

- BENNEMA, P. & GILMER, G. M. (1973). *Kinetics of Crystal Growth*. In *Crystal Growth: An Introduction*, edited by P. HARTMAN. Amsterdam: North-Holland.
- BIENFAIT, M. & KERN, R. (1964). *Bull. Soc. Fr. Minéral. Cristallogr.* **87**, 604–613.
- DONNAY, J. D. H. & HARKER, D. (1937). *Am. Mineral.* **22**, 446–467.
- DOWTY, E. (1976). *Am. Mineral.* **61**, 448–457.
- EUSTATHOPOULOS, N. (1974). Thèse de Docteur-ès-Sciences Physiques, Univ. de Grenoble.
- FELIUS, R. O. (1976). *Structural Morphology of Rutile and Trirutile Type Crystals*. Dutch Efficiency Bureau, Pijnacker.
- HARTMAN, P. (1965). *Absorption et Croissance Cristalline*, Colloque CNRS, Nancy.
- HARTMAN, P. (1973). *Structure and Morphology*. In *Crystal Growth: An Introduction*, edited by P. HARTMAN. Amsterdam: North-Holland.
- HARTMAN, P. (1978). *Bull. Soc. Fr. Minéral. Cristallogr.* **101**, 195–201.
- HAVINGA, E. E. (1972). *J. Less-Common Met.* **27**, 187–193.
- PAULING, L. (1940). *The Nature of the Chemical Bond*. Ithaca, New York: Cornell Univ. Press.
- Selected Values of Thermodynamic Properties of the Elements* (1973). ASM, Metal Park, Ohio.
- SMITHELLS, C. J. (1955). *Metal Reference Book*. London: Butterworth.
- TASSONI, D. (1978). Thèse de Docteur-Ingénieur, Univ. de Grenoble.
- TASSONI, D., RIQUET, J. P. & DURAND, F. (1978a). *Acta Cryst.* **A34**, 55–60.
- TASSONI, D., RIQUET, J. P. & DURAND, F. (1978b). *J. Cryst. Growth*, **44**, 241–246.
- Thermochemical Tables* (1971). 2nd ed. JANAF, NBS, Washington.
- TORRENS, I. M. (1972). *Interatomic Potentials*. New York: Academic Press.
- WULFF, G. (1901). *Z. Kristallogr. Mineral.* **34**, 449–530.

Acta Cryst. (1980). **A36**, 428–432

Intermolecular Energy and Structure of Tetrathiafulvalene (TTF) Stacks from Atom–Atom Potentials

BY H. A. J. GOVERS AND C. G. DE KRUIF

General Chemistry Laboratory, Chemical Thermodynamics Group, State University of Utrecht, Padualaan 8, Utrecht 2506, The Netherlands

(Received 26 October 1979; accepted 3 December 1979)

Abstract

The lattice energy of isolated, regular tetrathiafulvalene stacks was minimized for a longitudinal slip of the molecules relative to each other at constant intermolecular separation and transverse slip. The van der Waals and repulsive interactions were calculated from atom–atom potentials. A simple expression is presented for the electrostatic interaction in neutral and charged stacks. This electrostatic contribution was calculated from CNDO/2 atomic point charges. The latter contribution proved to be negligible for stacks built up from neutral molecules. For these stacks the minimum of the lattice energy is achieved at a slip of 0.1–0.2 Å below the observed values. Eclipsed stacks, with zero slip, appeared to be only 3.35 kJ mol⁻¹ less stable than slipped ones. In stacks built up from positively charged molecules the van der Waals and repulsive contributions are dominated completely by the electrostatic interaction. These stacks tend to a structure with infinite slip.

