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The Probabilistic Theory of the Three-Phase Structure Seminvariant in $P2_1$, with Applications

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Abstract

By embedding the three-phase structure seminvariant T_0 and its symmetry-related variants T_1, T_2 and T_3 in suitable quintets Q_0, Q_1, Q_2 and Q_3, respectively, one obtains the extensions Q_j of the seminvariants T_j. Owing to the space-group dependent relationships among the phases, the value of T_0 is simply related to the values of the Q_j's. Thus the probabilistic theory of the seminvariant T_0 is reduced to that of quintets, which is well developed. In particular the discriminant Δ of T_0 is defined in terms of the discriminant of the quintet, and extreme values of Δ are correlated with extreme values of T_0 in the sense that $T_0 \simeq 0$ or π according as $\Delta \gg 0$ or $\Delta \ll 0$, respectively. Applications to two real structures in $P2_1$ are described which show the usefulness of these results in the solution of crystal structures.

1. Introduction

Our major goal is to present a formula, (3.19), which will be useful in the identification and estimation of those three-phase structure seminvariants in $P2_1$ having the extreme values 0 or π. In order not to distract or confuse the reader interested in making the applications, no details of the derivations are presented. Instead, only a few introductory paragraphs are given connecting this paper with the earlier work on extensions and relating the present work to the probabilistic theory of quintets (*via* the neighborhood concept), in particular the quintet discriminant. The remainder of the paper is devoted simply to a description of the major result, equation (3.19), and to applications of (3.19) to two structures in $P2_1$. These applications show the usefulness of the three-phase structure seminvariants in the determination of crystal structures.

Suppose that

$$T_0 = \varphi_{h_1 k_1 l} + \varphi_{h_2 k_2 l_2} + \varphi_{h_3 k_3 l_3} \tag{1.1}$$

is a structure seminvariant in $P2_1$. Then

$$(h_1 k_1 l_1) + (h_2 k_2 l_2) + (h_3 k_3 l_3) \equiv 0 \bmod(202), \tag{1.2}$$

i.e. $h_1 + h_2 + h_3$ and $l_1 + l_2 + l_3$ are even integers and

$$k_1 + k_2 + k_3 = 0. \tag{1.3}$$

By embedding T_0 and its three symmetry related variants,

$$T_1 = \varphi_{\bar{h}_1 k_1 \bar{l}_1} + \varphi_{h_2 k_2 l_2} + \varphi_{h_3 k_3 l_3}, \tag{1.4}$$

$$T_2 = \varphi_{h_1 k_1 l_1} + \varphi_{\bar{h}_2 k_2 \bar{l}_2} + \varphi_{h_3 k_3 l_3}, \tag{1.5}$$

and

$$T_3 = \varphi_{h_1 k_1 l_1} + \varphi_{h_2 k_2 l_2} + \varphi_{\bar{h}_3 k_3 \bar{l}_3}, \tag{1.6}$$

in suitable quintets (five-phase structure invariants), Q_0, Q_1, Q_2, and Q_3, respectively, one obtains the extensions Q_j of T_j, $j = 0, 1, 2, 3$, (Hauptman, 1978; but see also Giacovazzo, 1977, for a similar concept). If one defines integers H_j and L_j, $j = 0, 1, 2, 3$, by means of

$$H_0 = \tfrac{1}{2}(h_1 + h_2 + h_3), \qquad L_0 = \tfrac{1}{2}(l_1 + l_2 + l_3), \tag{1.7}$$

$$H_1 = \tfrac{1}{2}(-h_1 + h_2 + h_3), \qquad L_1 = \tfrac{1}{2}(-l_1 + l_2 + l_3), \tag{1.8}$$

$$H_2 = \tfrac{1}{2}(h_1 - h_2 + h_3), \qquad L_2 = \tfrac{1}{2}(l_1 - l_2 + l_3), \tag{1.9}$$

$$H_3 = \tfrac{1}{2}(h_1 + h_2 - h_3), \qquad L_3 = \tfrac{1}{2}(l_1 + l_2 - l_3), \tag{1.10}$$

then the extensions Q_j of T_j are defined by

$$Q_j = T_j + \varphi_{\bar{H}_j K_j \bar{L}_j} + \varphi_{\bar{H}_j \bar{K}_j L_j}, \tag{1.11}$$

where the four (positive) integers K_j, $j = 0, 1, 2, 3$, are arbitrary. Then the Q_j are five-phase structure invariants (quintets). It then follows from the space-group dependent relationships among the phases (Hauptman, 1978) that

$$T_0 = Q_j + \pi[\tfrac{1}{2} - \tfrac{1}{2}\cos \pi(k_j + K_j)], \quad j = 0, 1, 2, 3, \tag{1.12}$$

provided that k_0 is defined by

$$k_0 = 0. \tag{1.13}$$

In this way the probabilistic theory of the three-phase structure seminvariant T_0 is reduced to the probabilistic theory of quintets, which is well developed. In particular, for fixed positive integers K_j, $j = 0, 1, 2, 3$, the second neighborhood of T_0 consists of the set-theoretic union of the second neighborhoods of the four extensions Q_j, $j = 0, 1, 2, 3$, *i.e.* 41 magnitudes $|E|$

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in all. Since the four integers $K_j, j = 0, 1, 2, 3$, are arbitrary, there are many second neighborhoods, one for each set of four positive integers K_j.

It should perhaps be stressed that the extension concept enables one merely to identify the neighborhoods of the structure seminvariants. There remains the more time consuming task of deriving the conditional probability distribution of the seminvariant, given the magnitudes in any of its neighborhoods, using a mathematical formalism previously described (*e.g.* Hauptman, 1975*a*,*b*; Fortier & Hauptman, 1977*a*; Hauptman & Fortier, 1977; van der Putten & Schenk, 1977). However, the problem of deriving distributions sufficiently accurate to be useful in the applications appears to be quite difficult in general and has been solved only in a few cases so far.

