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Space-Group Symmetry and the Joint Probability Distribution of the Magnitude and Phase of a Triple Product: An Unexpected Result in the Eleven Pairs of Chiral Space Groups

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Abstract

The main term of the probability distribution of a triple product in an arbitrary space group is derived *via* the central limit theorem. The results are in general identical to those obtained by Giacovazzo [*Direct Methods in Crystallography* (1980), p. 286. London: Academic Press], *i.e.* in any space group the well known distribution functions for $P1$ and $P\bar{1}$ are valid for general triple products and triple products with restricted phase angles, respectively, provided a suitable weight is applied. However, in the eleven pairs of enantiomorphously related space groups it is found that there are triple products for which the most probable phase angle assumes a value different from zero. As an example, in $P4_1$ the most probable phase for the triple product $E_{221}E_{\bar{4}01}E_{2\bar{2}\bar{2}}$, given its magnitude, appears to be −45°.

Introduction

The effect of space-group symmetry on the probability distribution of triplet invariants was described by Giacovazzo (1974*a*,*b*, 1980). *Via* the characteristic function he derived the joint probability distribution of three normalized structure factors $E_{\mathbf{h}_1}$, $E_{\mathbf{h}_2}$ and $E_{\mathbf{h}_3}$, ($\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = \mathbf{0}$), expressed in terms of multivariate cumulants and Hermite polynomials. In the derivation $\mathbf{h}_1$, $\mathbf{h}_2$ and $\mathbf{h}_3$ were fixed, while the atomic coordinates were regarded as the primitive random variables. After expanding the cumulants in terms of joint moments of the trigonometric parts of the contributing structure factors he used the linearization theory (Bertaut, 1959*a*,*b*) to obtain an analytical expression for the desired distribution function. Because of the relation between the variance of the distribution and the mean value of the trigonometric part of the triple product, his result can only be correct if the latter quantity is real valued. Therefore, his formulae are not applicable in those cases where the triple product must have a non-real component as a consequence of space-group symmetry. [For example, in $P2_12_12_1$ the triple product $E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}$, where $\mathbf{h}_1 = (g0u)$, $\mathbf{h}_2 = (0gu)$ and $\mathbf{h}_3 = (gg0)$.]

In this paper the distribution function of a triple product in an arbitrary space group is redetermined. We will calculate the main term of this distribution *via* the central limit theorem applied directly to the product of any three normalized structure factors. As we aim at an expression for triple products containing structure factors of an arbitrary class, we will define a general expression for the normalized structure factor $E_{\mathbf{h}}$ which can be used both for a centrosymmetric and a non-centrosymmetric arrangement of atoms. From this an explicit expression for the real and imaginary parts (A and B) of the triple product is derived.

Application of the central limit theorem then leads directly to a two-dimensional normal distribution of A and B if the triple product is of a general type, or to a one-dimensional normal distribution if the phase of the triple product is restricted to two possible values.

A generalized structure-factor expression

Amplitudes of normalized structure factors can be obtained from an observed data set using

$$|E_{\mathbf{h}}|^2 = |F_{\mathbf{h}}^{\text{obs}}|^2 \bigg/ \left[p_{\mathbf{h}} \sum_{i=1}^{N} f_i^2(h)\right], \tag{1}$$

where $F_{\mathbf{h}}^{\text{obs}}$ is a structure factor on an absolute scale, N is the number of atoms in the unit cell, $p_{\mathbf{h}}$ is the statistical weight of $E_{\mathbf{h}}$, and $f_i(h)$ is the scattering factor of the ith atom, temperature factor included. The statistical weight takes into account the fact that in most space groups the average intensity for certain classes of reflexions is expected to be larger than $\sum_{i=1}^{N} f_i^2(h)$.

The normalized structure factor can be written as

$$E_{\mathbf{h}} = p_{\mathbf{h}}^{-1/2} \sigma_2^{-1/2} \sum_{i=1}^{N} Z_i \exp(2\pi i \mathbf{h}.\mathbf{r}_i), \tag{2}$$

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where

$$\sigma_s = \sum_{i=1}^{N} Z_i^s$$

and Z_i is the atomic number of atom i. In a space group of order m there are $n = N/m$ independent atoms in the unit cell so, following Bertaut & Waser (1957) and excluding systematically absent reflexions,

$$E_{\mathbf{h}} = p_{\mathbf{h}}^{1/2}\sigma_2^{-1/2} \sum_{i=1}^{n} Z_i \sum_{j=1}^{m/p_{\mathbf{h}}} \exp[2\pi i\mathbf{h}.(R_j\mathbf{r}_i + \mathbf{t}_j)], \quad (3)$$

where R_j is a 3 × 3 matrix for the proper or improper rotational component of the jth symmetry operation, $\mathbf{t}_j$ is a three-dimensional vector describing the translational component of the jth symmetry operation, m is the total number of symmetry operations, a possible inversion included.

If $E_{\mathbf{h}}$ corresponds to a centrosymmetric arrangement of atoms, (3) reduces to a sum over $m/2p_{\mathbf{h}}$ cosine terms. This can lead to an expression for a triple product in which both cosine and exponential functions are present. To avoid this we proceed in the following way: if $E_{\mathbf{h}}$ corresponds to a centrosymmetric structure, one of the $m/p_{\mathbf{h}}$ symmetry operations, to be identified with label h, will be of such a form that $\mathbf{h}R_h = -\mathbf{h}$ so the hth term in the summation over the symmetry elements can be combined with the one arising from the identity operation:

$$\{\exp(2\pi i\mathbf{h}.\mathbf{r}_i) + \exp[2\pi i(-\mathbf{h}.\mathbf{r}_i + \mathbf{h}.\mathbf{t}_h)]\}. \quad (4)$$

As the set of $m/p_{\mathbf{h}}$ symmetry operations forms a mathematical group, the following reasoning holds:

if $(R_h,\mathbf{t}_h)$ and $(R_q,\mathbf{t}_q)$ are members of the group, then $(R_s,\mathbf{t}_s)$ also belongs to the group if $R_s = R_hR_q$ and $\mathbf{t}_s = \mathbf{t}_h + \mathbf{t}_q$. So, if $\mathbf{h}R_h = -\mathbf{h}$, then $\mathbf{h}R_hR_q = \mathbf{h}R_s = -\mathbf{h}R_q$.

