

Table 2. Results for the calculation of signs of $\Delta\varphi_H$'s for the 1000 largest E 's from RFC

%: percentage of reflections with the sign of $\Delta\varphi_H$ correctly determined.

ER: averaged phase error in degrees.

Group	Number of reflections	Method 1		Method 2		Method 3	
		%	ER	%	ER	%	ER
1	200	70.0	29	92.0	11	93.5	8
2	400	65.0	31	82.3	20	89.5	12
3	600	64.2	31	76.2	24	78.8	21
4	800	60.9	34	70.0	28	72.8	24
5	1000	56.9	38	65.9	27	67.8	25

example. The results of methods 2 and 3 are nearly the same and both are better than that of method 1.

It is concluded from the comparison that method 3 is the best among the three.

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Structure Analysis of Displacively Modulated Molecular Crystals

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Abstract

A structure-factor formalism for incommensurate modulated structures is derived. It allows for several simultaneous translational and rotational displacements of molecules or molecular segments, which are considered as being rigidly displaced. It incorporates treatment of several displacement waves in the crystal and makes full use of the four-dimensional symmetry description of de Wolff, Janssen & Janner [*Acta Cryst.* (1981), **A37**, 625-636]. A computer program based on the formalism has been applied to existing data sets on phenothiazine-TCNQ [Kobayashi (1974). *Acta Cryst.* **B30**, 1010-1017] and biphenyl [Baudour & Sanquer (1983). *Acta Cryst.* **B39**, 75-89], and to a new data set on [bis(ethylenedithio)-TTF]₂I₃ [Leung *et al.* (1984). *J. Am. Chem. Soc.* **106**, 7644-7646].

Introduction

It has become increasingly clear in the past years that modulated crystal structures are more common than

previously expected. In particular the recent interest in conducting organic solids has led to the discovery of a great many incommensurate phases of molecular crystals, each stable in a certain temperature domain, which can be described with formalisms developed for application to minerals, alloys and other inorganic solids. In many cases the transition to the modulated structure corresponds to a change from a metallic to an insulating state (*i.e.* a Peierls transition), in others the transport properties are much less affected. In all cases a knowledge of the geometry of the distortion is important for the understanding of the mechanism of the transition and the transport properties in the modulated state. Intermolecular distances and molecular overlap, for example, may show large local variations from the average over the whole crystal.

Scattering formalisms for modulated structures have been discussed by Overhauser (1971), de Wolff (1974), Axe (1980) and Yamamoto (Yamamoto, Nakazawa & Tokonami, 1979). They take into account substitutional or displacive modulations of each of the atoms in the crystal. In molecular crystals, however, a translational or rotational displacement of a molecule, or one of its segments, is more likely because of the stiffness of the intramolecular linkages between atoms. Such a *rigid body displacement analy-*

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sis is related to the well known treatments of thermal motion in crystal structure analysis. It has been applied to the molecular crystals of phenothiazine-7,7,8,8-tetracyano-*p*-quinodimethane (PTZ-TCNQ) by Kobayashi (1974) and to the low-temperature phase III of diphenyl by Baudour & Sanquer (1983). In both cases the phase of the molecular displacement was referred to the origin of the unit cell. This choice is adequate when the number of molecules in the cell is limited to one per chain, but not sufficiently general when the cell contains more molecules, or several non-symmetry-related chains. We discuss here a more general formalism in which the phase reference point can be anywhere in the unit cell, such as at the molecule's center of mass. The formalism allows for several simultaneous translational and rotational displacements of the rigidly displaced body, and includes the possibility of several coexisting waves in different parts of the crystal. This latter feature is of particular importance for organic salts, in which cation and anion displacements will in general be different. Full use is made of the four-dimensional symmetry description of one-dimensionally modulated structures developed by de Wolff, Janssen & Janner (1981). In its present form our algorithm is valid within the harmonic approximation; an extension to include higher harmonic terms will be considered in future work.