2. The second neighborhoods

In view of earlier work on quintets (Schenk, 1975; Hauptman, 1977), the second neighborhood of the special quintet Q_0 (1.11) is known to consist of fourteen magnitudes $|E|$, the four distinct 'main terms'

$$|E_{h_1k_1l_1}|, |E_{h_2k_2l_2}|, |E_{h_3k_3l_3}|, |E_{H_0K_0L_0}|, \quad (2.1)$$

and the ten 'cross-terms'

$$|E_{h_1+h_2,k_3,l_1+l_2}|, |E_{h_2+h_3,k_1,l_2+l_3}|, |E_{h_3+h_1,k_2,l_3+l_1}|,$$
$$|E_{H_1,k_1\pm K_0,L_1}|, |E_{H_2,k_2\pm K_0,L_2}|, |E_{H_3,k_3\pm K_0,L_3}|,$$
$$|E_{2H_0,0,2L_0}|, \quad (2.2)$$

where K_0 is an arbitrary positive integer. In a similar way the fourteen-magnitude second neighborhoods of Q_1, Q_2 and Q_3 are found. However only 41 of the $14 \times 4 = 56$ magnitudes constituting the four second neighborhoods of Q_0, Q_1, Q_2 and Q_3 turn out to be distinct. Thus the second neighborhood of T_0 is found to consist of the 41 magnitudes:

$$r_i = |E_{h_ik_il_i}|, \quad i = 1, 2, 3; \quad (2.3)$$
$$R_j = |E_{H_jK_jL_j}|, \quad j = 0, 1, 2, 3; \quad (2.4)$$
$$r_{12} = |E_{h_1+h_2,k_3,l_1+l_2}|, \quad r_{1\bar{2}} = |E_{h_1-h_2,k_3,l-l_2}|; \quad (2.5)$$
$$r_{23} = |E_{h_2+h_3,k_1,l_2+l_3}|, \quad r_{2\bar{3}} = |E_{h_2-h_3,k_1,l_2-l_3}|; \quad (2.6)$$
$$r_{31} = |E_{h_3+h_1,k_2,l_3+l_1}|, \quad r_{3\bar{1}} = |E_{h_3-h_1,k_2,l_3-l_1}|; \quad (2.7)$$
$$R_{0j} = |E_{2H_j,0,2L_j}|, \quad j = 0, 1, 2, 3; \quad (2.8)$$
$$R_{10} = |E_{H_1,k_1+K_0,L_1}|, \quad R_{1\bar{0}} = |E_{H_1,k_1-K_0,L_1}|; \quad (2.9)$$
$$R_{20} = |E_{H_2,k_2+K_0,L_2}|, \quad R_{2\bar{0}} = |E_{H_2,k_2-K_0,L_2}|; \quad (2.10)$$
$$R_{30} = |E_{H_3,k_3+K_0,L_3}|, \quad R_{3\bar{0}} = |E_{H_3,k_3-K_0,L_3}|, \quad (2.11)$$
$$R_{11} = |E_{H_0,k_1+K_1,L_0}|, \quad R_{1\bar{1}} = |E_{H_0,k_1-K_1,L_0}|; \quad (2.12)$$
$$R_{21} = |E_{H_3,k_2+K_1,L_3}|, \quad R_{2\bar{1}} = |E_{H_3,k_2-K_1,L_3}|; \quad (2.13)$$
$$R_{31} = |E_{H_2,k_3+K_1,L_2}|, \quad R_{3\bar{1}} = |E_{H_2,k_3-K_1,L_2}|; \quad (2.14)$$
$$R_{12} = |E_{H_3,k_1+K_2,L_3}|, \quad R_{1\bar{2}} = |E_{H_3,k_1-K_2,L_3}|; \quad (2.15)$$
$$R_{22} = |E_{H_0,k_2+K_2,L_0}|, \quad R_{2\bar{2}} = |E_{H_0,k_2-K_2,L_0}|; \quad (2.16)$$
$$R_{32} = |E_{H_1,k_3+K_2,L_1}|, \quad R_{3\bar{2}} = |E_{H_1,k_3-K_2,L_1}|; \quad (2.17)$$
$$R_{13} = |E_{H_2,k_1+K_3,L_2}|, \quad R_{1\bar{3}} = |E_{H_2,k_1-K_3,L_2}|; \quad (2.18)$$
$$R_{23} = |E_{H_1,k_2+K_3,L_1}|, \quad R_{2\bar{3}} = |E_{H_1,k_2-K_3,L_1}|; \quad (2.19)$$
$$R_{33} = |E_{H_0,k_3+K_3,L_0}|, \quad R_{3\bar{3}} = |E_{H_0,k_3-K_3,L_0}|. \quad (2.20)$$

The logical next step would be to derive the conditional probability distribution of T_0, given the 41 magnitudes in its second neighborhood, using techniques previously described (*e.g.* Hauptman & Fortier, 1977). However, owing to the enormity of this task, this attempt has not yet been made. Instead, a more modest goal was set. It was decided to derive the exponential form of the conditional probability distribution of each quintet Q_j (a relatively easy task), given the 14 magnitudes in its second neighborhood, in effect the discriminant of the quintet (Hauptman & Fortier, 1977; Fortier & Hauptman, 1977*b*). It is already known from this earlier work that extreme values of the discriminant, whether large and positive or large and negative, are well correlated with the extreme values, 0 or π respectively, of the quintet. Thus, by employing only those extensions Q_j, the magnitudes of whose discriminants are extremely large, one identifies, *via* (1.12), those structure seminvariants T_0 having the extreme values 0 or π, approximately. In view of the earlier work on the discriminant, only the final results are briefly summarized in the sequel.