This means that all exponential terms in (3) are two by two related in the same way as described in (4). Because $\mathbf{t}_s = \mathbf{t}_h + \mathbf{t}_q$ the phase difference between the two terms is always equal to $2\pi\mathbf{h}.\mathbf{t}_h$.

If we now define the parameter $\delta_{\mathbf{h}}$ so that $\delta_{\mathbf{h}} = 0$ if $E_{\mathbf{h}}$ is a general structure factor and $\delta_{\mathbf{h}} = 1$ if $E_{\mathbf{h}}$ corresponds to a centrosymmetric arrangement of atoms, then the general expression for the normalized structure factor becomes

$$E_{\mathbf{h}} = p_{\mathbf{h}}^{-1/2}\sigma_2^{-1/2} \sum_{i=1}^{n} \sum_{j=1}^{m_{\mathbf{h}}} G_{i,j}(\mathbf{h}), \quad (5)$$

where $m_{\mathbf{h}} = m/(p_{\mathbf{h}}2^{\delta_{\mathbf{h}}})$ and

$$G_{i,j}(\mathbf{h}) = Z_i\{\exp[2\pi i\mathbf{h}.(R_j\mathbf{r}_i + \mathbf{t}_j)] + \delta_{\mathbf{h}}\exp[2\pi i\mathbf{h}.\mathbf{t}_h] \times \exp[-2\pi i\mathbf{h}.(R_j\mathbf{r}_i + \mathbf{t}_j)]\}.$$

From this it follows that if $\delta_{\mathbf{h}} = 1$ the phase of the structure factor is restricted to two possible values: $(\pi\mathbf{h}.\mathbf{t}_h)$ or $(\pi\mathbf{h}.\mathbf{t}_h + \pi)$.

Algebraic and probabilistic description of the product $E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}$

From (5) it follows that

$$E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3} = (p_{\mathbf{h}_1}p_{\mathbf{h}_2}p_{\mathbf{h}_3})^{1/2}\sigma_2^{-3/2} \times \sum_{i_1\ldots i_3}\sum_{j_1\ldots j_3} G_{i_1,j_1}(\mathbf{h}_1)\,G_{i_2,j_2}(\mathbf{h}_2)\,G_{i_3,j_3}(\mathbf{h}_3), \quad (6)$$

where

$$\sum_{i_1\ldots i_3}\sum_{j_1\ldots j_3} \quad \text{means} \quad \sum_{i_1=1}^{n}\sum_{i_2=1}^{n}\sum_{i_3=1}^{n}\sum_{j_1=1}^{m_{\mathbf{h}_1}}\sum_{j_2=1}^{m_{\mathbf{h}_2}}\sum_{j_3=1}^{m_{\mathbf{h}_3}}.$$

Define

$$\left.\begin{aligned} T\gamma_1,\gamma_2,\gamma_3 &\equiv \sum_{k=1}^{3}\gamma_k\mathbf{h}_k.\mathbf{t}_{j_k} \\ R\gamma_1,\gamma_2,\gamma_3 &\equiv \sum_{k=1}^{3}\gamma_k\mathbf{h}_k.R_{j_k}\mathbf{r}_{i_k} \\ D\gamma_1,\gamma_2,\gamma_3 &\equiv \sum_{k=1}^{3}\gamma_k\mathbf{h}_k.\mathbf{t}_{h_k} \end{aligned}\right\}\ \gamma_1,\gamma_2,\gamma_3 \text{ are integers}, \quad (7)$$

and write

$$E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3} = A_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} + iB_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3},$$

then

$$\begin{aligned} A_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} = (p_{\mathbf{h}_1}p_{\mathbf{h}_2}p_{\mathbf{h}_3})^{1/2}\sigma_2^{-3/2} &\sum_{i_1\ldots i_3}\sum_{j_1\ldots j_3} Z_{i_1}Z_{i_2}Z_{i_3} \\ &\times \{\cos 2\pi(T_{111} + R_{111}) \\ &+ \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3}\cos 2\pi(D_{111} + T_{\bar{1}\bar{1}\bar{1}} + R_{\bar{1}\bar{1}\bar{1}}) \\ &+ \delta_{\mathbf{h}_1}\cos 2\pi(D_{100} + T_{\bar{1}11} + R_{\bar{1}11}) \\ &+ \delta_{\mathbf{h}_2}\cos 2\pi(D_{010} + T_{1\bar{1}1} + R_{1\bar{1}1}) \\ &+ \delta_{\mathbf{h}_3}\cos 2\pi(D_{001} + T_{11\bar{1}} + R_{11\bar{1}}) \\ &+ \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\cos 2\pi(D_{110} + T_{\bar{1}\bar{1}1} + R_{\bar{1}\bar{1}1}) \\ &+ \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_3}\cos 2\pi(D_{101} + T_{\bar{1}1\bar{1}} + R_{\bar{1}1\bar{1}}) \\ &+ \delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3}\cos 2\pi(D_{011} + T_{1\bar{1}\bar{1}} + R_{1\bar{1}\bar{1}})\}. \quad (8) \end{aligned}$$

The expression for $B_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ is analogous to (8), with the cosines replaced by sines.

Now let $\mathbf{h}_1$, $\mathbf{h}_2$ and $\mathbf{h}_3$ be fixed vectors in reciprocal space and let the atomic coordinates assume all possible values, then, after defining

$$A'_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} \equiv A_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} - \langle A_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}\rangle \text{ p.r.v.'s}$$

and

$$B'_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} \equiv B_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3} - \langle B_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}\rangle \text{ p.r.v.'s}, \quad (9)$$

where the p.r.v.'s are the primitive random variables (*i.e.* the atomic coordinates), both $A'_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and $B'_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ can be regarded as a sum over a large number of independent random variables. From (8) it can be seen that each random variable is a sum over eight trigonometric functions (eight cosines for $A'_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$ and eight sines for $B'_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$).

Application of the central limit theorem (see Appendix 1) now leads directly to the conclusion that the joint probability distribution of A' and B' will be a normal distribution:

$$P(A',B') = (2\pi)^{-1}\,U^{-1/2}\exp[-\tfrac{1}{2}U^{-1}(u_{22}A'^2 + u_{11}B'^2 - 2u_{12}A'\,B')], \qquad (10)$$

where u_{11}, u_{22} and u_{12} are the elements of the covariance matrix U of which U is the determinant.

