the n' atoms j of the z surrounding molecules k:

$$-\Delta H_{subl}^{calc} = \tfrac{1}{2}N \sum_k^z \sum_i^n \sum_j^{n'} E_{kij}(r_{kij}) \quad (4)$$

with

$$E_{kij}(r_{kij}) = -A_{tij}r_{kij}^{-6} + B_{tij}\exp(-C_{tij}r_{kij}) + \frac{e_ie_j}{r_{kij}}. \quad (5)$$

In (4) the factor $\frac{1}{2}$ is introduced to avoid double

Table 1. *Parameters of interatomic potentials and summation limits*

Units are: kcal mol⁻¹ Å⁻⁶ (A_{tij}); kcal mol⁻¹ (B_{tij}); Å⁻¹ (C_{tij}) and Å (s.l.$_{tij}$). The first row of each type *tij* is set 1, the second row is set 2.

tij	A_{tij}	B_{tij}	C_{tij}	s.l.$_{tij}$	Reference
CC	568	83630	3·6	6	Williams (1967)
	358	42000	3·579	15	Mirskaya & Nauchitel' (1972)
CH	125	8766	3·67	5·5	Williams (1967)
	130·5	35700	4·121	15	This work*
CN	375·3	11480	3·6	6	Govers (1975)
	305	42000	3·676	15	This work*
CS	1154	140189	3·5435	6	This work†
	916·9	99400	3·532	15	This work*
HH	27·3	2654	3·74	5	Williams (1967)
	41·3	30200	4·857	15	Mirskaya & Nauchitel' (1972)
HN	143	4833	3·67	5·5	Govers (1975)
	108·5	35700	4·25	15	This work*
HS	253	24974	3·6135	5·5	This work†
	337·7	84300	4·06	15	This work*
NN	760	105400	3·6	6	Govers (1975)
	259	42000	3·778	15	Mirskaya & Nauchitel' (1972)
NS	1335	157382	3·5435	6	This work†
	783	99400	3·627	15	This work*
SS	2345	235000	3·487	6	Nauchitel' & Mirskaya (1972)
	2345	235000	3·487	15	Nauchitel' & Mirskaya (1972)

* A_{XY}, B_{XY}, C_{XY} calculated from A_{XX}, A_{YY}, ... (set 2) by the combining laws of Mirskaya & Nauchitel' (1972) and Nauchitel' & Mirskaya (1972); $X \neq Y$ = C, H, N, S.

† Calculated by the combining laws $A_{XY} = [A_{XX}\,(\text{set 1})\,A_{YY}\,(\text{set 1})]^{1/2}$; $B_{XY} = [B_{XX}\,(\text{set 1})\,B_{YY}\,(\text{set 1})]^{1/2}$; $C_{XY} = \frac{1}{2}[C_{XX}\,(\text{set 1}) + C_{YY}\,(\text{set 1})]$; X = C, H, N; Y = S (Williams, 1967; Sams, 1964).

counting of pair interactions, N is the number of molecules in the lattice, and r_{kij} are the interatomic distances, which in our approach will be calculated from the known room-temperature crystal structure of TTF (Cooper, Edmonds, Wudl & Coppens, 1974), TCNQ (Long, Sparks & Trueblood, 1965) and TTF-TCNQ (Kistenmacher, Philips & Cowan, 1974). The parameters A_{tij}, B_{tij} and C_{tij} in (5) depend only on the ten different types tij of interatomic pairs CC, CH, CN, CS, ..., which exist for the C, H, N and S atoms of TTF and TCNQ. These parameters are listed in Table 1, together with the summation limits s.l.$_{tij}$, *i.e.* together with the interatomic distances beyond which the lattice summation is cut off. Two sets are given: set 1 demands the introduction of a factor 1·25 in $E_{\mathrm{vdW}} + E_{\mathrm{rep}}$, without which only 80% of the attractive and respulsive contribution is obtained (Govers, 1975, 1974; Williams, 1967); set 2 demands the inclusion of the dynamical contribution E_{dyn} in (3), as it has been derived with the explicit exclusion of lattice and gaseous dynamical contributions (Nauchitel' & Mirskaya, 1972; Mirskaya & Nauchitel', 1972). This contribution will be estimated as $2RT$ (Govers, 1974; Mirskaya & Nauchitel', 1972; Rae, 1969), where R is the gas constant and T is the absolute temperature.