3. The discriminant of T_0

The discriminant of the three-phase structure seminvariant T_0 is defined in terms of the discriminants of the extensions Q_j of $T_j, j = 0, 1, 2, 3$.

3.1. *The discriminant of the quintet* Q_0

For each value of

$$K_0 = 1, 2, 3, \ldots, \quad (3.1)$$

one calculates the discriminant of the quintet Q_0 by means of

$$\Delta_{K_0} = \frac{2}{\sigma_2^{9/2}} \left[\sigma_3^3 \sum_{15}^{K_0} - \sigma_3(3\sigma_3^2 - \sigma_2\sigma_4) \sum_{10}^{K_0} + (15\sigma_3^3 - 10\sigma_2\sigma_3\sigma_4 + \sigma_2^2\sigma_5)\right], \quad (3.2)$$

where

$$\sum_{10}^{K_0} = r_{12}^2 + r_{23}^2 + r_{31}^2 + R_{00}^2 + R_{10}^2 + R_{1\bar{0}}^2 + R_{20}^2 + R_{2\bar{0}}^2 + R_{30}^2 + R_{3\bar{0}}^2, \quad (3.3)$$

$$\sum_{15}^{K_0} = r_{12}^2(R_{00}^2 + R_{30}^2 + R_{30}^{2-}) + r_{23}^2(R_{00}^2 + R_{10}^2 + R_{10}^{2-}) + r_{31}^2(R_{00}^2 + R_{20}^2 + R_{20}^{2-}) + (R_{10}^2 R_{20}^{2-} + R_{20}^2 R_{30}^{2-} + R_{30}^2 R_{10}^{2-}) + (R_{10}^{2-} R_{20}^2 + R_{20}^{2-} R_{30}^2 + R_{30}^{2-} R_{10}^2), \tag{3.4}$$

$$\sigma_n = \sum_{j=1}^{N} f_j^n, \tag{3.5}$$

f_j is the zero-angle atomic scattering factor of the atom labeled j, and N is the number of atoms in the whole unit cell. In the X-ray diffraction case the f_j are equal to the atomic numbers Z_j and are therefore all positive; in the neutron diffraction case some of the f_j may be negative.

3.2. *The discriminant of the quintet* Q_1

For each value of

$$K_1 = 1, 2, 3, \ldots, \tag{3.6}$$

one calculates the discriminant of Q_1 by means of

$$\Delta_{K_1} = \frac{2}{\sigma_2^{9/2}} \left[\sigma_3^3 \sum_{15}^{K_1} - \sigma_3(3\sigma_3^2 - \sigma_2\sigma_4) \sum_{10}^{K_1} + (15\sigma_3^3 - 10\sigma_2\sigma_3\sigma_4 + \sigma_2^2\sigma_5)\right], \tag{3.7}$$

where

$$\sum_{10}^{K_1} = r_{12}^{2-} + r_{23}^2 + r_{31}^{2-} + R_{01}^2 + R_{11}^2 + R_{11}^{2-} + R_{21}^2 + R_{21}^{2-} + R_{31}^2 + R_{31}^{2-} \tag{3.8}$$

and

$$\sum_{15}^{K_1} = r_{12}^{2-}(R_{01}^2 + R_{31}^2 + R_{31}^{2-}) + r_{23}^2(R_{01}^2 + R_{11}^2 + R_{11}^{2-}) + r_{31}^{2-}(R_{01}^2 + R_{21}^2 + R_{21}^{2-}) + (R_{11}^2 R_{21}^{2-} + R_{21}^2 R_{31}^{2-} + R_{31}^2 R_{11}^{2-}) + (R_{11}^{2-} R_{21}^2 + R_{21}^{2-} R_{31}^2 + R_{31}^{2-} R_{11}^2). \tag{3.9}$$

3.3. *The discriminant of the quintet* Q_2

For each value of

$$K_2 = 1, 2, 3, \ldots, \tag{3.10}$$

one calculates the discriminant of Q_2 by means of

$$\Delta_{K_2} = \frac{2}{\sigma_2^{9/2}} \left[\sigma_3^3 \sum_{15}^{K_2} - \sigma_3(3\sigma_3^2 - \sigma_2\sigma_4) \sum_{10}^{K_2} + (15\sigma_3^3 - 10\sigma_2\sigma_3\sigma_4 + \sigma_2^2\sigma_5)\right], \tag{3.11}$$

where

$$\sum_{10}^{K_2} = r_{12}^{2-} + r_{23}^{2-} + r_{31}^2 + R_{02}^2 + R_{12}^2 + R_{12}^{2-} + R_{22}^2 + R_{22}^{2-} + R_{32}^2 + R_{32}^{2-} \tag{3.12}$$

and

$$\sum_{15}^{K_2} = r_{12}^{2-}(R_{02}^2 + R_{32}^2 + R_{32}^{2-}) + r_{23}^{2-}(R_{02}^2 + R_{12}^2 + R_{12}^{2-}) + r_{31}^2(R_{02}^2 + R_{22}^2 + R_{22}^{2-}) + (R_{12}^2 R_{22}^{2-} + R_{22}^2 R_{32}^{2-} + R_{32}^2 R_{12}^{2-}) + (R_{12}^{2-} R_{22}^2 + R_{22}^{2-} R_{32}^2 + R_{32}^{2-} R_{12}^2). \tag{3.13}$$