For the calculations of the mean values we refer to Appendices II and III. The final results are

$$\begin{aligned}\langle A\rangle\ \text{p.r.v.'s} = {} & (p_{\mathbf{h}_1}p_{\mathbf{h}_2}p_{\mathbf{h}_3})^{1/2}\,m^{-1}\,\sigma_3\,\sigma_2^{-3/2}\\ & \times \Bigg\{\overset{(0)}{\sum}[\cos 2\pi(T_{111})\\ & + \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3}\cos 2\pi(D_{111} + T_{\bar{1}\bar{1}\bar{1}})]\\ & + \overset{(1)}{\sum}[\delta_{\mathbf{h}_1}\cos 2\pi(D_{100} + T_{\bar{1}11})\\ & + \delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3}\cos 2\pi(D_{011} + T_{1\bar{1}\bar{1}})]\\ & + \overset{(2)}{\sum}[\delta_{\mathbf{h}_2}\cos 2\pi(D_{010} + T_{1\bar{1}1})\\ & + \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_3}\cos 2\pi(D_{101} + T_{\bar{1}1\bar{1}})]\\ & + \overset{(3)}{\sum}[\delta_{\mathbf{h}_3}\cos 2\pi(D_{001} + T_{11\bar{1}})\\ & + \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\cos 2\pi(D_{110} + T_{\bar{1}\bar{1}1})]\Bigg\}, \qquad (11)\end{aligned}$$

where $\overset{(n)}{\sum}$ means

$$\sum_{j_1}^{m_{\mathbf{h}_1}}\sum_{j_2}^{m_{\mathbf{h}_2}}\sum_{j_3}^{m_{\mathbf{h}_3}}$$

with

$$\sum_{i=1}^{3}(-1)^{\delta_{i,n}}\,\mathbf{h}_i R_{j_i} = \mathbf{0},$$

where $\delta_{i,n}$ is the Kronecker delta.

The expression for $\langle B\rangle$ is analogous to (11), with the cosines replaced by sines.

$$\begin{aligned}u_{11} = {} & \tfrac{1}{2}p_{\mathbf{h}_1}p_{\mathbf{h}_2}p_{\mathbf{h}_3}\sigma_2^{-3}\,m_{\mathbf{h}_1}m_{\mathbf{h}_2}m_{\mathbf{h}_3}\\ & \times\sum_{i_1}\sum_{i_2}\sum_{i_3}Z_{i_1}^2Z_{i_2}^2Z_{i_3}^2\,\{1 + \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3} + \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\\ & + \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_3} + \delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3} + \delta_{\mathbf{h}_1} + \delta_{\mathbf{h}_2} + \delta_{\mathbf{h}_3}\\ & + 8\delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3}\cos 2\pi D_{111}\}. \qquad (12)\end{aligned}$$

Define μ as the number of structure factors in the triple product having a restricted phase (*i.e.* $\mu = \delta_{\mathbf{h}_1} + \delta_{\mathbf{h}_2} + \delta_{\mathbf{h}_3}$) then

$$u_{11} = \tfrac{1}{2} + \tfrac{1}{2}\delta_{\mu,3}\cos 2\pi D_{111}. \qquad (13)$$

Using the same definitions we get

$$u_{22} = \tfrac{1}{2} - \tfrac{1}{2}\delta_{\mu,3}\cos 2\pi D_{111} \qquad (14)$$

and

$$u_{12} = u_{21} = \tfrac{1}{2}\delta_{\mu,3}\sin 2\pi D_{111}. \qquad (15)$$

In (12)–(15) terms of order N^{-1} were neglected.

From (13), (14) and (15) the value of the determinant is

$$U = \tfrac{1}{4} - \tfrac{1}{4}\delta_{\mu,3}. \qquad (16)$$

It may be noted that the various contributions to $\langle A\rangle$ and $\langle B\rangle$ are obtained by rotating the reciprocal vectors according to the symmetry operations of the space group and taking into account all combinations for which $\mathbf{h}_1R_{j_1} \pm \mathbf{h}_2R_{j_2} \pm \mathbf{h}_3R_{j_3} = \mathbf{0}$. This set of symmetry-related triple products is usually referred to as the first representation of the invariant phase combination $(\varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3})$. From (11) it follows that it is essential to take the complete first representation into account, which is in agreement with the results of the representation theory of Giacovazzo (1977).

General triple products

If at least one of the structure factors participating in the triple product is of a non-centrosymmetric nature (*i.e.* $\mu \neq 3$), the covariance matrix of A' and B' becomes diagonal with $U = \tfrac{1}{4}$ and $u_{11} = u_{22} = \tfrac{1}{2}$.

From (9) and (10) we find

$$P(A,B) = \pi^{-1}\exp[-A^2 - B^2 + 2A\langle A\rangle + 2B\langle B\rangle - \langle A\rangle^2 - \langle B\rangle^2], \qquad (17)$$

where $\langle A\rangle$ and $\langle B\rangle$ are defined in (11). Put $A = R\cos\Phi$, $B = R\sin\Phi$ and

$$\langle A\rangle + i\langle B\rangle = \sigma_3\,\sigma_2^{-3/2}\,Q\exp(iq), \qquad (18)$$

then (17) gives

$$P(R,\Phi) = \pi^{-1}R\exp(-R^2)\exp[2\sigma_3\,\sigma_2^{-3/2}RQ \times\cos(\Phi - q)] \qquad (19)$$

and

$$P(\Phi|R) = (2\pi)^{-1}I_0^{-1}(2\sigma_3\,\sigma_2^{-3/2}RQ)\exp[2\sigma_3\,\sigma_2^{-3/2}RQ \times\cos(\Phi - q)], \qquad (20)$$

where $I_0(x)$ is the modified Bessel function of order 0. This type of distribution is usually referred to as a circular normal distribution or a von Mises distribution (Heinerman, Krabbendam & Kroon, 1977). The mode of (20) is at $\Phi = q$ and the argument of the Bessel function is a measure of its sharpness.