Scattering formalism

Let us consider a displacively modulated crystal in which the ν th atom in the unit cell defined by \mathbf{n} is located at

$$\mathbf{r}_{\mathbf{n}\nu} = \mathbf{r}_\nu^0 + \mathbf{n} + \mathbf{u}_\nu\{\mathbf{q} \cdot (\mathbf{g}_\nu + \mathbf{n})\}, \quad (1)$$

where \mathbf{r}_ν^0 is the average position of atom ν , \mathbf{u}_ν is the periodic vector field $\mathbf{u}_\nu(x) = \mathbf{u}_\nu(x+1)$, \mathbf{q} is the modulation vector and the vector \mathbf{g}_ν determines the phase reference point of the displaced entity, which may be chosen in several ways:

In the *atomic displacement model* (e.g. de Wolff, 1977), we have

$$\mathbf{g}_\nu = \mathbf{r}_\nu^0, \quad (2a)$$

while in a *molecular displacement model*

$$\mathbf{g}_\nu = \mathbf{R}, \quad (2b)$$

where \mathbf{R} is common to all atoms in a molecule or molecular segment. A convenient, but not unique, choice for \mathbf{R} is the center of mass, $\mathbf{R} = \sum \mathbf{m}_i \mathbf{r}_i^0 / \sum m_i$ of the rigidly displaced body.

A third choice described by Kobayashi (1974) is

$$\mathbf{g}_\nu = \mathbf{0}, \quad (2c)$$

which implies that the displacement phases of all atoms in the unit cell are referred to the same point at the origin.

We will assume that the displacement vector field \mathbf{u}_ν is a harmonic function, so that

$$\mathbf{r}_{\mathbf{n}\nu} = \mathbf{r}_\nu^0 + \mathbf{n} + \mathbf{U}_\nu \sin \{2\pi \mathbf{q} \cdot (\mathbf{g}_\nu + \mathbf{n}) - \varphi_\nu\}, \quad (3)$$

where \mathbf{U}_ν and φ_ν are the displacement wave's amplitude and phase respectively.

The contribution of the ν th atom to the structure factor is described as

$$F_\nu(\mathbf{Q}) = f_\nu(\mathbf{Q}) \sum_{\mathbf{n}=(0,0,0)}^{(N_1, N_2, N_3)} \exp \{2\pi i \mathbf{Q} \cdot (\mathbf{r}_\nu^0 + \mathbf{n}) + \mathbf{U}_\nu \sin [2\pi \mathbf{q} \cdot (\mathbf{g}_\nu + \mathbf{n}) - \varphi_\nu]\}, \quad (4)$$

where $f_\nu(\mathbf{Q})$ is the atomic scattering factor and \mathbf{Q} the scattering vector.

With the Jacobi-Auger expansion:

$$\exp(iz \sin \alpha) = \sum_{-\infty}^{\infty} \exp(-im\alpha) J_{-m}(z),$$

(4) becomes

$$\begin{aligned} F_\nu(\mathbf{Q}) &= f_\nu(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_\nu^0) \\ &\times \sum_{m=-\infty}^{\infty} J_{-m}(2\pi \mathbf{Q} \cdot \mathbf{U}_\nu) \\ &\times \exp(-2\pi i m \mathbf{q} \cdot \mathbf{g}_\nu) \exp(im\varphi_\nu) \\ &\times \sum_{\mathbf{n}=(0,0,0)}^{(N_1, N_2, N_3)} \exp[2\pi i \mathbf{n} \cdot (\mathbf{Q} - m\mathbf{q})]. \end{aligned} \quad (5)$$

For $N_i \gg 1$ the sum over \mathbf{n} leads to the delta function $\delta(\mathbf{H} - \mathbf{Q} + m\mathbf{q})$, where $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$. This means that reflections occur for $\mathbf{Q} = \mathbf{H} + m\mathbf{q}$. Main reflections representing the average structure have $m = 0$, while satellites are defined by $m \neq 0$.