3.4. *The discriminant of the quintet* Q_3

For each value of

$$K_3 = 1, 2, 3, \ldots, \tag{3.14}$$

one calculates the discriminant of Q_3 by means of

$$\Delta_{K_3} = \frac{2}{\sigma_2^{9/2}} \left[\sigma_3^3 \sum_{15}^{K_3} - \sigma_3(3\sigma_3^2 - \sigma_2\sigma_4) \sum_{10}^{K_3} + (15\sigma_3^3 - 10\sigma_2\sigma_3\sigma_4 + \sigma_2^2\sigma_5)\right], \tag{3.15}$$

where

$$\sum_{10}^{K_3} = r_{12}^2 + r_{23}^{2-} + r_{31}^{2-} + R_{03}^2 + R_{13}^2 + R_{13}^{2-} + R_{23}^2 + R_{23}^{2-} + R_{33}^2 + R_{33}^{2-} \tag{3.16}$$

and

$$\sum_{15}^{K_3} = r_{12}^2(R_{03}^2 + R_{33}^2 + R_{33}^{2-}) + r_{23}^{2-}(R_{03}^2 + R_{13}^2 + R_{13}^{2-}) + r_{31}^2(R_{03}^2 + R_{23}^2 + R_{23}^{2-}) + (R_{13}^2 R_{23}^{2-} + R_{23}^2 R_{33}^{2-} + R_{33}^2 R_{13}^{2-}) + (R_{13}^{2-} R_{23}^2 + R_{23}^{2-} R_{33}^2 + R_{33}^{2-} R_{13}^2). \tag{3.17}$$

3.5. *The discriminant of the structure seminvariant* T_0

For each fixed structure seminvariant T_0, arrange the collection

$$r_1 r_2 r_3(R_0^2 - 1)\Delta_{K_0}, \quad r_1 r_2 r_3(R_1^2 - 1)\Delta_{K_1}, \quad r_1 r_2 r_3(R_2^2 - 1)\Delta_{K_2}, \quad r_1 r_2 r_3(R_3^2 - 1)\Delta_{K_3}, \quad K_j = 1, 2, 3, \ldots; \quad j = 0, 1, 2, 3, \tag{3.18}$$

in decreasing order of magnitude and select the largest n of them where n is some small number, *e.g.* $n = 1, 2, 3, 4$ or 5. Using these n numbers construct, in view of (1.12), the 'discriminant' of T_0,

$$\Delta = \langle r_1 r_2 r_3(R_j^2 - 1)\Delta_{K_j} \cos \pi(k_j + K_j) \rangle_{K_j} \tag{3.19}$$

where the average is taken over the n K_j's corresponding to the n largest values of

$$|r_1 r_2 r_3(R_j^2 - 1)\Delta_{K_j}|, \quad K_j = 1, 2, 3, \ldots, \quad j = 0, 1, 2, 3, \tag{3.20}$$

and, by definition,

$$k_0 = 0. \tag{3.21}$$

If $n = 1$ then only one term contributes to (3.19), that one of (3.18) whose magnitude is largest. In this way one obtains a discriminant Δ for each structure seminvariant T_0 [in actuality several discriminants, one for each value of n, the number of contributors to the average in (3.19); however, as described in the sequel, the initial applications suggest that only the case $n = 1$ is needed].

Arrange the $|\Delta|$'s in decreasing order. Recall that according as $r_1 r_2 r_3(R_j^2 - 1)\,\Delta_{K_j}$ is large and positive or

Table 1. *Identity of* 200 *cosines of three-phase structure seminvariants calculated to be* ± 1 *employing* (3.19) *for aldosterone monohydrate,* $C_{21}H_{28}O_5 . H_2O$, *space group* $P2_1$