0567-7394/80/030428-05\$01.00

Introduction

The existence of segregated stacks of acceptor and donor molecules (Soos, 1974) is an important condition for high electrical conductivity and other one-dimensional properties of compounds like tetrathiafulvalene–tetracyanoquinodimethane, TTF–TCNQ (Kistenmacher, Phillips & Cowan, 1974). In TTF compounds two different kinds of stacking are found. In the first (Kistenmacher, Phillips & Cowan, 1974; Cooper, Edmonds, Wudl & Coppens, 1974), the flat TTF molecules are slipped relative to each other along the longitudinal molecular axis by $\delta = 1.6\text{--}1.7$ Å. In the second (Scott, La Placa, Torrance, Silverman & Welber, 1977; Wudl, Schafer, Walsh, Rupp, Di Salvo, Waszczak, Kaplan & Thomas, 1977), the molecules eclipse with $\delta \approx 0.0$ Å. In both kinds the slip, ϵ , in the transverse direction of the short molecular axis is about 0.0 Å. A range of 3.3 to 3.8 Å is observed for the intermolecular separation, R .

A second condition is the existence of partial charge
© 1980 International Union of Crystallography

transfer, ρ , from the electron-donor to the electron-acceptor molecule (Soos, 1974). From the viewpoint of classical electrostatic or Madelung interaction (Metzger & Bloch, 1975) one can describe this in a uniform model, in which all molecules bear identical charges plus or minus ρ , or in a Wigner chain, in which some molecules are neutral and others are completely charge-transferred, monovalent ions. In pure TTF, all molecules are neutral and no charge transfer is observed. In TTF-TCNQ, $\rho = 0.59e$ (Metzger, 1977).

It has been shown recently (Silverman, 1979a) that the energy of isolated TTF dimers exhibits a minimum for the eclipsed geometry only. However, this quantum-mechanical calculation conflicts with a packing analysis (Silverman, 1979b), which shows that only the slipped stacking geometry of TTF in TTF-TCNQ and in pure TTF is consistent with the close packing of hard spheres having atomic van der Waals radii.

The atom-atom potential method (Kitaigorodskii, 1973) can be considered to be of intermediate sophistication between a close-packing analysis and a quantum-mechanical calculation. This method has been shown to be useful for the calculation of the lattice energies of TTF-TCNQ crystals (Govers, 1978;* Sandman, Epstein, Chickos, Ketchum, Fu & Scheraga, 1979). Here, it is our aim to predict the observed TTF stack structures *via* this approximation, with a one-dimensional chain model. As far as we know no simple method exists for the calculation of the electrostatic interaction in chains built up from large numbers, of the order of Avogadro's number, of charged molecules. Therefore, we will also derive an expression for this interaction. This work precedes a more complete three-dimensional analysis *via* the atom-atom approximation (Silverman & Govers, 1980). Therefore we are interested only in a simple calculation with no variation of R , ε , atom-atom potential parameters and charge distribution models.

Method

The lattice energy, E , is considered to be a pairwise sum of the 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, 1978):

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

with

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

In (1) the factor $\frac{1}{2}$ is introduced to avoid double counting of pair interactions, N is the number of

* The corrected values (in kcal mol⁻¹ \equiv 4.19 kJ mol⁻¹) of $E_{\text{electr}}^{\text{calc}}$ in Table 2 of this reference are -0.04, -0.01, +0.58 and +0.01, and in Table 3 -0.38, -1.78, -9.09, -1.88 and -6.35.

molecules in the stack and r_{kij} are the interatomic distances, which in our approach were calculated from the molecular geometry of TTF and from the value of the molecular separation, $R = 3.47$ Å, observed in TTF-TCNQ (Kistenmacher, Phillips & Cowan, 1974). As transverse slip we used the model value $\varepsilon = 0.00$ Å. The distance, b , between the centres of two neighbour molecules in the stack was calculated from the relation $b^2 = R^2 + \delta^2$. Therefore b varies with the longitudinal slip, δ , Fig. 1.