We shall use the assumption that the modulation is incommensurate, so that at least one component of $\mathbf{q}(\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*)$ is not a rational fraction. In this case the satellites do not overlap and we get

$$\begin{aligned} F_\nu(h, k, l, m) &= f_\nu(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_\nu^0) \\ &\times J_m(2\pi \mathbf{Q} \cdot \mathbf{U}_\nu) (-1)^m \\ &\times \exp(-2\pi i m \mathbf{q} \cdot \mathbf{g}_\nu) \\ &\times \exp(im\varphi_\nu). \end{aligned} \quad (6)$$

Using (2a), (2b) and (2c) we get respectively:

$$\begin{aligned} F_\nu(h, k, l, m) &= f_\nu(\mathbf{Q}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_\nu^0) \\ &\times J_m(2\pi \mathbf{Q} \cdot \mathbf{U}_\nu) \\ &\times (-1)^m \exp(im\varphi_\nu) \end{aligned} \quad (7a)$$

$$\begin{aligned} F_\nu(h, k, l, m) &= f_\nu(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_\nu^0) \\ &\times \exp(-2\pi i m \mathbf{q} \cdot \mathbf{R}) \\ &\times J_m(2\pi \mathbf{Q} \cdot \mathbf{U}_\nu) \\ &\times (-1)^m \exp(im\varphi_\nu) \end{aligned} \quad (7b)$$

and

$$F_\nu(h, k, l, m) = f_\nu(\mathbf{Q}) \exp[2\pi i \mathbf{Q} \cdot \mathbf{r}_\nu^0] J_m(2\pi \mathbf{Q} \cdot \mathbf{U}_\nu) \times (-1)^m \exp(im\varphi_\nu), \quad (7c)$$

where φ_ν is the phase of the phase reference point \mathbf{g} .

As shown by Overhauser (1971) and by Axe (1980) phase and amplitude fluctuations around the equilibrium value give rise to an additional satellite temperature factor, which has, for small phase fluctuations, the effect of replacing

$$J_m(2\pi \mathbf{Q} \cdot \mathbf{U}_\nu)$$

by

$$J_m(2\pi \mathbf{Q} \cdot \boldsymbol{\eta}_\nu) \exp[-|m|(|m|-1)\langle\varphi_\nu^2\rangle/2]$$

(Axe, 1980), where $\boldsymbol{\eta}_\nu$ is the average value of \mathbf{U}_ν around which fluctuations occur, while \mathbf{U}_ν is the amplitude of the modulation wave in the hypothetical case in which no fluctuations would occur, and $\langle\varphi_\nu^2\rangle$ is the mean-square phase fluctuation. For cases where only satellites with $m = \pm 1$ are observable the only effect is the replacement of \mathbf{U}_ν by $\boldsymbol{\eta}_\nu$. But for higher-order satellites a strong reduction in intensity occurs, which must be allowed for wherever fluctuations are evident.

Treatment of symmetry

Incommensurate crystals with one-dimensional modulation can be described as periodic arrangements in four-dimensional space (de Wolff, 1974; de Wolff, Janssen & Janner, 1981). A new coordinate axis \mathbf{a}_4 perpendicular to the three-dimensional hyperplane R_3 is introduced. The real electron density ρ is in R_3 , the section of four-dimensional space defined by t (=displacement coordinate) = 0. A four-dimensional symmetry operation S

$$S \begin{pmatrix} \mathbf{r} \\ t \end{pmatrix} = \begin{pmatrix} \mathbf{r}' \\ t' \end{pmatrix}, \quad \tilde{\rho}(\mathbf{r}', t') = \tilde{\rho}(\mathbf{r}, t),$$

(where $\tilde{\rho}$ is the four-dimensional electron density) is described by

$$\begin{aligned} \mathbf{r}' &= \mathcal{R}\mathbf{r} + \mathbf{s} \\ t' &= \varepsilon t + \delta - \mathbf{q} \cdot \mathbf{s}. \end{aligned} \quad (8)$$

Here \mathcal{R} and \mathbf{s} are respectively the rotational and translational parts of the three-dimensional symmetry element, $\varepsilon = \pm 1$ and δ is a rotational and/or translational part of the symmetry in the additional direction.