Triple products with restricted phase angles

If $\mu = 3$, then $U = 0$ (see 16), so the two-dimensional normal distribution (10) can no longer be applied. In these cases all three structure factors in the triple product have restricted phases. Clearly then the phase $\Phi_{\mathbf{h}_1\mathbf{h}_2}$ of the triple product is also restricted to two possible values:

$$\Phi_{\mathbf{h}_1\mathbf{h}_2} = \pi(\mathbf{h}_1 . \mathbf{t}_{h_1} + \mathbf{h}_2 . \mathbf{t}_{h_2} + \mathbf{h}_3 . \mathbf{t}_{h_3}) + n_{\mathbf{h}_1\mathbf{h}_2}\pi$$
$$(n_{\mathbf{h}_1\mathbf{h}_2} = 0 \text{ or } 1),$$

so

$$\Phi_{\mathbf{h}_1\mathbf{h}_2} = \pi D_{111} \quad \text{or} \quad \Phi_{\mathbf{h}_1\mathbf{h}_2} = \pi(D_{111} + 1). \tag{21}$$

This means that A' and B' are linearly related *via*

$$B' = \tan(\pi D_{111}) A',$$

and therefore $P(A',B')$ is not defined.

Instead of treating their real and imaginary part, these triple products should preferably be described in terms of their amplitude and their direction along the axis on which they are restricted. To avoid cumbersome notation, we postpone this transformation. The probability distribution will first be derived in terms of A and B, after which the transformation is straightforward.

Because

$$P(A') = \int_{-\infty}^{\infty} P(A',B')\,\mathrm{d}B', \tag{22}$$

the desired one-dimensional distribution can be determined from (10). It appears that

$$P(A') = (2\pi u_{11})^{-1/2} \exp(-\tfrac{1}{2} u_{11}^{-1} A'^2), \tag{23}$$

which is independent of the determinant of the covariance matrix. If the variance of A' happens to be equal to zero,

$$\lim_{u_{11}\to 0} [P(A')] = \delta(A',0), \tag{24}$$

where $\delta(A',0)$ is the Dirac delta function. The same procedure can be used to derive $P(B')$ and to show

$$\lim_{u_{22}\to 0} [P(B')] = \delta(B',0). \tag{25}$$

Depending on the value of D_{111}, both $P(A')$ and $P(B')$ are given by (23) or one of them is a delta function. If $P(A')$ is not a delta function the probability distribution of the real part of the triple product follows from (9) and (23).*

$$P(A) = (2\pi u_{11})^{-1/2} \exp[-\tfrac{1}{2} u_{11}^{-1}(A^2 - 2A\langle A\rangle + \langle A\rangle^2)]. \tag{26}$$

Because $\delta_{\mathbf{h}_1} = \delta_{\mathbf{h}_2} = \delta_{\mathbf{h}_3} = 1$, (11) can be written as

$$\langle A\rangle = 2(p_{\mathbf{h}_1} p_{\mathbf{h}_2} p_{\mathbf{h}_3})^{1/2} \sigma_3 \sigma_2^{-3/2} W \cos(\pi D_{111}) m^{-1}, \tag{27}$$

where

$$W = \sum^{(0)} \cos \pi(D_{\bar{1}\bar{1}\bar{1}} + T_{222}) + \sum^{(1)} \cos \pi(D_{1\bar{1}\bar{1}} + T_{\bar{2}22})$$
$$+ \sum^{(2)} \cos \pi(D_{\bar{1}1\bar{1}} + T_{2\bar{2}2})$$
$$+ \sum^{(3)} \cos \pi(D_{\bar{1}\bar{1}1} + T_{22\bar{2}}).$$

By the transformation

$$A = R \cos(\pi D_{111} + n_{\mathbf{h}_1\mathbf{h}_2}\pi), \tag{28}$$

where R is the amplitude of the triple product and $n_{\mathbf{h}_1\mathbf{h}_2} = 0$ or 1, and because

$$u_{11}^{-1} \cos^2(\pi D_{111}) = 1, \tag{29}$$

the following distribution function is obtained:

$$P(n_{\mathbf{h}_1\mathbf{h}_2},R) = C \exp[-\tfrac{1}{2}R^2 + R(p_{\mathbf{h}_1} p_{\mathbf{h}_2} p_{\mathbf{h}_3})^{1/2}$$
$$\times \sigma_3 \sigma_2^{-3/2} m^{-1} W\, 2 \cos(n_{\mathbf{h}_1\mathbf{h}_2}\pi)], \tag{30}$$

where C is a suitable normalizing constant.

From (30) the probability that the phase of the triple product is πD_{111} (*i.e.* $n_{\mathbf{h}_1\mathbf{h}_2} = 0$), given the amplitude R, is easily calculated:

$$P(\Phi_{\mathbf{h}_1\mathbf{h}_2} = \pi D_{111}) = \tfrac{1}{2} + \tfrac{1}{2} \tanh[2(p_{\mathbf{h}_1} p_{\mathbf{h}_2} p_{\mathbf{h}_3})^{1/2}$$
$$\times m^{-1} \sigma_3 \sigma_2^{-3/2} WR]. \tag{31}$$

Discussion and conclusions

The results in this paper, as formulated in (20) and (31), clearly show that space-group symmetry influences the main term of the conditional probability distribution of the phase of a triple product.

From (20) it is seen that in any space group the phase of a general triple product can be described by a von Mises distribution. Equation (18) shows that if $\langle B\rangle = 0$ then (20) becomes analogous to the well-known distribution function for $P1$. Under this condition our results are in agreement with Giacovazzo's conclusion (Giacovazzo, 1980) that the distribution function for $P1$ can be used in any non-centrosymmetric space group provided a suitable weight is applied. If $\langle B\rangle = 0$ the mean value of the trigonometric part of the triple product in Giacovazzo's formulae can be replaced by $\langle A\rangle$, after which it can be shown that in these cases the weight he applies is identical to our parameter Q.

Triple products with restricted phase angles are described by (31) which gives the probability that the phase $\Phi_{\mathbf{h}_1\mathbf{h}_2}$ is equal to one of the two possible values.

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* If $u_{11} = 0$ the following derivation is not correct. However, in these cases the same results are obtained *via* $P(B')$.