The parameters e_i and e_j in (5) are the point charges on the atoms i and j. Several charge distributions will be examined for the calculation of E_{electr}. These distributions were used for calculation on TTF–TCNQ by other investigators and are listed in Table 2 (for neutral TTF) and in Table 3 (for neutral TCNQ). The numbering of atoms in TTF and TCNQ is given in Fig. 2. The electrostatic contributions in TTF and TCNQ will be calculated by the Ewald method with convergence acceleration (Williams, 1971).

For TTF–TCNQ, which is considered to be completely ordered, the total lattice energy is calculated as the average of the two energies which are obtained if a TTF or a TCNQ molecule is chosen as the central one (Govers, 1977). The 0·07 Å shift of the position of the hydrogen-atom attraction and repulsion centre, which has to be performed in potential set 1, will not be applied for the sake of simplicity. This introduces an error in the calculated energies of less than 2% (Govers, 1974). The rapid summation cut off for set 1 introduces errors of less than 4% (Govers, 1974, 1975). The summation limits of set 2 introduce errors of less

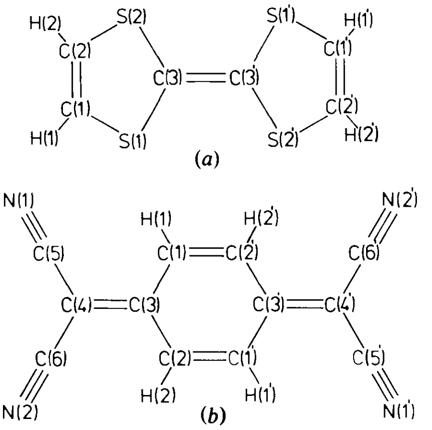

Fig. 2. The numbering of atoms in (*a*) TTF and (*b*) TCNQ.

Table 2. *Atomic point charges* (e) *and electrostatic lattice energy* (*kcal mol*$^{-1}$) *of TTF*

	CNDO/2(a) Metzger	CNDO/2(b) Lipari	CNDO–SCF(c) Lipari	CNDO/2(d) Ratner
C(1,1')*	0·0048	0·0060	−0·1523	−0·0240
C(2,2')	0·0045	0·0060	−0·1523	−0·0240
C(3,3')	0·0364	0·0464	−0·1139	−0·0050
H(1,1')	0·0416	0·0258	0·0882	0·0085
H(2,2')	0·0354	0·0258	0·0882	0·0085
S(1,1')	−0·0664	−0·0550	0·1210	0·0180
$E_{\mathrm{electr}}^{\mathrm{calc}}$	0·10	0·10	−9·32	−0·14

References: (*a*) Metzger & Bloch (1975), first column, Table 4; (*b*) Epstein *et al.* (1976), set 1, Table 3; (*c*) Epstein *et al.* (1976), set 2, Table 3; (*d*) Epstein *et al.* (1976), set 3, Table 3.

* The numbering of atoms is as given in Fig. 2.

Table 3. *Atomic point charges* (e) *and electrostatic lattice energy* (*kcal mol*$^{-1}$) *of TCNQ*

	PPP(a) Lowitz 1	PPP(b) Lowitz 2	*Ab initio*(c) Jonkman	CNDO/2(d) Lipari	CNDO–SCF(e) Lipari
C(1,1',2,2')*	0·0047	0·0142	−0·102	−0·0127	−0·0941
C(3,3')	0·0150	0·0435	−0·212	0·0628	0·0802
C(4,4')	−0·0042	−0·0123	0·188	0·0259	−0·0108
C(5,5',6,6')	0·0760	0·1493	0·088	0·1026	0·1988
H(1,1',2,2')	0·0000	0·0000	0·288	0·0277	0·1477
N(1,1',2,2')	−0·0861	−0·1791	−0·262	−0·1619	−0·2869
$E_{\mathrm{electr}}^{\mathrm{calc}}$	−0·38	−1·78	−30·83	−2·14	−16·63

References: (*a*) Metzger & Bloch (1975), *Qm*, Table 5; (*b*) Metzger & Bloch (1975), *Qn*, Table 5; (*c*) Metzger & Bloch (1975), fourth column, Table 5; (*d*) Epstein *et al.* (1976), set 1, Table 2; (*e*) Epstein *et al.* (1976), set 2, Table 2.