The parameters A_{ij} , B_{ij} , C_{ij} in (2) depend only on the six different types, tij , of interatomic pairs CC, CH, CS, HH, HS and SS, which exist for the C, H and S atoms of TTF. We used set 1 of Table 1 by Govers (1978). These parameters determine the van der Waals, E_{vdw} , and repulsive, E_{rep} , contributions to the lattice energy and were used as previously, *i.e.* in combination with summation limits of about 5.5 Å yielding 80% of the lattice energy (Govers, 1978).

The parameters e_i and e_j in (2) are the point charges on the atoms i and j . These determine the electrostatic contribution, E_{electr} , to the lattice energy. We used the CNDO/2 charge distributions for TTF⁰ (neutral) and TTF⁺ (monovalent) molecules from the sets 1 and 4, respectively, of Table 3 by Epstein, Lipari, Sandman & Nielsen (1976).* The total electrostatic contribution to the chain energy cannot be calculated *via* a simple lattice sum of contributions $e_i e_j / r_{kij}$, which is caused by bad convergence properties. We used the expression

$$E_{\text{electr}} = E_{\text{electr}}^{z'} + (Ne/b)[\ln N - \ln(\frac{1}{2}z' + 1) - 1], \quad (3)$$

with

$$e = \sum_i^n \sum_j^{n'} e_i e_j. \quad (4)$$

In (3) $E_{\text{electr}}^{z'}$ is a direct sum of interactions $e_i e_j / r_{kij}$ between the atoms of a central molecule and those of z' neighbouring molecules. It was calculated in the normal way *via* (1). The quantity e in (3) and (4) is an

* Note that the charge on H(2) of TTF⁺ (set 4, Table 3) should be 0.0814 instead of 0.0184 (Epstein, 1978).

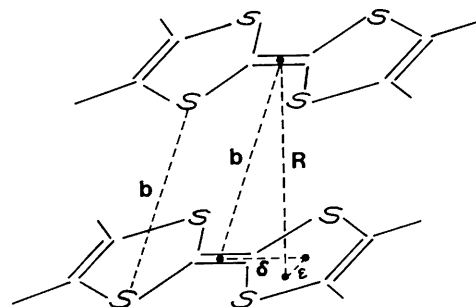


Fig. 1. Nearest-neighbour molecules in a TTF stack; definition of intermolecular separation, R longitudinal slip, δ , transverse slip, ε , and distance between the molecular centres, b .

intermolecular sum over the products of the charges on the atoms i and j . For neutral TTF⁰ molecules this sum is zero. Thus only E_{electr}^z remains in (3). The derivation of (3) is given in the Appendix.

An overall error of <5% in the calculated lattice energies is caused by the rapid summation cut-off of the van der Waals and repulsive contribution, by the neglect of a 0.07 Å shift of the position of the H-atom attraction and repulsion centre and by approximations in (3). This does not, however, influence the relative values of the lattice energies at different values of δ to a high degree.

Calculations and results

The calculated lattice energies as a function of δ of stacks built up from neutral molecules are given in Fig. 2 and Table 1. Within the physically interesting range

Table 1. Lattice energy, E , electrostatic contribution, E_{electr} , and the contribution E_{SS} , of neighbour S atoms related by a translation, b , (Fig. 1) for neutral TTF stacks as a function of the longitudinal slip, δ

Energies are in kJ mol⁻¹, δ in Å.

δ	E	E_{electr}	E_{SS}
0.0	-51.37	+0.80	+5.32
0.2	-51.04	+0.80	+5.07
0.4	-52.08	+0.75	+4.27
0.6	-53.00	+0.71	+3.14
0.8	-53.34	+0.63	+1.76
1.0	-53.59	+0.54	+0.42
1.2	-54.09	+0.50	-0.75
1.4	-54.34	+0.42	-1.67
1.6	-54.26	+0.33	-2.22
1.8	-53.00	+0.25	-2.47
2.0	-51.96	+0.21	-2.43