If the space group is centrosymmetric this formula can be simplified by choosing the conventional setting with the origin of the unit cell at the inversion centre, by which all D functions become equal to zero. Therefore, in centrosymmetric space groups the parameter W as defined in (27) can always be calculated *via*

$$W = \overset{(0)}{\sum} \cos 2\pi(T_{111}) + \overset{(1)}{\sum} \cos 2\pi(T_{\bar{1}11})$$

$$+ \overset{(2)}{\sum} \cos 2\pi(T_{1\bar{1}1}) + \overset{(3)}{\sum} \cos 2\pi(T_{11\bar{1}}).$$

In $P\bar{1}$, for example, the following parameters are valid for all triple products:

$$p_{\mathbf{h}_1} = p_{\mathbf{h}_2} = p_{\mathbf{h}_3} = 1 \quad \text{and} \quad m_{\mathbf{h}_1} = m_{\mathbf{h}_2} = m_{\mathbf{h}_3} = 1$$

$$\text{so} \quad W = 1,$$

which leads to the formula of Cochran & Woolfson (1955). Restricted triple products in non-centrosymmetric space groups, however, can only be described by (31). A well-known example of this type occurs in space group $P2_12_12_1$, where a triple product can be constructed from three structure factors in the parity groups ($g0u$), ($0gu$) and ($gg0$), so $\Phi_{\mathbf{h}_1\mathbf{h}_2}$ is restricted to $\pm\pi/2$ by space-group symmetry. Because $W = 0$ for this type of invariant (as is shown in Appendix IV), the probability that $\Phi_{\mathbf{h}_1\mathbf{h}_2} = \pi/2$ is exactly equal to the probability that $\Phi_{\mathbf{h}_1\mathbf{h}_2} = -\pi/2$.

The fact that there is no phase information about this triple product could have been expected because a preference for one of the two possible phases would implicitly mean a choice for one of the possible enantiomorphic solutions. The mere knowledge of three structure-factor amplitudes without any information about Bijvoet differences is of course insufficient for this kind of conclusion. These arguments are more generally applicable: because the von Mises distribution for general triple products (equation 20) is unimodal between 0 and 2π, it is not possible to find phase indications different from 0 or π as long as we have not specified which of the two enantiomorphic solutions we want to describe.

Therefore, it is not surprising that our results are in agreement in most cases with Giacovazzo's conclusions because the fixation of an enantiomorph in normal direct-methods procedures occurs after the determination of the probability distributions. However, there are situations in which phase indications are obtained that differ from 0: in the eleven pairs of enantiomorphously related space groups the enantiomorph is fixed by the choice of one of the two possible space groups, so there is in principle no objection against enantiomorph-dependent phase indications. For example, in $P4_1$ the triple product $E_{221}E_{\bar{4}01}E_{2\bar{2}\bar{2}}$ is expected to have a phase of $-45°$ because $\langle A\rangle = +\sigma_3\sigma_2^{-3/2}$ and $\langle B\rangle = -\sigma_3\sigma_2^{-3/2}$, as can be seen from Appendix V. In space group $P4_3$ the most probable phase of the same invariant is $+45°$ because now $\langle B\rangle = +\sigma_3\sigma_2^{-3/2}$.

An interesting consequence of this probabilistic result in chiral space groups is the possibility of indicating the most probable space group, without determining the structure. For this purpose it is sufficient to consider triple products, the most probable phases of which differ from zero or π according to (20). Following Heinerman, Krabbendam, Kroon & Spek (1978), the phases of these triple products can be estimated from the measured Bijvoet differences, without knowing the positions of the anomalous scatterers. Only one of the two possible space-group-dependent theoretical distribution functions will match the experimental one, thus indicating the space group. Once the space group has been specified in this way, the absolute configuration of the compound is completely fixed by the measured intensities even in the absence of anomalous scattering (ignoring the possibility of 'homometric' solutions). The subsequent determination of the structure in the indicated space group will therefore directly lead to the corresponding absolute configuration of the compound.

It should be noted that the latter procedure is of a statistical nature and only gives the most probable enantiomorph, even if the phases could be determined without error. In such an ideal situation the use of the so-called identities (Kroon, Pontenagel, Krabbendam & Peerdeman, 1982) would give an absolute answer. For practical purposes, however, the statistical solution seems the most favourable.

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APPENDIX I

The central limit theorem for complex vectors

Let T be a complex vector defined by

$$T = A + iB, \tag{I.1}$$

and let A and B be sums over a large number of *independent* random contributions, *i.e.*

$$A = \sum_i a_i, \quad B = \sum_i b_i$$

$$\left.\begin{array}{ll} \text{and} & \langle a_i a_j\rangle \text{ p.r.v.'s} = 0 \\ \text{and} & \langle b_i b_j\rangle \text{ p.r.v.'s} = 0 \end{array}\right] \text{ for } i \neq j, \tag{I.2}$$

where the p.r.v.'s are the primitive random variables of the problem in which the a_i's and b_i's are expressed.

If, in addition, $\langle A\rangle = 0$ and $\langle B\rangle = 0$, application of the central limit theorem leads to a two-dimensional normal distribution for A and B:

$$P(A,B) = (2\pi)^{-1}\, U^{-1/2} \exp[-\tfrac{1}{2}U^{-1}(u_{22}A^2 + u_{11}B^2 - 2u_{12}AB)], \tag{I.3}$$

where

$$u_{11} = \sum_i \langle a_i^2\rangle, \quad u_{22} = \sum_i \langle b_i^2\rangle, \quad u_{12} = \sum_i \langle a_i b_i\rangle \tag{I.4}$$

and

$$U = u_{11}u_{22} - u_{12}^2.$$

APPENDIX II

Calculation of $\langle A\rangle$, $\langle B\rangle$, u_{11}, u_{22} and u_{12}

From (8) we obtain

$$\langle A\rangle = C \sum_{i_1\ldots i_3}\sum_{j_1\ldots j_3} Z_{i_1}Z_{i_2}Z_{i_3}[\langle\cos 2\pi(T_{111} + R_{111})\rangle + \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3}\langle\cos 2\pi(D_{111} + T_{\bar1\bar1\bar1} + R_{\bar1\bar1\bar1})\rangle + \ldots], \tag{II.1}$$

where C is a constant of order $N^{-3/2}$. Each of the individual averages gives rise to a contribution of order $N^{-1/2}$ to $\langle A\rangle$ if $i_1 = i_2 = i_3$, provided j_1, j_2, j_3 assume values for which $\gamma_1\mathbf{h}_1R_{j_1} + \gamma_2\mathbf{h}_2R_{j_2} + \gamma_3\mathbf{h}_3R_{j_3} = \mathbf{0}$, as described in case (*c*) of Appendix III. The result is easily obtained and is given in (11).