* The numbering of atoms is as given in Fig. 2.

than 1% (Kitaigorodskii, Mirskaya & Tovbis, 1968), as does the convergence-acceleration method for the calculation of E_{electr} (Williams, 1971). We shall use overall errors in the calculated $E_{\text{vdW}} + E_{\text{rep}}$ of 4% for set 1 of Table 1 and of about 3% for set 2. Errors in the calculated E_{electr} as a consequence of structural inaccuracies are considered to be unimportant relative to those caused by inaccuracies in the charge distributions of TTF and TCNQ.

Calculations and results

The results of the calculations of the van der Waals and repulsive energies are given in Table 4. The results of the calculation of the electrostatic energy are given in Table 2 for TTF and in Table 3 for TCNQ.

Table 4. *Van der Waals and repulsive contributions (kcal mol⁻¹) to the lattice energies of TTF, TCNQ and TTF–TCNQ*

Compound	Energy	Set 1 of Table 1	Set 2 of Table 1
TTF	E_{vdW}	−37·18	−32·02
	E_{rep}	14·30	9·46
	$E_{\text{vdW}} + E_{\text{rep}}$	−22·88 ± 0·9	−22·56 ± 0·5
TCNQ	E_{vdW}	−37·15	−24·40
	E_{rep}	12·14	9·19
	$E_{\text{vdW}} + E_{\text{rep}}$	−25·02 ± 1·1	−15·21 ± 0·5
TTF–TCNQ	E_{vdW}	−49·61	−35·00
	E_{rep}	26·21	15·25
	$E_{\text{vdW}} + E_{\text{rep}}$	−23·39 ± 0·9	−19·76 ± 0·5

With regard to sets 1 and 2 in Table 4 remarkable differences have been obtained for the van der Waals and repulsive contributions in TTF–TCNQ and also for the van der Waals contributions in TCNQ. These differences are caused mainly by the differences in the CN, HN and NN potential parameters of Table 1, and the latter differences may be caused in turn by the presence of rather large electrostatic (Rae, 1969) or even charge-transfer (Britton, 1974) interactions in cyano compounds, as the parameters of set 1 were derived on the basis of *e.g.* the heats of sublimation of cyanogen and dicyanoacetylene (Govers, 1975), while those of set 2 have the heat of sublimation of pure nitrogen as their main basis (Mirskaya & Nauchitel', 1972). Moreover, other parameters, which were not derived from the heats of sublimation of cyano compounds, also produced low lattice energies for cyano compounds (Govers, 1975). Therefore we expect the parameters of set 1, in contrast to those of set 2, to contain a large fraction of electrostatic or other interactions, which are typical for single-component cyano compounds. However, this type of interaction is not contained completely in the parameters of set 1, as this set produces the value 13·6 kcal mol⁻¹ for the heat of sublimation of tetracyanoethylene (Govers, 1975), while the experimental value amounts to 19·4 ± 1·5 kcal mol⁻¹ (Boyd, 1963).

With regard to the influence of the charge distributions on the electrostatic contribution to the lattice energy, the results of Tables 2 and 3 show large differences. The need for more reliable charge distributions seems evident. The results can be divided into a group of lower values and a group of higher ones. The lower values are 0·0 ± 0·1 kcal mol⁻¹ for the CNDO/2 distributions of TTF and −1·4 ± 0·5 kcal mol⁻¹ for the Pariser–Pople–Parr and CNDO/2 models of TCNQ. The high values are −9·32 kcal mol⁻¹ (CNDO–SCF) for TTF and −16·63 kcal mol⁻¹ (CNDO–SCF) or even −30·83 kcal mol⁻¹ (*ab initio*) for TCNQ. These differences are remarkable in view of the relatively low and constant values which were found by other investigators for TTF–TCNQ, as shown in Table 5. From the results of Table 5 for TTF^0–TCNQ^0 we conclude that the lower values of our calculations are more reliable than the higher ones. This conclusion is supported by Epstein *et al.* (1976) who consider the CNDO/2 charge distribution more reliable than the CNDO–SCF version.