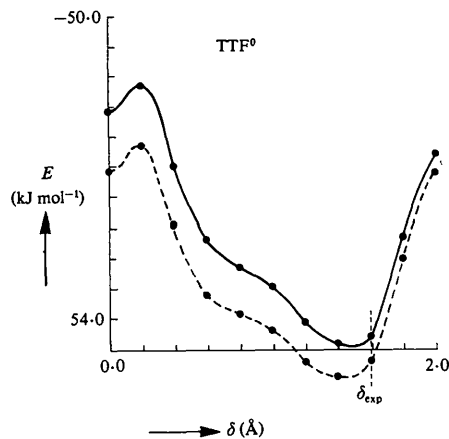


Fig. 2. Lattice energy, E , of TTF⁰ stacks as a function of the longitudinal slip, δ , at $R = 3.47$ Å and $\epsilon = 0.00$ Å. Solid curve: total lattice energy; dashed curve: van der Waals + repulsive contribution.

of δ three extrema are found in the $E(\delta)$ curve. An absolute minimum of -54.4 kJ mol⁻¹ is found at $\delta = 1.54$ Å, about 0.06 and 0.19 Å beneath the observed values of δ in TTF-TCNQ (Kistenmacher, Phillips & Cowan, 1974) and in TTF (Cooper, Edmonds, Wudl & Coppens, 1974), respectively. A relative minimum of -51.5 kJ mol⁻¹ is obtained at $\delta = 0.0$ Å, *i.e.* at the eclipsed stack geometry. This minimum is close to a maximum of -51.1 kJ mol⁻¹ at $\delta = 0.2$ Å. It might even be coalescent with this maximum in view of calculational inaccuracy. Both this relative minimum and the maximum are about 3.35 kJ mol⁻¹ above the absolute minimum in the $E(\delta)$ curve, which is symmetrical in $\delta = 0.0$ Å.

The electrostatic contribution decreases from $+0.8$ kJ mol⁻¹ at $\delta = 0.0$ Å to $+0.21$ kJ mol⁻¹ at $\delta = 2.0$ Å (Table 1). It shows a maximum at the eclipsed structure and no further extrema. However, it is so small that it does not influence the general form of the $E(\delta)$ curve.

A more detailed analysis of the contribution of close intermolecular contacts shows that the close contacts between S atoms, which are immediately above each other in the eclipsed stack structure (Fig. 1), can explain this feature to some degree. If we only count these SS contributions to the stack energy, a maximum of $+5.32$ kJ mol⁻¹ is obtained at $\delta = 0.0$ Å and a minimum of -2.47 kJ mol⁻¹ at about $\delta = 1.8$ Å (Table 1). Other (close) contacts vary less drastically with δ , but change this SS curve extrema into the total $E(\delta)$ curve by their large number. In Fig. 3 the calculated electrostatic lattice energies are given as a function of the slip, δ , for a uniform and a Wigner-type stack, built up from (partly) charged molecules.

The electrostatic energy of the uniform stack was calculated with a charge of $\rho = +0.59e$ (Metzger, 1977) on every molecule of the stack. A value of $E_{\text{electr}}(\rho = 0.59e) = \rho^2 E_{\text{electr}}(\rho = 1e)$ was applied as we had to use the CNDO/2 distribution of TTF⁺¹. From this

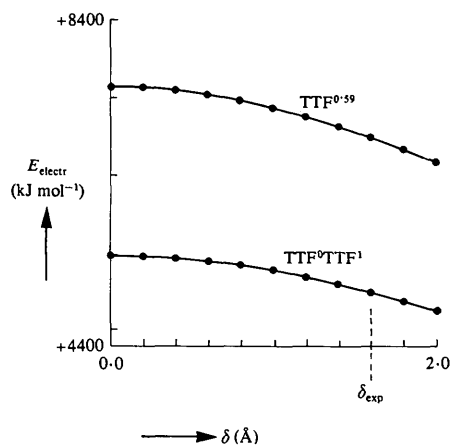


Fig. 3. Electrostatic lattice energy, E_{electr} , of TTF⁰⁻⁵⁹ (uniform) stacks and of TTF⁰ TTF⁺¹ (Wigner) stacks as a function of the longitudinal slip, δ , at $R = 3.47$ Å and $\epsilon = 0.00$ Å.

relation one immediately sees that the general form would not have changed if we had used other values of ρ .