$\langle B\rangle$ can be calculated in the same way after replacing all cosines by sines. From Appendix I, using (8), it follows that the variance of A' (*i.e.* u_{11}) is

$$u_{11} = C \sum_{i_1\ldots i_3}\sum_{j_1\ldots j_3}{}^{*} Z_{i_1}^2Z_{i_2}^2Z_{i_3}^2\{\langle\cos^2 2\pi(T_{111} + R_{111})\rangle + 2\delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3}\langle\cos 2\pi(T_{111} + R_{111}) \times \cos 2\pi(D_{111} + T_{\bar1\bar1\bar1} + R_{\bar1\bar1\bar1})\rangle + 2\delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3} \times \langle\cos 2\pi(T_{111} + R_{111}) \times \cos 2\pi(D_{011} + T_{1\bar1\bar1} + R_{1\bar1\bar1})\rangle + \ldots\}, \tag{II.2}$$

where C is a constant of order N^{-3}.

This expression contains eight quadratic terms of the type $\cos^2(x)$; since $\cos^2(x) = \frac{1}{2} + \frac{1}{2}\cos(2x)$, each term of this kind gives rise to a constant contribution; the total contribution of the quadratic terms to the average is

$$\tfrac{1}{2}C \sum_{i_1\ldots i_3} Z_{i_1}^2Z_{i_2}^2Z_{i_3}^2(1 + \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3} + \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2} + \delta_{\mathbf{h}_1}\delta_{\mathbf{h}_3} + \delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3} + \delta_{\mathbf{h}_1} + \delta_{\mathbf{h}_2} + \delta_{\mathbf{h}_3}). \tag{II.3}$$

In addition there are 28 terms of the type

$$\langle\cos 2\pi(D_{\nu_1} + T_{\eta_1} + R_{\omega_1})\cos 2\pi(D_{\nu_2} + T_{\eta_2} + R_{\omega_2})\rangle = \tfrac{1}{2}[\langle\cos 2\pi(D_{\nu_1+\nu_2} + T_{\eta_1+\eta_2} + R_{\omega_1+\omega_2})\rangle + \langle\cos 2\pi(D_{\nu_1-\nu_2} + T_{\eta_1-\eta_2} + R_{\omega_1-\omega_2})\rangle]. \tag{II.4}$$

Order n^3 contributions, necessary to compensate for the $0(N^{-3})$ factor C, are only possible if $i_1 \neq i_2 \neq i_3$ [see case (*a*) of Appendix III]. This is the case if in $R_{\omega_1+\omega_2}$ or $R_{\omega_1-\omega_2}$ the symbols $\omega_1 + \omega_2$ or $\omega_1 - \omega_2$ stand for (0,0,0), so $R_{\omega_1+\omega_2} = 0$ or $R_{\omega_1-\omega_2} = 0$ (and, as it appears, $T_{\eta_1+\eta_2} = 0$ or $T_{\eta_1-\eta_2} = 0$). Out of the 56 terms of this type only four fulfil the above conditions; their total contribution to the average is

$$C \sum_{i_1\ldots i_3}\sum_{j_1\ldots j_3} 4\delta_{\mathbf{h}_1}\delta_{\mathbf{h}_2}\delta_{\mathbf{h}_3}\cos 2\pi D_{111}. \tag{II.5}$$

The final expression for u_{11} is given by (12).

u_{22} and u_{12} can be calculated along the same lines. The results are given in (14) and (15).

APPENDIX III

Order of the contributions to the mean values

In all expressions concerned the terms are of the form

$$C \sum_{i_1\ldots i_3}\sum_{j_1\ldots j_3} Z_{i_1}^qZ_{i_2}^qZ_{i_3}^q\langle\cos 2\pi(T + D + R_{\gamma_1\gamma_2\gamma_3})\rangle_{\mathbf{r}_{i_1},\mathbf{r}_{i_2},\mathbf{r}_{i_3}}, \tag{III.1}$$

in which

$$R_{\gamma_1\gamma_2\gamma_3} = \gamma_1\mathbf{h}_1 . R_{j_1}\mathbf{r}_{i_1} + \gamma_2\mathbf{h}_2 . R_{j_2}\mathbf{r}_{i_2} + \gamma_3\mathbf{h}_3 . R_{j_3}\mathbf{r}_{i_3}$$

and C is a constant of order $(N^{-3/2})$ and $q = 1$ in the expressions for $\langle A\rangle$ and $\langle B\rangle$, while C is of order (N^{-3}) and $q = 2$ in the expressions for the elements of the covariance matrix.

If we assume that the number of atoms in the asymmetric unit is large compared to the number of symmetry operations ($n \gg m_{\mathbf{h}_1}m_{\mathbf{h}_2}m_{\mathbf{h}_3}$), then the following three cases must be explored:

(*a*) $i_1 \neq i_2 \neq i_3$ (*order n^3 contributions*). $\langle\cos 2\pi(T + D + R)\rangle \neq 0$ if simultaneously $\gamma_1\mathbf{h}_1R_{j_1} = \mathbf{0}$ and $\gamma_2\mathbf{h}_2R_{j_2} = \mathbf{0}$ and $\gamma_3\mathbf{h}_3R_{j_3} = \mathbf{0}$. Excluding triplets in which $\mathbf{h}_i = \mathbf{0}$ $(i = 1, 2, 3)$, we obtain $\gamma_1 = \gamma_2 = \gamma_3 = 0$ for order n^3 contributions. These are the important contributions to the elements of the covariance matrix, as the $0(n^3)$ contributions compensate for the $0(N^{-3})$ constant in the expressions.

(*b*) $i_1 = i_2 \neq i_3$ (*order n^2 contributions*). $\langle\cos 2\pi(T + D + R)\rangle \neq 0$ if simultaneously $\gamma_3\mathbf{h}_3R_{j_3} = \mathbf{0}$ (*i.e.* $\gamma_3 = 0$) and $\gamma_1\mathbf{h}_1R_{j_1} + \gamma_2\mathbf{h}_2R_{j_2} = \mathbf{0}$; this case is not relevant to the calculation of $\langle A\rangle$ and $\langle B\rangle$, where γ_3 is not equal to zero, and can be neglected compared to the $0(n^3)$ contributions in the calculation of the elements of the covariance matrix.