Table 5. *The electrostatic contribution to the lattice energies of neutral and charge-transferred TTF–TCNQ calculated by other investigators*

Units are kcal mol⁻¹. Note that the other investigators published their values in eV mol⁻¹ of donor–acceptor dimer. Therefore we multiplied their values by the factor 23·0693/2 in order to obtain values in kcal mol⁻¹ of monomer molecules.

Charge-distribution model		E_{electr}	
TTF	TCNQ	$\rho = 0$	$\rho = 0{\cdot}59$
CNDO/2 (Lipari)	CNDO/2 (Lipari)	0·00[a]	9·11[a]*
CNDO–SCF (Lipari)	CNDO–SCF (Lipari)	1·38[a]	−9·96[a]*
CNDO/2 (Lipari)	PPP (Lowitz 1)	0·12[a]	7·83[a]*
CNDO SCF (Lipari)	PPP (Lowitz 1)	0·58[a]	−8·91[a]*
CNDO/2 (Lipari)	PPP (Lowitz 2)	0·12[a]	−8·55[a]*
CNDO–SCF (Lipari)	PPP (Lowitz 2)	1·27[a]	−9·60[a]*
CNDO/2 (Lipari)	ABINITIO (Jonkman)	−1·50[a]	−6·87[a]*
CNDO SCF (Lipari)	ABINITIO (Jonkman)	0·92[a]	−7·70[a]*
CNDO/2 (Ratner)	CNDO/2 (Lipari)	0·81[a]	−9·32[a]*
CNDO/2 (Metzger)	PPP (Lowitz 1)	−0·09[b]	−8·54[b]
CNDO/2 (Metzger)	PPP (Lowitz 2)	−0·01[b]	−10·01[b]
Klimenko ?	Lowitz ?	0·00[c]?	−8·03[c]*
Mean value		0·62 ± 0·5	−8·71 ± 1·0

References: (*a*) Epstein *et al.* (1976), Tables 4 and 5; (*b*) Metzger & Bloch (1975), Table 6; (*c*) Klimenko *et al.* (1976).

* Calculated by $E_{\text{electr}}(\rho) = \rho^2 E_{\text{electr}}(\rho = 1)$ (Epstein *et al.*, 1976).

Conclusions

The final test of the reliability of our calculations has to come from a comparison with experimental results. The relevant thermodynamic quantities and their mutual relations are shown in Fig. 1. In Table 6 the values of the experimental and corresponding calculated quantities are listed. For the calculation of the heat of sublimation and the lattice energy of TTF$^{\varrho+}$–TCNQ$^{\varrho-}$, TTF and TCNQ we used the expressions (1)–(3). The heat of dissociation of TTF$^{\varrho+}$–TCNQ$^{\varrho-}$ was calculated from

$$\Delta H^{\mathrm{calc}}_{\mathrm{diss}}(c) = \tfrac{1}{2}[2\Delta H^{\mathrm{calc}}_{\mathrm{subl}}(\mathrm{TTF}^{\varrho+}\text{–}\mathrm{TCNQ}^{\varrho-}) - \Delta H^{\mathrm{calc}}_{\mathrm{subl}}(\mathrm{TTF}) - \Delta H^{\mathrm{calc}}_{\mathrm{subl}}(\mathrm{TCNQ})]. \quad (6)$$

The values of $E_{\mathrm{vdW}} + E_{\mathrm{rep}}$ are given in Table 4. For E_{electr} (TTF) and E_{electr} (TCNQ) we used the average of the lower values of Tables 2 and 3: 0·0 ± 0·1 and −1·4 ± 0·5 kcal mol^{-1} respectively. As stated before, it is doubtful that the inclusion of a completely extra E_{electr} in $\Delta H^{\mathrm{calc}}_{\mathrm{subl}}$ (TCNQ, set 1) gives the right result, as the atom–atom parameters of set 1 may contain electrostatic interaction. However, by doing this we cannot introduce a large error, as E_{electr} (TCNQ) seems to be small. For E_{electr} (TTF$^{\varrho+}$–TCNQ$^{\varrho-}$) we used the mean value −8·7 ± 1·0 kcal mol^{-1}, as calculated from a large number of results published by other investigators (see Table 5). For $2RT$ we used the room-temperature value 1·2 ± 0·5 kcal mol^{-1}. The experimental heats of sublimation of TTF and TCNQ were extrapolated to $T = 298{\cdot}15$ K by a temperature dependence of −15 ± 10 cal K^{-1} mol^{-1}. The values for ρ, $I(g)$ and $A(g)$ were those mentioned by Metzger (1977). The experimental heats of sublimation and dissociation of TTF$^{\varrho+}$–TCNQ$^{\varrho-}$ were calculated from