The electrostatic energy of the Wigner stack was calculated for a stack with molecules charged alternately zero and +1, *i.e.* for a mean charge transfer of $\rho = 0.5e$. Therefore we could apply directly the molecular charge distributions of TTF⁰ and TTF⁺¹. The direct part, E'_{electr} of (3) could be calculated in the normal way, but in the second part of (3) we now had to use the values $N = \frac{1}{2}$ times Avogadro's number, $\frac{1}{2}z' = 15$ and $b = 2(3.47^2 + \delta^2)^{1/2}$ Å. By doing this, we have neglected the small contribution of the electrostatic interaction between zero and +1 charged molecules in this second part.

The van der Waals and repulsive contributions, which are identical for neutral and charged stacks in our method, appeared to be much smaller than the electrostatic contribution. These cause only small local extrema, which do not change the general form of Fig. 3. Both curves of Fig. 3 show that the stacks tend to a structure with infinite slip as a consequence of the repulsion of the positive charges on the molecules. This fact is less surprising than the very high values of more than +4200 kJ mol⁻¹, which are calculated for this repulsion. Furthermore, it appeared that the short-range contribution, E'_{electr} , to the total energy, E_{electr} , amounted to only 7 and 6% for the uniform and Wigner stacks, respectively. (See also Table 2 in the Appendix.) Therefore an analysis of close atomic contacts is not important in this case. A comparison of the energy of the Wigner stack ($\rho = 0.5e$) with the energy of a uniform stack with $\rho = 0.5e$ instead of $\rho = 0.59e$, showed that the Wigner stack was only 1% less unstable than the uniform one.

Conclusions

The huge values of the electrostatic energies calculated for (partly) charged TTF stacks clearly show the importance of the inclusion of interstack interaction. In real charge-transfer crystals there are equal amounts of positively and negatively charged stacks and the resulting total electrostatic energy is of the order of -42 kJ mol⁻¹ (Govers, 1978) instead of more than +4200 kJ mol⁻¹. Therefore an isolated stack model can work only in TTF compounds with very small charge transfer or with no charge transfer at all. Yet our neutral TTF stack energy calculations show a minimum at only 0.06 Å beneath the observed value of $\delta = 1.60$ Å in TTF-TCNQ. The reason for this might be that the total electrostatic energy of TTF-TCNQ is only slightly dependent on δ . The fact that this energy is slightly dependent on the charge distribution model (Metzger & Bloch, 1975; Epstein, Lipari, Sandman & Nielsen, 1976) seems to support this view.

The slip predicted for the neutral TTF stack is about 0.19 Å beneath the observed value of $\delta = 1.73$ Å in pure TTF. The reason for this could well be that in our calculation we have applied R , ϵ values and a TTF molecular geometry as observed in TTF-TCNQ, which are slightly different from those observed in pure TTF. A more important contribution to this deviation is probably the influence of three-dimensional interstack van der Waals and repulsive interactions. The isolated stack energy, about -54.4 kJ mol⁻¹, accounts for only 57% of the observed heat of sublimation of TTF (de Kruijff & Govers, 1980; Sandman *et al.*, 1979). This three-dimensional effect will be studied elsewhere (Silverman & Govers, 1980).

The interstack interaction might be especially important for a calculation of the relative stability and realizability of eclipsed structures with respect to slipped stacks. In our present calculation the eclipsed structure in neutral TTF compounds is only 3.35 kJ mol⁻¹ less stable than the slipped one, but interstack interaction might decrease or increase this value.