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* If $i_1 = i_2 = i_3$ all terms for which $\mathbf{h}_1R_{j_1} \pm \mathbf{h}_2R_{j_2} \pm \mathbf{h}_3R_{j_3} = \mathbf{0}$ are omitted.

(*c*) $i_1 = i_2 = i_3$ (*order n contributions*). $\langle \cos 2\pi(T + D + R)\rangle \neq 0$ if $\gamma_1 \mathbf{h}_1 R_{j_1} + \gamma_2 \mathbf{h}_2 R_{j_2} + \gamma_3 \mathbf{h}_3 R_{j_3} = \mathbf{0}$. This case is essential in the calculation of $\langle A\rangle$ and $\langle B\rangle$. Example: if $\gamma_1 = -1$ and $\gamma_2 = \gamma_3 = 1$ then the expression is

$$C \sum_{i=1}^{n} Z_i^3 \sum^{(1)} \cos 2\pi(T + D)$$

with

$$\sum^{(1)} = \sum_{j_1}^{m_{\mathbf{h}_1}} \sum_{j_2}^{m_{\mathbf{h}_2}} \sum_{j_3}^{m_{\mathbf{h}_3}},$$

where j_1, j_2, j_3 are restricted to those values for which $-\mathbf{h}_1 R_{j_1} + \mathbf{h}_2 R_{j_2} + \mathbf{h}_3 R_{j_3} = \mathbf{0}$.

APPENDIX IV

Example of the calculations for a special triple product in $P2_12_12_1$

Consider the triple product $E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_3}$, where

$$\mathbf{h}_1 = (2,0,1), \quad \mathbf{h}_2 = (0,4,\bar{1}), \quad \mathbf{h}_3 = (\bar{2},\bar{4},0).$$

In Table 1 all symmetry-related structure factors of interest are collected together with their phase shifts, which can be calculated from the equivalent positions as given in *International Tables for X-ray Crystallography* (1969)

(x,y,z), $(\frac{1}{2} - x, -y, \frac{1}{2} + z)$, $(\frac{1}{2} + x, \frac{1}{2} - y, -z)$,
$(-x, \frac{1}{2} + y, \frac{1}{2} - z)$.

From Table 1 we obtain:

$$p_{\mathbf{h}_1} = p_{\mathbf{h}_2} = p_{\mathbf{h}_3} = 1.$$

Because $\mathbf{h}_1 R_4 = (-\mathbf{h}_1)$: $\delta_{\mathbf{h}_1} = 1$; $\mathbf{h}_1 . \mathbf{t}_{h_1} = \frac{1}{2}$; $m_{\mathbf{h}_1} = 2$ (nos. 1 and 3); because $\mathbf{h}_2 R_3 = (-\mathbf{h}_2)$: $\delta_{\mathbf{h}_2} = 1$; $\mathbf{h}_2 . \mathbf{t}_{h_2} = 0$; $m_{\mathbf{h}_2} = 2$ (nos. 1 and 2); because $\mathbf{h}_3 R_2 = (-\mathbf{h}_3)$: $\delta_{\mathbf{h}_3} = 1$; $\mathbf{h}_3 . \mathbf{t}_{h_3} = 0$; $m_{\mathbf{h}_3} = 2$ (nos. 1 and 3).

With these parameters (27) can be used to calculate the following contributions to W:

$\sum^{(0)}$ type: $\cos \pi(-\frac{1}{2} + 0)$

because $\mathbf{h}_1 R_1 + \mathbf{h}_2 R_1 + \mathbf{h}_3 R_1 = \mathbf{0}$

$\cos \pi(-\frac{1}{2} + 1)$

because $\mathbf{h}_1 R_1 + \mathbf{h}_2 R_2 + \mathbf{h}_3 R_3 = \mathbf{0}$;

$\sum^{(1)}$ type: no contributions;

$\sum^{(2)}$ type: $\cos \pi(-\frac{1}{2} + 0)$

because $\mathbf{h}_1 R_3 - \mathbf{h}_2 R_1 + \mathbf{h}_3 R_3 = \mathbf{0}$

$\cos \pi(-\frac{1}{2} - 1)$

because $\mathbf{h}_1 R_3 - \mathbf{h}_2 R_2 + \mathbf{h}_3 R_1 = \mathbf{0}$;

$\sum^{(3)}$ type: no contributions.

Therefore, for this triple product $W = 0$, so (31) leads to

$$P(\Phi_{\mathbf{h}_1 \mathbf{h}_2} = \tfrac{1}{2}\pi) = \tfrac{1}{2}.$$

Table 1. *Symmetry-related structure factors and phase shifts in $P2_12_12_1$*

Symmetry operation		$\mathbf{h}_1 = (2,0,1)$	$\mathbf{h}_2 = (0,4,\bar{1})$	$\mathbf{h}_3 = (\bar{2},\bar{4},0)$
(1)	$\mathbf{h}R_1$	(2,0,1)	(0,4,$\bar{1}$)	($\bar{2}$,$\bar{4}$,0)
	$\mathbf{h}.\mathbf{t}_1$	(0)	(0)	(0)
(2)	$\mathbf{h}R_2$	($\bar{2}$,0,1)	(0.$\bar{4}$,$\bar{1}$)	(2,4,0)
	$\mathbf{h}.\mathbf{t}_2$	($\frac{1}{2}$)	($\frac{1}{2}$)	(0)
(3)	$\mathbf{h}R_3$	(2,0,$\bar{1}$)	(0,$\bar{4}$,1)	($\bar{2}$,4,0)
	$\mathbf{h}.\mathbf{t}_3$	(0)	(0)	(0)
(4)	$\mathbf{h}R_4$	($\bar{2}$,0,$\bar{1}$)	(0,4,1)	(2,$\bar{4}$,0)
	$\mathbf{h}.\mathbf{t}_4$	($\frac{1}{2}$)	($\frac{1}{2}$)	(0)

APPENDIX V

Example of the calculations for a special triple product in $P4_1$

Consider the triple product $E_{\mathbf{h}_1} E_{\mathbf{h}_2} E_{\mathbf{h}_3}$, where

$$\mathbf{h}_1 = (2,2,1); \quad \mathbf{h}_2 = (\bar{4},0,1); \quad \mathbf{h}_3 = (2,\bar{2},\bar{2}).$$

According to *International Tables for X-ray Crystallography* (1969) the equivalent positions are:

(x,y,z); $(\bar{x}, \bar{y}, \frac{1}{2} + z)$; $(\bar{y}, x, z + \frac{1}{4})$; $(y, \bar{x}, z - \frac{1}{4})$.