	Seminvariant Triple													
Serial	h_1	k_1	ℓ_1	h_2	k_2	ℓ_2	h_3	k_3	ℓ_3	A	No. of Quintets	No. of Cross Terms	Discr.	Calc Cos	True Cos
1	1	0	-12	10	0	-14	11	0	-2	6.15	7	7	-418.3	-1	-1.00
2	6	0	-10	3	0	8	11	0	-2	6.15	20	10	-389.0	-1	-1.00
3	9	0	-2	7	1	-10	4	-1	8	4.66	20	10	-323.3	-1	-0.97
4*	10	1	-2	9	0	-2	1	-1	0	7.39	17	9	-319.4	-1	-0.83
5	9	0	-2	11	1	-14	0	-1	12	5.45	12	10	-300.3	-1	-0.93
6	5	0	-4	4	0	2	11	0	-2	5.90	23	10	-251.0	-1	-1.00
7	10	1	-2	3	0	8	5	-1	-10	4.47	20	10	234.6	+1	0.79
8*	6	0	-10	1	1	0	7	-1	-10	7.23	17	9	-225.0	-1	-0.99
9*	10	1	-2	1	-1	0	11	0	-2	5.74	17	9	211.5	+1	0.83
10	1	0	-12	10	1	-2	9	-1	-14	4.92	11	10	207.3	+1	0.52
11	9	0	-2	4	0	2	7	0	-4	3.42	25	10	-203.5	-1	-1.00
12	5	0	-4	10	1	-2	3	-1	2	5.74	23	10	197.7	+1	0.91
13	7	1	-10	9	-2	-2	4	1	8	4.29	17	10	-186.4	-1	-0.99
14	9	0	-2	3	0	8	8	0	-10	3.47	21	10	-181.0	-1	-1.00
15	6	0	-10	9	0	-2	5	0	8	4.06	20	10	-173.8	-1	-1.00
16*	10	1	-2	3	0	8	7	-1	-10	6.91	10	6	-166.6	-1	-0.88
17	10	1	-2	3	-2	8	5	1	-10	3.53	17	10	161.2	+1	0.96
18	9	2	-2	11	-1	-14	0	-1	12	5.01	14	10	-159.6	-1	-0.92
19	1	1	0	11	0	-2	8	-1	-2	2.25	22	10	-156.3	-1	-0.83
20	9	2	-2	11	0	-2	0	-2	0	2.59	20	8	-152.8	-1	-0.99
21	11	0	-2	4	1	8	5	-1	-10	2.34	20	10	-151.8	-1	-0.92
22*	1	0	-12	10	1	-2	11	-1	-14	7.50	5	6	-149.1	-1	-0.95
23	6	2	-10	3	-2	8	11	0	-2	3.36	18	10	-147.2	-1	-0.95
24	5	0	-4	11	1	-14	4	-1	-10	5.26	19	10	146.3	+1	1.00
25*	10	1	-2	1	1	0	9	-2	-2	6.80	16	9	-145.8	-1	-1.00
26	6	0	-10	5	0	-4	7	0	10	5.78	20	8	140.2	+1	1.00
27	4	0	2	11	1	-14	5	-1	8	4.89	16	6	-138.3	-1	-1.00
28	5	0	-4	7	1	-10	0	-1	6	4.99	23	10	-133.2	-1	-0.93
29	10	0	-14	5	0	-10	7	0	-4	3.09	16	9	-133.1	-1	-1.00
30*	6	0	-10	-1	1	0	5	-1	-10	4.67	17	9	130.6	+1	1.00
31	9	0	-2	6	3	-9	5	-3	7	4.23	15	10	-130.4	-1	-1.00
32	6	1	-4	11	0	-2	3	-1	2	3.07	23	8	-129.6	-1	-0.94
33	0	1	12	11	0	-2	9	-1	-14	2.78	12	10	-125.8	-1	-0.95
34	11	0	-14	7	1	-10	6	-1	-4	5.35	15	7	-122.5	-1	-0.92
35*	1	1	0	7	1	-10	6	-2	-10	4.99	16	9	-121.4	-1	-0.92
36*	6	0	-10	10	1	-2	4	-1	8	6.31	10	6	-120.9	-1	-0.97
37	8	4	-7	11	0	-2	1	-4	5	3.26	11	10	-120.9	-1	-0.97
38	10	1	-2	7	-1	-10	5	0	8	3.55	20	10	120.8	+1	0.88
39*	10	1	-2	4	0	2	6	-1	-4	6.18	19	7	-120.7	-1	-1.00
40*	10	1	-2	10	0	-14	0	-1	12	6.80	7	6	-120.1	-1	-0.76
41	10	1	-2	4	-1	8	8	0	-10	2.76	20	10	119.6	+1	0.97
42	10	1	-2	3	0	8	1	-1	0	7.31	24	10	-119.3	-1	-0.83
43*	10	0	-14	1	1	0	11	-1	-14	6.27	5	8	-118.7	-1	-0.96
44*	5	0	-4	1	1	0	6	-1	-4	6.61	21	9	-117.9	-1	-0.88
45	9	0	-2	7	0	-11	4	0	9	2.84	20	10	-115.9	-1	-1.00
46	5	1	8	11	0	-2	4	-1	-10	3.28	17	10	-115.7	-1	-1.00
47	3	0	8	7	1	-10	8	-1	-2	2.71	22	10	115.2	+1	0.88
48	10	0	-14	0	1	12	8	-1	-2	2.67	15	10	110.7	+1	0.77
49	1	0	-12	11	1	-14	8	-1	-2	2.94	15	10	109.5	+1	0.95
50	5	0	-10	11	0	-2	4	0	8	2.44	20	7	-108.9	-1	-1.00
51*	1	0	-12	1	1	0	0	-1	12	6.57	14	9	-108.0	-1	-0.99
52	4	0	2	6	1	-4	8	-1	-2	2.43	23	10	107.3	+1	1.00
53	1	1	0	11	0	-14	8	-1	10	4.59	17	6	-107.0	-1	-0.66
54	11	0	-14	3	2	8	4	-2	2	3.10	17	8	106.8	+1	1.00
55	6	0	-10	4	1	8	8	-1	-2	2.47	20	10	106.3	+1	0.97
56*	6	0	-10	9	0	-2	3	0	8	7.93	8	7	106.0	+1	1.00
57	11	0	-14	11	0	-2	2	0	-12	3.19	4	7	-104.1	-1	-1.00
58	9	0	-2	8	1	10	3	-1	-12	2.88	15	10	-104.1	-1	-0.95
59	9	0	-2	3	4	4	8	-4	-6	3.78	12	10	-103.8	-1	-1.00
60*	1	1	0	7	-1	-10	8	0	-10	3.17	17	9	102.1	+1	0.99

Table 1 (*cont.*)