Since ε and δ have to be specified for every symmetry element of the four-dimensional space group prior to structure analysis we will briefly discuss their selection.

All combinations of $(\mathcal{R}, \varepsilon)$ are restricted by the condition of uniqueness of the modulation vector \mathbf{q}

$$\varepsilon \mathbf{q} - \mathcal{R}\mathbf{q} = \mathbf{n}^* \quad (9a)$$

(de Wolff, 1977), where \mathbf{n}^* is a vector in the reciprocal three-dimensional lattice. This implies for example

- (a) if $\mathcal{R} = E$ (pure translation) then $\varepsilon = 1$,
 (b) if $\mathcal{R} = -E$ (inversion center) then $\varepsilon = -1$,

(c) if $\mathcal{R} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ (twofold axis) then $\varepsilon = 1$ for $\mathbf{q} \parallel 2$; $\varepsilon = -1$ for $\mathbf{q} \perp 2$.

This condition restricts the number of four-dimensional space groups to which modulated structures can belong. Furthermore, the separation of the coordinates in three-dimensional space and the fourth coordinate t in (8) imply that every superspace group has to be a (3+1) reducible group. For every space-group element there exists a smallest finite number n for which S^n is equal to some translational element of the superspace group. Because of the (3+1) reducibility this means that

$$\mathcal{R}^n = E, \quad \varepsilon^n = 1 \quad \text{and} \quad \delta + \varepsilon\delta + \dots + \varepsilon^{n-1}\delta = \text{integer}. \quad (9b)$$

Possible δ values for $\varepsilon = 1$ are therefore limited to $\pm j/n$, where $j = 0, 1, \dots, n-1$, while for superspace group elements with $\varepsilon = -1$ no limitation exists. For $\varepsilon = +1$ the values of δ are specified in the superspace group symbol, for $\varepsilon = -1$ we use the following method to find δ .

Let G^+ and G^- be the subsets of symmetry elements of superspace group G with $\varepsilon = +1$ and $\varepsilon = -1$ respectively. Every $S_j^- \in G^-$ can be written as

$$S_j^- = S_j^+ S_0^-, \quad (10)$$

where S_0^- is one element in G^- for which we can set $\delta = 0$ because of the particular choice of origin along the distortion coordinate t . This freedom can also be understood as the possibility of choosing the origin (*i.e.* the 'first' cell) in the three-dimensional modulated crystal. This means that $\delta(S_j^-)$ can be derived by use of (10) combined with (8).

It is useful to define a new value τ , the intrinsic rational increment in t , as:

$$\tau = \delta - \mathbf{q}_r \cdot \mathbf{s} \quad (11)$$

(de Wolff, Janssen & Janner, 1981), where \mathbf{q}_r is the rational part of the modulation vector. All restrictions for τ are related to restrictions in δ .

In order to sum over all atoms related by the four-dimensional symmetry operations we must express the displacement \mathbf{u}_ν^j of the atom generated by S_j to that of the 'source' atom \mathbf{u}_ν . From de Wolff *et al.* (1981, expression 3.16) we have:

$$\mathbf{u}_\nu^j(\mathbf{q} \cdot \mathbf{g}_\nu^j) = \mathcal{R}^j \mathbf{u}_\nu \{ \varepsilon_j(\mathbf{q} \cdot \mathbf{g}_\nu^j - \delta_j + \mathbf{m}_j^* \cdot \mathbf{g}_\nu) \}, \quad (12a)$$

where \mathbf{m}_j^* is a reciprocal-lattice vector equal to $\varepsilon_j \mathbf{q} - \mathcal{R}_j^{-1} \mathbf{q}$ (9), and \mathbf{g}_ν^j is the phase reference point for the atom generated by S_j .