Table 2 gives symmetry-related structure factors with their phase shifts.

As

$$p_{\mathbf{h}_1} = p_{\mathbf{h}_2} = p_{\mathbf{h}_3} = 1 \quad \text{and} \quad \delta_{\mathbf{h}_1} = \delta_{\mathbf{h}_2} = \delta_{\mathbf{h}_3} = 0,$$

(11) gives the following contributions to $\langle A\rangle$:

Table 2. *Symmetry-related structure factors and phase shifts in $P4_1$*

Symmetry operation		$\mathbf{h}_1 = (2,2,1)$	$\mathbf{h}_2 = (\bar{4},0,1)$	$\mathbf{h}_3 = (2,\bar{2},\bar{2})$
(1)	$\mathbf{h}R_1$	(2,2,1)	($\bar{4}$,0,1)	(2,$\bar{2}$,$\bar{2}$)
	$\mathbf{h}.\mathbf{t}_1$	(0)	(0)	(0)
(2)	$\mathbf{h}R_2$	($\bar{2}$,$\bar{2}$,1)	(4,0,1)	($\bar{2}$,2,$\bar{2}$)
	$\mathbf{h}.\mathbf{t}_2$	($\frac{1}{2}$)	($\frac{1}{2}$)	(0)
(3)	$\mathbf{h}R_3$	(2,$\bar{2}$,1)	(0,4,1)	($\bar{2}$,$\bar{2}$,$\bar{2}$)
	$\mathbf{h}.\mathbf{t}_3$	($\frac{1}{4}$)	($\frac{1}{4}$)	($\frac{1}{2}$)
(4)	$\mathbf{h}R_4$	($\bar{2}$,2,1)	(0,$\bar{4}$,1)	(2,2,$\bar{2}$)
	$\mathbf{h}.\mathbf{t}_4$	($\frac{3}{4}$)	($\frac{3}{4}$)	($\frac{1}{2}$)

$\overset{(0)}{\sum}$ type: $\cos 2\pi(0 + 0 + 0)$

because $\mathbf{h}_1 R_1 + \mathbf{h}_2 R_1 + \mathbf{h}_3 R_1 = \mathbf{0}$

$\cos 2\pi(\frac{1}{2} + \frac{1}{2} + 0)$

because $\mathbf{h}_1 R_2 + \mathbf{h}_2 R_2 + \mathbf{h}_3 R_2 = \mathbf{0}$

$\cos 2\pi(\frac{1}{4} + \frac{1}{4} + \frac{1}{2})$

because $\mathbf{h}_1 R_3 + \mathbf{h}_2 R_3 + \mathbf{h}_3 R_3 = \mathbf{0}$

$\cos 2\pi(\frac{3}{4} + \frac{3}{4} + \frac{1}{2})$

because $\mathbf{h}_1 R_4 + \mathbf{h}_2 R_4 + \mathbf{h}_3 R_4 = \mathbf{0}$

$\cos 2\pi(0 + \frac{3}{4} + 0)$

because $\mathbf{h}_1 R_1 + \mathbf{h}_2 R_4 + \mathbf{h}_3 R_2 = \mathbf{0}$

$\cos 2\pi(\frac{1}{2} + \frac{1}{4} + 0)$

because $\mathbf{h}_1 R_2 + \mathbf{h}_2 R_3 + \mathbf{h}_3 R_1 = \mathbf{0}$

$\cos 2\pi(\frac{1}{4} + 0 + \frac{1}{2})$

because $\mathbf{h}_1 R_3 + \mathbf{h}_2 R_1 + \mathbf{h}_3 R_4 = \mathbf{0}$

$\cos 2\pi(\frac{3}{4} + \frac{1}{2} + \frac{1}{2})$

because $\mathbf{h}_1 R_4 + \mathbf{h}_2 R_2 + \mathbf{h}_3 R_3 = \mathbf{0}$.

Therefore, $\langle A \rangle = \sigma_3 \sigma_2^{-3/2} 4^{-1}(4 + 0) = \sigma_3 \sigma_2^{-3/2}$.

For the calculation of $\langle B \rangle$ the same contributions can be used with the cosines replaced by sines, so

$$\langle B \rangle = \sigma_3 \sigma_2^{-3/2} 4^{-1}(0 - 4) = -\sigma_3 \sigma_2^{-3/2}.$$

From (18) and (20) the most probable phase for this triple product in $P4_1$ appears to be

$$q = \arctan[\langle B \rangle / \langle A \rangle] = -45°.$$

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Modeling the Phase Change in Crystalline Biphenyl by using a Temperature-Dependent Potential*

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Abstract

The structures of two crystalline phases of biphenyl ($C_{12}H_{10}$) were modeled using an exp-6-1 nonbonded potential and $(1 - \cos^2 \varphi)$ terms for the phenyl–phenyl conjugation energy. Preliminary calculations were made by minimizing the energy of a model starting from the 110 K structure, space group $P2_1/a$, with planar molecules. Doubling the b axis and relaxing all symmetry caused the model to transform to a structure with twisted molecules, space group Pa, essentially the same as the approximate structure reported from neutron diffraction studies at 22 K. Increasing the contribution of the conjugation energy reversed the transformation, and calculations show that the potential that produces planar molecules in the crystal predicts twisted molecules in the gas phase, in agreement with experiment. A new temperature-dependent potential is described in which the nonbonded terms are modified according to the thermal motions of the atoms involved. Motion parallel to the interaction vector tends to push atoms apart, whereas motion perpendicular to it permits their mean positions to get closer together. Ways of combining the motions of the two atoms involved are considered. This new potential was applied to biphenyl to calculate successfully the observed unit-cell volumes and thermal expansion. The model reproduces the torsion angles in the 22 K

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