Anyhow, we feel confident that our simple atom-atom approximation and the expression for the electrostatic energy of charged stacks are valuable tools in the prediction of the structure of TTF compounds. This view is supported by the even more simple close-packing analysis by Silverman (1979*b*). In this analysis the R value of closest intermolecular approach obtains a minimum at $\delta \approx 1.8$ Å and a maximum at $\delta \approx 0.0$ Å, at which the large S atoms are beside and straight above each other, respectively. This result is very similar to the contribution, E_{SS} , calculated by us for the separate SS interaction as a function of δ . Furthermore, the atom-atom approximation seems to have some advantages over quantum-mechanical calculations. It can be applied easily to whole stacks instead of to dimers only and it seems to treat the closed-shell interaction more adequately than, *e.g.*, a CNDO/2 calculation, as the latter predicts an energy minimum for the eclipsed neutral TTF dimer (Silverman, 1979*a*) instead of a maximum.

We thank J. Voogd, H. de Wit and J. L. Derissen of the Structural Chemistry Group, State University, Utrecht for their discussion of the derivation of the expression for the electrostatic stack energy.

APPENDIX

Consider a stack of N equidistant and parallel molecules, $k' = 1 \dots N$, at a distance b from each other. Let $Z = \frac{1}{2}z'$ be the number of molecules which neighbour a certain central molecule, $k' = m$, in both directions of the chain and let Z be chosen so large that for more distant neighbours we can write

$$\sum_{i,j} e e_j / r_{k',ij} = e/bk', \quad (A1)$$

with e given in (4), Fig. 4. Then the electrostatic lattice energy of this chain is

$$E_{\text{electr}} = \frac{1}{2} \sum_{m=Z+2}^{N-Z} \left[(e/b) \sum_{k'=Z+1}^{m-1} (1/k') + \sum_{k'=m-1}^{m-Z} \sum_i \sum_j e_i e_j / r_{k'ij} + \sum_{k'=m+1}^{m+Z} \sum_i \sum_j e_i e_j / r_{k'ij} + (e/b) \sum_{k'=Z+1}^{N-m} (1/k') \right]. \quad (A2)$$

The four contributions in (A2) are shown in Fig. 4 and the factor $\frac{1}{2}$ is introduced to avoid double counting of pair interactions. The expression is not quite exact as the sum over m extends from $Z + 2$ to $N - Z$. Therefore it only holds for $N \gg Z$. The same neglect of boundary effects is used in the further simplification of (A2) in combination with the Euler theorem (Hyslop, 1959):

$$\sum_{k'=Z+1}^{m-1} (1/k') = \ln(m-1) - \ln(Z+1), \quad (A3)$$

which holds within 4‰ if $Z, m \geq 30$, and in combination with the Stirling approximation (Hyslop, 1959)

$$\ln[(N-Z)!/(Z+1)!] = N \ln N - N, \quad (A4)$$

Table 2. Influence of the number of neighbours, Z , on the electrostatic chain energy, calculated by (3) for an eclipsed and charged TTF stack as specified in the text

$E_{\text{electr}}(\rho = 0.59) = (0.59)^2 E_{\text{electr}}(\rho = 1.0)$ is used. Both energies are in kJ mol⁻¹. $Z = \frac{1}{2}z'$.

Note that even at $Z = 1000$, with a calculation of $E_{\text{electr}}^{z'}$ extending to neighbours at 3470 Å in both directions of the chain, $E_{\text{electr}}^{z'}$ amounts to only 13% of the total electrostatic contribution. At $Z = 30$, our choice, this amount is 6.5%.