Substitution of this expression in (12a) leads to

$$\mathbf{u}_\nu^j(\mathbf{q} \cdot \mathbf{g}_\nu^j) = \mathcal{R}^j \mathbf{u}_\nu \{ \mathbf{q} \cdot \mathbf{g}_\nu + \varepsilon_j(\mathbf{q} \cdot \mathbf{s}_j - \delta_j) \}, \quad (12b)$$

which is more suitable for computational purposes.

The structure-factor expression (4) becomes, after summation over all symmetry-related atoms N_s ,

$$\begin{aligned} F_\nu(\mathbf{Q}) = & \sum_{j=1}^{N_s} f_\nu(\mathbf{Q}) \\ & \times \sum_{\mathbf{n}=(0,0,0)}^{(N_1, N_2, N_3)} \exp(2\pi i \mathbf{Q} \cdot (\mathbf{r}_\nu^j + \mathbf{n})) \\ & + \mathcal{R}^j U \sin \{ 2\pi \mathbf{q} \cdot \mathbf{g}_\nu \\ & + 2\pi [\varepsilon_j \mathbf{q} \cdot \mathbf{n} + \varepsilon_j(\mathbf{q} \cdot \mathbf{s}_j - \delta_j)] - \varphi_\nu \} \end{aligned} \quad (13)$$

or after summation over all unit cells:

$$\begin{aligned} F_\nu(\mathbf{Q}) = & \sum_{j=1}^N f_\nu(\mathbf{Q}) \exp(2\pi i \mathbf{Q} \cdot \mathbf{r}_\nu^j) \\ & \times J_m(2\pi \mathbf{Q} \cdot \mathbf{U}_\nu^j) (-\varepsilon_j)^m \\ & \times \exp(-2\pi i m \varepsilon_j \mathbf{q} \cdot \mathbf{g}_\nu) \\ & \times \exp \{ im [2\pi(\delta_j - \mathbf{q} \cdot \mathbf{s}_j) + \varepsilon_j \varphi_\nu] \}. \end{aligned} \quad (14)$$

Combination of several displacement waves

In many modulated structures encountered in practice several modulation waves with the same \mathbf{q} are superimposed. In the molecular case these may be rotational in addition to transverse and longitudinal displacements. It is possible to incorporate the separate waves into a structure-factor formalism. Such a treatment, however, leads to an expression with products of Bessel functions, which becomes particularly cumbersome in the case of more than two contributing vector fields.

Let us have n modulation sine waves for some atom in the structure:

$$\mathbf{u}_\nu = \sum_{i=1}^n \mathbf{U}_{\nu i} \sin(2\pi \mathbf{q} \cdot \mathbf{g}_\nu - \varphi_i), \quad (15)$$

where $\mathbf{U}_{\nu i}$, φ_i are the amplitude and the phase of the i th wave respectively. This equation can be rewritten as

$$\mathbf{u}_\nu = \mathbf{U}_\nu^x \sin(2\pi \mathbf{q} \cdot \mathbf{g}_\nu) - \mathbf{U}_\nu^y \cos(2\pi \mathbf{q} \cdot \mathbf{g}_\nu) \quad (16)$$

with $\mathbf{U}_\nu^x = \sum_i \mathbf{u}_{\nu i} \cos \varphi_i$ and $\mathbf{U}_\nu^y = \sum_i \mathbf{u}_{\nu i} \sin \varphi_i$.

This means that the $(3+1) \times n$ (i.e. $\mathbf{u}_{\nu i}$, φ_i , $i = 1, \dots, n$) parameters of (15) have been reduced to six parameters (i.e. components of \mathbf{U}_ν^x and \mathbf{U}_ν^y).