Serial	Seminvariant Triple h_1	k_1	ℓ_1	h_2	k_2	ℓ_2	h_3	k_3	ℓ_3	A	No. of Quintets	No. of Cross Terms	Discr.	Calc Cos	True Cos
61	10	1	-2	9	0	-2	7	-1	-10	6.99	20	8	-101.8	-1	-0.88
62	6	0	-10	6	1	-4	8	-1	10	4.72	20	7	-100.4	-1	-0.94
63	5	0	-4	4	1	8	3	-1	-12	3.44	22	10	-99.6	-1	-0.67
64	6	1	-4	5	0	-10	9	-1	-14	2.94	18	10	98.6	+1	0.60
65	5	0	-4	1	1	0	14	-1	0	3.85	22	7	-97.7	-1	-0.93
66	5	0	-4	11	0	-2	14	0	-6	4.17	15	7	-97.5	-1	-1.00
67	10	0	-14	6	1	-4	6	-1	-10	3.37	16	9	-97.2	-1	-0.91
68	9	0	-2	5	1	8	6	-1	-10	3.15	20	10	-96.9	-1	-0.73
69	1	0	-12	11	0	-2	8	0	10	3.76	5	7	-96.7	-1	-1.00
70	6	0	-10	11	0	-14	7	0	-4	4.01	15	7	-95.9	-1	-1.00
71	1	0	-12	9	0	-2	2	0	6	6.04	22	8	-95.7	-1	-1.00
72	1	1	0	6	1	-4	13	-2	0	3.81	20	8	-94.8	-1	-0.99
73	11	0	-2	2	0	9	7	0	-11	2.36	17	10	-94.1	-1	-1.00
74	11	0	-2	4	3	-9	5	-3	7	2.38	15	10	-93.5	-1	-1.00
75*	10	1	-2	7	1	-10	3	-2	8	5.47	8	6	-93.2	-1	-0.99
76	3	0	8	11	0	-14	4	0	2	6.43	20	8	93.1	+1	1.00
77	9	0	-2	3	1	2	14	-1	0	2.30	20	8	92.6	+1	0.98
78	11	0	-2	8	1	10	1	-1	-12	2.35	5	7	-92.2	-1	-0.88
79	6	1	-4	4	-1	8	10	0	-8	2.68	22	8	-92.0	-1	-0.99
80	10	0	-14	5	1	8	3	-1	2	3.90	17	8	90.4	+1	1.00
81	5	0	-4	11	0	-14	8	0	-10	3.90	15	7	-89.7	-1	-1.00
82	4	0	2	3	1	-12	5	-1	-10	2.38	22	10	89.4	+1	0.32
83	11	0	-2	3	1	9	6	-1	-11	2.48	20	10	-88.7	-1	-0.99
84	6	0	-10	3	2	8	11	-2	-2	2.61	18	10	-88.6	-1	-0.93
85	2	2	-12	11	0	-2	7	-2	10	2.52	10	8	-87.8	-1	-0.99
86	1	1	0	11	0	-14	0	-1	6	4.52	21	9	-87.5	-1	-0.89
87*	9	0	-2	1	1	0	8	-1	-2	2.90	19	9	86.3	+1	0.83
88	0	1	12	6	-1	-4	4	0	8	2.79	20	10	-85.6	-1	-0.82
89	7	1	-10	6	-1	-4	7	0	10	3.48	20	7	-85.1	-1	-0.92
90	7	1	-10	2	-2	-12	3	1	2	3.78	20	10	84.6	+1	0.66
91	9	2	-2	3	-2	8	8	0	-10	2.53	19	10	-84.5	-1	-0.97
92*	1	1	0	6	-2	-10	5	1	-10	3.22	16	9	84.4	+1	0.84
93	10	1	-2	1	1	0	3	-2	8	5.78	20	10	-84.2	-1	-0.98
94	9	0	-2	9	3	-7	2	-3	5	2.59	16	8	-83.4	-1	-0.83
95	5	0	-4	9	0	-2	2	0	-12	4.79	23	10	82.8	+1	1.00
96*	1	1	0	9	-2	-2	8	1	-2	2.67	17	9	82.8	+1	1.00
97	6	3	-9	11	0	-2	3	-3	7	3.01	15	10	-82.7	-1	-0.82
98	10	1	-2	4	-1	-10	4	0	8	3.01	20	10	82.3	+1	0.95
99	7	1	11	11	0	-2	2	-1	-13	2.79	5	7	-81.6	-1	-0.92
100*	1	1	0	6	-1	-4	7	0	-4	2.98	21	9	79.7	+1	0.88
101	9	0	-2	10	4	-7	1	-4	5	2.69	12	10	-79.4	-1	-0.68
102	0	3	11	11	0	-2	9	-3	-13	2.67	11	8	-79.3	-1	-0.98
103	6	1	-4	1	-2	-6	5	1	-10	2.35	20	10	78.7	+1	1.00
104	11	1	-14	4	0	-4	5	-1	-10	2.31	19	10	78.6	+1	0.94
105	0	1	12	5	0	-10	3	-1	2	3.41	21	10	78.2	+1	0.96
106*	9	0	-2	6	2	-10	3	-2	8	4.32	7	7	77.5	+1	0.95
107	5	0	-4	5	0	-10	2	0	6	5.23	23	10	-76.9	-1	-1.00
108	9	0	-2	1	1	0	4	-1	8	4.93	24	10	-76.5	-1	-0.94
109	10	0	-14	4	0	-4	8	0	-10	2.24	16	9	-76.5	-1	-1.00
110	10	1	-2	7	0	10	1	-1	-12	3.02	15	9	76.4	+1	0.73
111	7	1	-10	9	2	-2	4	-3	8	2.74	15	10	-76.2	-1	-0.78
112*	10	1	-2	6	-2	-10	4	1	8	4.35	8	6	-75.7	-1	-0.91
113	3	0	8	6	1	-4	1	-1	-12	3.70	22	10	74.4	+1	0.67
114	0	1	12	5	-1	8	7	0	-4	2.55	19	10	73.9	+1	0.96
115	10	1	-2	7	1	-10	9	-2	-2	6.43	18	8	-73.6	-1	-0.99
116*	10	0	-14	1	1	0	9	-1	-14	4.12	8	9	73.4	+1	0.91
117	3	0	8	6	2	-10	11	-2	-2	2.28	18	10	-73.3	-1	-0.78
118*	3	0	8	1	1	0	4	-1	8	4.87	17	9	-72.1	-1	-0.94
119	4	0	2	7	1	-10	1	-1	-12	3.87	22	10	71.5	+1	0.33
120	10	1	-2	2	0	9	6	-1	-11	3.01	20	10	71.4	+1	1.00
121	5	0	-4	3	0	8	14	0	-6	5.32	20	10	71.0	+1	1.00
122	1	0	-12	10	0	-14	3	0	8	7.84	15	7	70.5	+1	1.00
123	4	0	2	5	1	8	9	-1	-14	3.21	17	6	70.4	+1	0.82
124*	10	1	-2	5	0	-10	5	-1	8	5.21	10	6	-70.3	-1	-0.92
125	2	2	-12	3	-2	8	7	0	-4	2.47	20	10	-70.0	-1	-0.95
126	3	0	8	7	1	-10	4	-1	8	4.61	21	9	-69.9	-1	-0.97
127	5	0	-4	9	2	-2	2	-2	-12	6.45	20	10	69.7	+1	0.86
128	7	1	-10	3	-1	2	2	0	-12	2.59	22	10	69.4	+1	1.00
129*	10	1	-2	1	1	0	11	-2	-2	3.08	16	9	69.0	+1	0.84
130	9	0	-2	11	0	-14	0	0	12	3.04	11	10	-68.9	-1	-1.00