$$\Delta H^{\mathrm{exp}}_{\mathrm{diss}}(c) = \tfrac{1}{2}[\Delta H^{\mathrm{exp}}_{f}(\mathrm{TTF},c) + \Delta H^{\mathrm{exp}}_{f}(\mathrm{TCNQ},c) - 2\Delta H^{\mathrm{exp}}_{f}(\mathrm{TTF}^{\varrho+}\text{–}\mathrm{TCNQ}^{\varrho-})] \quad (7)$$

$$\Delta H^{\mathrm{exp}}_{\mathrm{subl}}(\mathrm{TTF}^{\varrho+}\text{–TCN–}^{\varrho-}) = \tfrac{1}{2}[2\Delta H^{\mathrm{exp}}_{\mathrm{diss}}(c) + \Delta H^{\mathrm{exp}}_{\mathrm{subl}}(\mathrm{TTF}) + \Delta H^{\mathrm{exp}}_{\mathrm{subl}}(\mathrm{TCNQ})]. \quad (8)$$

The expressions (6)–(8) follow directly from Fig. 1.

The following conclusions can be drawn from the values of Table 6. First, the atom–atom approximation in the form of set 1 and in combination with the electrostatic contributions as calculated by other investigators produces values for the heat of sublimation and the lattice binding energy of TTF$^{\varrho+}$–TCNQ$^{\varrho-}$ which are equal to the corresponding experimental values within the error ranges. Therefore this approximation seems to be a very useful and simple way to obtain the values of these kinds of quantities for TCNQ compounds. We shall proceed on these lines, *e.g.* by the calculation of substitutional and orientational disorder phenomena. It is shown that the atom–atom approximation can replace extensive quantum-mechanical calculations for these purposes. The calculated heat of dissociation of TTF$^{\varrho+}$–TCNQ$^{\varrho-}$ is about 3 kcal mol^{-1} higher than the experimental one. This is because the value for the calculated heat of sublimation of TCNQ is 0·5–5·0 kcal mol^{-1} lower than the experimental one. For this reason more reliable quantum-mechanical calculations of the electrostatic energy in this compound have to be performed and more accurate knowledge of the experimental temperature dependence of the experimental heat of sublimation is needed. Nevertheless this comparison of the atom–atom approximation with the heat of dissociation determined on the basis of experimental heats of formation offers an interesting new possibility of deriving and testing atom–atom potential parameters. Moreover, it is shown that the complex is stable against dissociation into its components. The heat of sublimation of TTF is calculated in complete accordance with experiment.

Table 6. *Calculated and experimental heats of sublimation, lattice energies and heats of dissociation of TTF, TCNQ and TTF$^{\varrho+}$–TCNQ$^{\varrho-}$*

Units are kcal mol^{-1}.