We note that (16) is in full agreement with equation (1.1) of McConnell & Heine (1984), which states that incommensurate structures can always be expressed in the form of two different components, one modulated with $\cos \mathbf{q} \cdot \mathbf{r}$ and the other with $\sin \mathbf{q} \cdot \mathbf{r}$.

For the structure-factor expression (4) only the projection $\mathbf{Q} \cdot \mathbf{u}_\nu$ is needed. From (16) we have:

$$\begin{aligned} (\mathbf{Q} \cdot \mathbf{u}_\nu) = & (\mathbf{Q} \cdot \mathbf{U}_\nu^x) \sin(2\pi \mathbf{q} \cdot \mathbf{g}_\nu) \\ & - (\mathbf{Q} \cdot \mathbf{U}_\nu^y) \cos(2\pi \mathbf{q} \cdot \mathbf{g}_\nu). \end{aligned} \quad (17)$$

Introducing U_ν and χ_ν such that

$$U_\nu = \{ (\mathbf{Q} \cdot \mathbf{U}_\nu^x)^2 + (\mathbf{Q} \cdot \mathbf{U}_\nu^y)^2 \}^{1/2} \quad (18)$$

$$\sin \chi_\nu = \mathbf{Q} \cdot \mathbf{U}_\nu^x / U_\nu, \quad \cos \chi_\nu = \mathbf{Q} \cdot \mathbf{U}_\nu^y / U_\nu,$$

we get

$$\mathbf{Q} \cdot \mathbf{u}_\nu = U_\nu \sin(2\pi \mathbf{q} \cdot \mathbf{g}_\nu - \chi_\nu), \quad (19)$$

which is particularly convenient for calculational purposes. In expression (4), $\mathbf{Q} \cdot \mathbf{U}_\nu$ and φ_ν are replaced by U_ν and χ_ν respectively. This method represents a considerable simplification compared with expressions containing products of Bessel functions. It can be understood as a projection of the combination of waves with the same wavelength leading to a simple sine wave.

For symmetry-related atoms \mathbf{U}_ν^x and \mathbf{U}_ν^y in (18) are replaced by $\mathcal{R} \mathbf{U}_\nu^x$ and $\mathcal{R} \mathbf{U}_\nu^y$ before substitution into (14).

Molecular displacement model

The molecular displacement model defined by (2b) assumes a molecule (or part of a molecule) to be displaced as a rigid unit. In other words, the soft modes that lead to a modulation of the structure below the transition point are assumed to be low-frequency phonon modes. The number of parameters in this model is small and limited to translational and librational displacement coordinates. For all atoms in the rigid body

$$\mathbf{u}_\nu = \mathbf{u}^t \{ \mathbf{q} \cdot (\mathbf{R} + \mathbf{n}) \} \quad (20)$$

for translations, and

$$\mathbf{u}_\nu = \mathbf{u}^r \{ \mathbf{q} \cdot (\mathbf{R} + \mathbf{n}) \} \times (\mathbf{r}_\nu - \mathbf{R}) \quad (21)$$

for rotations within a rectilinear approximation, where \mathbf{u}^r is a rotational displacive vector field, which defines the direction and magnitude of the rotation. In the harmonic approximation the functions \mathbf{u}^r and \mathbf{u}^t are again harmonic functions defined by an amplitude and phase for every molecular displacement field.

Computer program

A least-squares program *JANA* has been written using (14) with the rigid-body approximations (20) and (21) and the combination of waves defined by (16) and (19). The program is based on the general routine *LINEX77* and allows simultaneous refinement of atomic positional and thermal parameters, and extinction parameters, in addition to the displacement

coordinates. Thus, although the rigid-body displacement assumption is used, the geometry of each molecule is fully adjustable.

The input to the program requires specification of the four-dimensional superspace group, including ϵ and δ values for each of the symmetry elements. Since many molecular crystals of interest have two or more molecular components, up to eight rigidly displaced bodies can be specified. This feature also allows separate treatment of more flexible parts of a molecule if desirable.