Z	$E_{\text{electr}}^{z'}(\rho = 0.59)$	$\ln(\frac{1}{2}z' + 1)$	$E_{\text{electr}}(\rho = 0.59)$
2	+159.0603	1.0986	+7505.5738
5	262.9679	1.7916	7512.7751
8	322.6382	2.1972	7515.8758
11	364.4492	2.4849	7517.5497
30	490.6804	3.4340	7511.3671
100	666.405	4.6151	7522.3021
300	813.0104	5.7071	7516.5553
1000	986.9565	6.9088	7522.8494

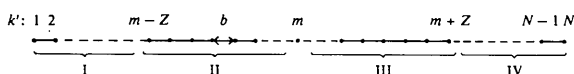


Fig. 4. Model of the derivation of (3) for the electrostatic energy, E_{electr} , of a stack built up from charged molecules. I, II, III and IV are molecular groups which contribute interactions with a central molecule, m , as denoted in the four terms of (A2). See text for the definition of symbols.

which holds almost exactly if $Z \ll N$ and N is Avogadro's number. Substitution of (A3) and (A4) into (A2) then results in (3).

We next have to show that (A1) holds if $Z \geq 30$, for example. For a stack with $b = 4.0$ Å, built up from flat centrosymmetrical molecules with a longitudinal diameter of about 8 Å as observed in TTF, the largest percentage deviation, $bk' - r_{k'ij}$, for a molecule at $k' = m + 30$ amounts to $\pm 7\%$, when the molecules are arranged in a direct line with each other. Thus for a symmetrical molecule these deviations counterbalance each other to a large degree. Moreover, the molecules are often far from being in a direct line with each other and only a small fraction of all $r_{k'ij}$ has this largest deviation. Numerical calculations for eclipsed TTF stacks with $\rho = 0.59$, in a uniform model, with a CNDO/2 charge distribution with $R = b = 3.47$ Å, as described in the Method, and performed for various values of Z yield results as given in Table 2. These results, which were calculated via (3), show that already at $Z = 5$, the total electrostatic energy, E_{electr} , is calculated with an uncertainty of $< 1.5\%$.

References

- COOPER, W. F., EDMONDS, J. W., WUDL, F. & COPPENS, P. (1974). *Cryst. Struct. Commun.* **3**, 23–26.
- EPSTEIN, A. J. (1978). Private communication.
- EPSTEIN, A. J., LIPARI, N. O., SANDMAN, D. J. & NIELSEN, P. (1976). *Phys. Rev. B*, **13**, 1569–1579.
- GOVERS, H. A. J. (1978). *Acta Cryst.* **A34**, 960–965.
- HYSLOP, J. M. (1959). *Infinite Series*, p. 51. New York: Interscience Publ. Inc.
- KISTENMACHER, T. J., PHILLIPS, T. E. & COWAN, D. O. (1974). *Acta Cryst.* **B30**, 763–768.
- KITAIGORODSKII, A. I. (1973). *Molecular Crystals and Molecules*. New York: Academic Press.
- KRUIF, C. G. DE & GOVERS, H. A. J. (1980). In preparation.
- METZGER, R. M. (1977). *J. Chem. Phys.* **66**, 2525–2533.
- METZGER, R. M. & BLOCH, A. N. (1975). *J. Chem. Phys.* **63**, 5098–5107.
- SANDMAN, D. J., EPSTEIN, A. J., CHICKOS, J. S., KETCHUM, J., FU, J. S. & SCHERAGA, H. A. (1979). *J. Chem. Phys.* **70**, 305–313.
- SCOTT, B. A., LA PLACA, S. J., TORRANCE, J. B., SILVERMAN, B. D. & WELBER, B. (1977). *J. Am. Chem. Soc.* **99**, 6631–6639.
- SILVERMAN, B. D. (1979a). In preparation.
- SILVERMAN, B. D. (1979b). In preparation.
- SILVERMAN, B. D. & GOVERS, H. A. J. (1980). In preparation.
- SOOS, Z. G. (1974). *Ann. Rev. Phys. Chem.* **25**, 121–153.
- WUDL, F., SCHAFFER, D. E., WALSH, W. M. JR, RUPP, L. W., DI SALVO, F. J., WASZCZAK, J. V., KAPLAN, M. L. & THOMAS, G. A. (1977). *J. Chem. Phys.* **66**, 377–385.