	TTF	TCNQ	TTF$^{\varrho+}$–TCNQ$^{\varrho-}$
$\Delta H^{\mathrm{calc}}_{\mathrm{subl}}$ (set 1)	22·9 ± 1·0	26·5 ± 1·2	32·1 ± 1·3
$\Delta H^{\mathrm{calc}}_{\mathrm{subl}}$ (set 2)	21·3 ± 0·7	15·4 ± 0·9	27·3 ± 1·3
$\Delta H^{\mathrm{exp}}_{\mathrm{subl}}$	23·2 ± 1·7$^{(a)}$	27·0 ± 2·5$^{(b)}$	29·6 ± 3·1$^{(b)}$
		31·5 ± 1·3$^{(c)}$	31·9 ± 2·2$^{(c)}$
$-U^{\mathrm{calc}}$ (set 1)			60·3 ± 1·9
$-U^{\mathrm{calc}}$ (set 2)			55·3 ± 1·8
$-U^{\mathrm{exp}}$			57·8 ± 3·4$^{(b)}$
			60·1 ± 2·6$^{(c)}$
$\Delta H^{\mathrm{calc}}_{\mathrm{diss}}(c)$ (set 1)			7·4 ± 1·5
$\Delta H^{\mathrm{calc}}_{\mathrm{diss}}(c)$ (set 2)			9·0 ± 1·3
$\Delta H^{\mathrm{exp}}_{\mathrm{diss}}(c)$			4·5 ± 0·4$^{(d)}$

(*a*) Calculated from $\Delta H^{\mathrm{exp}}_{\mathrm{subl}} = 22{\cdot}1 \pm 1{\cdot}5$ kcal mol^{-1} at 373 K (Metzger, 1977). (*b*) Calculated on the basis of the experimental vapour pressures of Boyd (1963), which give $\Delta H^{\mathrm{exp}}_{\mathrm{subl}}$(TCNQ) = 24·5 ± 1·8 kcal mol^{-1} at 465 K. (*c*) Calculated on the basis of the experimental vapour pressures of de Kruif (1978), which give $\Delta H^{\mathrm{exp}}_{\mathrm{subl}}$(TCNQ) = 29·8 ± 0·5 kcal mol^{-1} at 414 K. (*d*) Calculated from the experimental heats of formation of Metzger (1977).

With regard to the atom–atom approximation in the form of set 2 the results are markedly poorer. The heat of sublimation of TTF is calculated in accordance with experiment. The heat of sublimation and the lattice energy of TTF$^{\varrho+}$–TCNQ$^{\varrho-}$ only agree with the experimental values if the lower experimental values hold. However, these lower values are based on the experimental heat of sublimation of TCNQ of Boyd (1963), which was obtained by the McLeod method. This method seems to be less reliable than the torsion–effusion method (Thomson, 1963; de Kruif, 1978), which produces a value 5 kcal mol^{-1} higher. As concerns the heat of sublimation of TCNQ and the heat of dissociation of TTF$^{\varrho+}$–TCNQ$^{\varrho-}$, set 2 is even poorer.

I thank J. L. Derissen and J. Voogd of the Structural Chemistry Group, State University, Utrecht, for their assistance with the calculations of the electrostatic energies of TTF and TCNQ and C. G. de Kruif of our Laboratory for his prompt determination of the heat of sublimation of TCNQ.

References

André, J. M. & Ladik, J. (1975). *Electronic Structure of Polymers and Molecular Crystals*. New York: Plenum.

Boyd, R.H. (1963). *J. Chem. Phys.* **38**, 2529–2535.

Britton, D. (1974). *Acta Cryst.* B**30**, 1818–1821.

Cooper, W. F., Edmonds, J. W., Wudl, F. & Coppens, P. (1974). *Cryst. Struct. Commun.* **3**, 23–26.

Epstein, A. J., Lipari, N. O., Sandman, D. J. & Nielsen, P. (1976). *Phys. Rev. B*, **13**, 1569–1579.

Govers, H. A. J. (1974). *Calculation of Lattice Energies of Unitary and Binary Molecular Crystals.* Thesis, Rijksuniversiteit te Utrecht.

Govers, H. A. J. (1975). *Acta Cryst.* A**31**, 380–385.

Govers, H. A. J. (1977). *J. Chem. Phys.* **67**, 4199–4205.

Kistenmacher, T. J., Phillips, T. E. & Cowan, D. O. (1974). *Acta Cryst.* B**30**, 763–768.

Kitaigorodskii, A. I. (1973). *Molecular Crystals and Molecules*. New York: Academic Press.

Kitaigorodskii, A. I., Mirskaya, K. V. & Tovbis, A. B. (1968). *Sov. Phys. Crystallogr.* **13**, 176–180.

Klimenko, V. E., Krivnov, V. Y., Ovchinnikov, A. A., Ukrainskii, I. I. & Shvets, A. F. (1976). *Sov. Phys. J. Exp. Theor. Phys.* **42**, 123–127.