Application

The algorithms described above have been applied to three modulated structures. They range from phenothiazine-7,7,8,8-tetracyano-*p*-quinodimethane (PTZ-TCNQ), in which a very large amplitude modulation is induced by hydrogen-bonding requirements (Kobayashi, 1974), and the 20 K phase of biphenyl in which the central-bond torsion angle varies along the modulation wave (Baudour & Sanquer, 1983), to the ambient pressure low-temperature superconductor [bis(ethylenedithio)-tetrathiafulvalene]₂triiodide [(BEDT-TTF)₂I₃], in which two separate waves with the same \mathbf{q} are found in the organic and iodine components (Leung *et al.*, 1984). The first two data sets were obtained from the literature, while the (BEDT-TTF)₂I₃ data were as measured by Leung *et al.* Each case is discussed below.

PTZ-TCNQ

The 1:1 complex of phenothiazine and 7,7,8,8-tetracyano-*p*-quinodimethane shows large transverse displacements of about 0.8 Å relative to the average structure (Kobayashi, 1974). On the basis of the modulation vector $\mathbf{q} = 0.232 \mathbf{b}^*$, the absence of satellites of $0k0$ reflections and the space group of the average structure, the space group $P_{21}^{C2/m}$ was selected for our analysis. Satellites of first, second and third order were observed by Kobayashi in his photographic data. However, his analysis does not give evidence for an extra satellite temperature factor, which suggests that fluctuations around the average modulation are small in this case. This may be understood in terms of the relative rigidity of the hydrogen bond, compared with other intermolecular interactions.

Refined fractional components of the displacement amplitude are $[-0.1172(10), 0, 0.0708(8)]$, in good agreement with previous values $(-0.121, 0, 0.0714)$ estimated from the zero intensity of main reflections and the zero point of the Bessel function $J_0(x)$. The final $R(F)$ factor is 0.191 compared with values of 0.195, 0.200 and 0.178 obtained in the earlier analysis, in which the structure was refined in an enlarged 'pseudo-commensurate' cell with a larger number of independent atoms than used in the present treatment.

Table 1. Modulation waves for biphenyl

Top line: from Baudour & Sanquer (1983); bottom line: this study.

	Amplitude	
Torsion around L^*	11.0 (2)°	9°‡
	11.2 (2)°	12 (3)°
Libration around N^\dagger	1.0 (1)°	99°‡
	1.0 (1)°	94 (11)°
Translation along L^*	0.035 (5) Å	9°‡
	0.032 (4) Å	19 (28)°

* L = long molecular axis.

† N = normal to mean molecular plane.

‡ Not refined.

Introduction of rotational modulations, phase parameters and independent displacements of the PTZ and TCNQ molecules did not lead to significant improvements between the observed and calculated structure factors.

Biphenyl, 20 K

The modulated structure of the 20 K phase of biphenyl was analyzed with a set of neutron diffraction data by Baudour & Sanquer (1983) in the superspace group P_{21}^{Pa} . The main modulation is a torsion of the central C-C bond of the molecule, but, in addition Baudour & Sanquer found evidence for a librational and translational molecular displacement.

The structure is of particular interest for testing purposes because of the coexistence of these three types of displacement waves (with the same $\mathbf{q} = 0.46 \mathbf{b}^*$). Baudour & Sanquer did not refine the relative phases; these were adjusted separately until a minimum of R was found. The same treatment was used for the phase difference between the waves in the two symmetry-related columns.

In our treatment all phases were refined in the least-squares procedure, while the relative phase of the glide-plane-related columns depends only on the symmetry operation, through (12*b*). The possibility to adjust the phases of every modulation wave is specific for space groups including elements with $\epsilon = -1$; if only $\epsilon = +1$ elements occur one of the phases can arbitrarily be chosen as zero. The choice of phase difference between the two columns by Baudour & Sanquer can be shown to be equivalent to the refinement of all three (rather than two) phases in our treatment.