Table 1 (*cont.*)

Serial	Seminvariant Triple									A	No. of Quintets	No. of Cross Terms	Discr.	Calc Cos	True Cos
	h_1	k_1	ℓ_1	h_2	k_2	ℓ_2	h_3	k_3	ℓ_3						
131	9	0	-2	3	2	8	8	-2	-10	2.43	19	10	-68.8	-1	-0.25
132	10	1	-2	11	0	-14	3	-1	-12	4.42	14	7	-68.7	-1	-0.83
133	6	0	-10	6	3	-9	2	-3	-1	4.73	16	10	-68.1	-1	-0.79
134	1	1	0	11	-1	-14	8	0	10	3.85	15	6	-68.0	-1	-0.96
135	5	0	-4	2	0	-12	5	0	8	2.43	20	10	-67.3	-1	-1.00
136	1	0	-12	7	1	-10	14	-1	-6	3.28	9	7	-67.0	-1	-0.92
137*	6	3	-9	4	0	2	10	-3	-7	6.08	11	7	-66.8	-1	-0.98
138	10	1	-2	6	-1	-4	14	0	-6	4.38	15	7	-66.8	-1	-1.00
139	5	0	-4	3	0	8	4	0	2	7.51	26	10	66.6	+1	1.00
140	6	1	-4	6	-2	-10	8	1	10	3.26	17	7	-66.1	-1	-0.66
141	7	1	-10	4	0	-4	9	-1	-14	2.35	19	10	65.5	+1	0.86
142	10	1	-2	0	-1	12	2	0	6	5.18	20	8	65.3	+1	0.76
143	9	0	-2	11	0	-14	14	0	-6	4.61	15	7	65.2	+1	1.00
144*	6	0	-10	9	2	-2	3	-2	8	5.77	7	7	64.6	+1	0.97
145	10	1	-2	0	-1	12	8	0	10	4.18	12	7	-64.6	-1	-0.76
146*	10	1	-2	4	0	2	14	-1	0	3.60	11	7	-64.1	-1	-0.98
147	9	0	-2	11	0	-14	4	0	2	6.51	18	9	63.5	+1	1.00
148	1	0	-12	9	0	-2	4	0	-4	4.78	23	10	63.2	+1	1.00
149	6	0	-10	7	1	-10	5	-1	-10	4.42	19	7	63.2	+1	0.99
150*	11	0	-14	9	2	-2	2	-2	-12	5.52	5	6	62.4	+1	0.86
151*	10	1	-2	6	1	-4	4	-2	2	3.77	17	7	-62.4	-1	-0.96
152	4	0	2	7	1	-10	9	-1	4	2.90	21	9	-62.2	-1	-0.98
153	10	0	-14	7	1	-10	11	-1	-14	5.92	16	7	-62.1	-1	-0.99
154	10	1	-2	2	-2	-12	0	1	6	4.55	20	9	-61.7	-1	-1.00
155*	3	0	8	9	2	-2	6	-2	-10	5.03	7	7	61.5	+1	1.00
156*	6	3	-9	1	1	0	5	-4	-9	4.16	10	9	-61.3	-1	-0.99
157	6	1	-4	3	-2	8	1	1	-12	2.92	19	10	60.7	+1	0.51
158	7	1	-10	6	1	-4	7	-2	10	2.89	17	7	-60.1	-1	-0.80
159	10	1	-2	7	-1	-10	11	0	-2	5.43	19	7	59.9	+1	0.88
160	9	0	-2	0	1	6	3	-1	-12	2.84	22	9	-59.8	-1	-0.76
161	1	1	0	11	0	-2	4	-1	8	3.83	23	10	59.7	+1	0.94
162	10	1	-2	0	-1	6	2	0	-12	3.11	22	9	-59.6	-1	-0.99
163	11	0	-14	2	2	-12	3	-2	8	4.69	12	7	59.5	+1	0.95
164	1	1	0	7	1	-10	0	-2	0	3.27	20	10	-59.2	-1	-0.80
165	5	0	-4	3	0	8	10	0	-8	4.89	21	9	59.1	+1	1.00
166*	6	3	-9	1	-1	0	5	-2	-9	4.87	14	9	-58.4	-1	-0.96
167	3	0	8	11	0	-14	2	0	-12	4.06	15	7	58.1	+1	1.00
168	11	1	-14	5	1	8	4	-2	2	2.98	14	6	-57.8	-1	-0.94
169	6	0	-10	0	1	6	14	-1	0	2.71	20	7	-57.8	-1	-1.00
170	5	0	-4	7	1	-10	8	-1	10	5.06	19	6	-57.5	-1	-0.73
171	9	0	-2	2	2	-12	1	-2	-6	4.08	20	8	57.5	+1	0.77
172	5	0	-4	6	1	-4	5	-1	-10	4.04	23	10	57.5	+1	0.84
173	1	1	0	9	-2	-2	4	1	8	4.53	20	10	-57.3	-1	-0.97
174	7	1	11	6	-1	-4	7	0	-11	3.38	20	7	-57.2	-1	-0.94
175*	5	0	-4	0	1	12	5	-1	8	5.67	15	6	-57.0	-1	-0.96
176	1	0	-12	8	4	-7	9	-4	5	5.09	10	10	-56.9	-1	-0.99
177	7	1	-10	3	-2	8	4	1	8	3.64	19	8	-55.7	-1	-0.93
178	10	1	-2	4	3	-9	4	-4	7	2.60	11	10	55.6	+1	0.78
179	5	0	-4	4	0	9	3	0	-13	2.54	20	10	-55.5	-1	-1.00
180	1	1	0	11	0	-14	6	-1	-4	5.66	22	9	-55.2	-1	-0.98
181	9	0	-2	0	2	5	11	-2	-7	2.25	20	10	-55.2	-1	-0.69
182	1	1	0	11	-1	-14	4	0	-4	3.78	22	10	-55.1	-1	-0.96
183*	9	0	-2	7	0	10	2	0	-12	2.67	11	8	55.0	+1	1.00
184	10	1	-2	1	-1	0	5	0	-10	6.22	24	10	54.9	+1	0.83
185*	1	1	0	4	3	-9	5	-4	-9	3.02	10	9	54.9	+1	0.98
186	1	1	0	11	-1	-14	2	0	6	4.78	21	8	54.8	+1	0.96
187	7	1	-10	4	0	9	9	-1	-1	2.34	20	10	54.6	+1	0.60
188	9	2	-2	6	-2	-10	5	0	8	2.58	18	10	-54.5	-1	-1.00
189	6	0	-10	2	0	9	10	0	-1	2.45	20	10	-54.0	-1	-1.00
190	1	1	0	10	0	-8	3	-1	-12	2.53	22	8	-53.9	-1	-0.38
191	6	0	-10	3	1	2	9	-1	4	2.51	22	9	53.7	+1	0.97
192*	1	1	0	5	2	-9	4	-3	-9	3.52	14	9	53.6	+1	0.98
193	10	1	-2	1	-2	-6	3	1	-12	3.00	19	7	-53.6	-1	-0.22
194	5	0	-4	7	1	-10	6	-1	-4	6.25	23	9	-53.5	-1	-0.92
195	7	4	8	11	0	-2	2	-4	-10	2.22	8	8	-53.3	-1	-0.48
196	5	0	-4	9	1	-14	6	-1	-10	2.58	19	10	53.0	+1	0.21
197	1	0	-12	7	1	-10	0	-1	12	6.21	17	7	-52.9	-1	-0.98
198	10	1	-2	10	0	-14	8	-1	-8	4.31	15	6	52.8	+1	0.84
199	4	0	2	7	1	-10	9	-1	-8	3.14	22	10	52.4	+1	0.72
200*	1	1	0	5	0	-10	4	-1	-10	4.24	17	9	52.3	+1	0.96