Kruif, C. G. de (1978). Private communication.

Long, R. E., Sparks, R. A. & Trueblood, K. N. (1965). *Acta Cryst.* **18**, 932–939.

Metzger, R. M. (1977). *J. Chem. Phys.* **66**, 2525–2533.

Metzger, R. M. & Bloch, A. N. (1975). *J. Chem. Phys.* **63**, 5098–5107.

Mirskaya, K.V. & Nauchitel', V. V. (1972). *Sov. Phys. Crystallogr.* **17**, 56–59.

Nauchitel', V. V. & Mirskaya, K. V. (1972). *Sov. Phys. Crystallogr.* **16**, 891–892.

Rae, A. I. M. (1969). *Mol. Phys.* **16**, 257–273.

Sams, J. R. (1964). *Trans. Faraday Soc.* **60**, 149–156.

Scott, B. A. La Placa, S. J., Torrance, J. B., Silverman, B. B. & Welber, B. (1977). *J. Am. Chem. Soc.* **99**, 6631–6639.

Shmueli, U. & Goldberg, I. (1973). *Acta Cryst.* B**29**, 2466–2471.

Smit, P. H. (1978). *Intermolecular Interactions in Crystals of Carboxylic Acids.* Thesis, Rijksuniversiteit te Utrecht.

Thomson, G. W. (1963). *Techniques of Organic Chemistry.* Vol. I, part I, edited by A. Weissberger, pp. 457–465. New York: Interscience.

Torrance, J. B. & Silverman, B.D. (1977). *Phys. Rev. B*, **15**, 788–801.

Williams, D. E. (1967). *J. Chem. Phys.* **47**, 4680–4684.

Williams, D. E. (1971). *Acta Cryst.* A**27**, 452–455.

Acta Cryst. (1978). A**34**, 965–968

Ferroelasticity and Phase Transformation in $Rb_2Hg(CN)_4$ Spinel

By S. Haussühl

Institut für Kristallographie der Universität zu Köln, 5000 *Köln* 1, *Zülpicher Strasse* 49, *Federal Republic of Germany*

(*Received* 27 *February* 1978; *accepted* 9 *June* 1978)

The low-temperature form of $Rb_2Hg(CN)_4$ [space group $R\bar{3}c$, $Z = 12$, $a_1 = 9{\cdot}076$, $a_3 = 46{\cdot}050$ Å (273 K)] possesses a slightly distorted spinel structure with parameters similar to those of cubic cyanospinels. It transforms into a cubic spinel modification at *ca* 398 K ($a = 13{\cdot}140$ Å at 399 K). Below the transition temperature the crystals exhibit ferroelastic properties, which allow the switching of the distortion directions into any one of four equivalent states. The critical stress is less than 1×10^{-3} kp mm^{-2}. The resulting deformations do not exceed 2×10^{-2}. Larger twinned crystals return to their primary state after the release of stress. They behave like extremely soft elastic springs. The crystals belong to the ferroelastic Aizu species $m3mF\bar{3}m$. The transition shows a constant hysteresis of *ca* 12 K in all crystals investigated. The pressure derivatives of the upper and lower transition temperatures are observed to be almost equal and constant over a wide temperature range ($dT/dP \approx 0{\cdot}245$ K bar^{-1}). The observed enthalpy of transformation is $1{\cdot}03$ J g^{-1} in fair agreement with the prediction of the Clapeyron–Clausius relation. Crystals of $K_2Hg(CN)_4$ exhibit similar properties; their transition temperature, hysteresis, enthalpy of transformation, and dT/dP are considerably less.

Crystallographic characterization; ferroelastic behaviour

Following an earlier investigation on cyanospinels of the type $K_2M(CN)_4$ [with M = Zn, Cd, and Hg (Haussühl, 1976)] crystals of $Rb_2Hg(CN)_4$ with dimensions of *ca* 20 mm were grown from aqueous solutions at *ca* 310 K by the controlled lowering of temperature. The crystals exhibit trigonal symmetry, though their morphology is almost identical to that observed in cubic cyanospinels, namely octahedron {111}, icositetrahedron {311}, and cube {100}. The existence of a