Results are compared in Table 1. The results agree with those reported earlier within the standard deviations of the least-squares values. $R(F)$ factors for main and satellite reflections are 0.088 (0.088) and 0.176 (0.175) respectively, where the bracketed values are as published by Baudour & Sanquer.

(BEDT-TTF)₃I₃ (ET₂I₃)

The 2:1 salt of BEDT-TTF [bis(ethylenedithio)-tetrathiafulvalene] and I₃⁻ shows ambient-pressure

Table 2. Modulation parameters in (BEDT-TTF)₂I₃⁻

Refinement 1, rigid-body translations only

	Magni- tude (Å)	x	y	z	ψ(°)
I ₃ ⁻	0.281 (1)	0.0428 (2)	0.0008 (2)	-0.022 (1)	0
ET	0.124 (3)	0.0151 (3)	-0.0047 (3)	0.0022(1)	13.8 (9)

Refinement 2, non-rigid iodide ion, both translations and rotations for ET, using combination of waves expression (19)

Translations (in fractions of the unit cell edge)

	U ^x	U ^y
I ₁ [*]	0.0392 (2) 0.0009 (2) -0.0039 (2)	— — —
Magnitude	0.271 Å	
I ₂ [*]	0.0431 (2) 0.0022 (1) -0.0003 (1)	0.0030 (2) -0.0076 (2) -0.0030 (2)
Magnitude	0.277 Å	0.088 Å
ET†	0.0143 (2) -0.0042 (1) -0.0013	0.0017 (2) -0.0021 (1) 0.0021 (1)
Magnitude	0.113 Å	0.041 Å
Rotation		
ET†	0.00232 (6) 0.00172 (5) -0.00067 (5)	
Magnitude	1.24°	

* φ = 0 at the origin of the cell, which is the position of the central iodine atom.

† φ = 0 at ET molecular center.

superconductivity at temperatures 0.3–3 K higher than those observed in other organic conductors (Yagubski *et al.*, 1984; Leung *et al.*, 1984). When the crystals are cooled below 200 K strong first-order satellite reflections occur with a **q** vector of 0.08 **a*** + 0.27 **b*** + 0.205 **c*** at 125 K and superspace group $P^{P\bar{1}}$. Initial refinements were done on 3346 main reflections with $I > 3\sigma(I)$ and 1041 strong satellite reflections with $I > 25\sigma(I)$.

In a first model one translational wave of variable amplitude U_ν was introduced for each of the molecular species I₃⁻ and ET. This treatment led to $R(F) = 0.036$ and 0.163 for the two sets of reflections respectively, and showed large modulations of I₃⁻ [$|U_\nu| = 0.281$ (1) Å] directed along **a** and ET [$|U_\nu| = 0.124$ (3) Å] directed almost exactly along one of the inertial axes in the average plane of the ET (molecule).

Since the R factor on the satellite intensities is higher than expected from the estimated accuracy of

the intensities, the constraints of the model were relaxed by: (1) introducing separate motion of the two independent atoms in I₃⁻; (2) using both sine and cosine terms as in (17) for the terminal I atom (the phase of the central I atom is fixed by the center of symmetry) and the ET molecule; and (3) introducing rotational displacements for ET.

$R(F)$ factors for this refinement are 0.034 and 0.098 for main reflections and strong satellites respectively, a considerable improvement over the restricted model. A final refinement included 3209 satellite reflections with $I > 3\sigma(I)$ and gave an R factor of 0.076 for all reflections.

The results summarized in Table 2 show a significant deviation from pure translational displacement for I₃⁻, which is in part rotational, and in part due to internal distortions. The magnitudes of the displacement amplitudes are, however, little affected. For ET the magnitude of the translational displacement is again similar, though the cosine and sine components differ in magnitude and direction. In addition a small but significant rotational displacement with amplitude equal to 1.24° is observed.

A more detailed description of these results will be given in a separate publication.

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