large and negative the value of the special quintet Q_j is approximately 0 or π, respectively. Then, in view of (3.19) and (1.12), the T_0's are correlated with the Δ's in the sense that $T_o \simeq 0$ when Δ is large and positive and $T_o \simeq \pi$ when Δ is large and negative. Alternatively, cos $T_0 \simeq +1$ or -1 according as $\Delta \gg 0$ or $\Delta \ll 0$, respectively.

4. The applications

Two applications of the procedure described in § 3 have been made on known structures, the first to aldosterone monohydrate, $C_{21}O_5H_{28}.H_2O$, and the second to valinomycin $C_{54}H_{90}N_6O_{18}$, one molecule per asymmetric unit in both cases.

For aldosterone monohydrate the 221 phases corresponding to the (experimentally determined) $|E|$'s > 1·5 were used to generate the 30 000 three-phase structure seminvariants having the largest values of

$$A = \frac{2\sigma_3}{\sigma_2^{3/2}} r_1 r_2 r_3. \tag{4.1}$$

The discriminants Δ (3.19) were calculated and arranged in decreasing order of $|\Delta|$. In Table 1 are shown the first 200 three-phase structure seminvariants T_0 listed in decreasing order of $|\Delta|$ for the case

Table 2. *Identity of* 100 *cosines of three-phase structure seminvariants calculated to be* ± 1 *employing* (3.19) *for valinomycin,* $C_{54}H_{90}N_6O_{18}$, *space group* $P2_1$

	Seminvariant Triple													
Serial	h_1	k_1	ℓ_1	h_2	k_2	ℓ_2	h_3	k_3	ℓ_3	A	No. of Quintets	No. of Cross Terms	Discr.	Calc Cos	True Cos
1	21	0	4	4	0	-7	7	0	-5	5.52	39	10	-109.9	-1	-1.00
2	21	0	4	2	0	-7	1	0	9	3.67	38	8	-100.5	-1	-1.00
3	21	0	4	8	5	-10	5	-5	-12	4.16	19	6	80.4	+1	0.92
4	3	0	2	17	2	-9	4	-2	13	3.21	36	8	-77.8	-1	-1.00
5	21	0	4	12	5	-9	9	-5	-11	4.35	21	7	72.3	+1	1.00
6	3	0	2	2	0	-7	23	0	-3	5.39	40	9	-71.4	-1	-1.00
7	21	0	4	3	5	-12	0	-5	14	5.24	7	6	-70.7	-1	-0.97
8	3	0	2	2	1	14	19	-1	-10	4.18	33	7	-70.4	-1	-0.99
9	21	0	4	18	3	-9	21	-3	-7	3.94	22	6	65.5	+1	1.00
10	8	1	11	3	0	2	13	-1	-7	3.33	39	9	-65.3	-1	-1.00
11	21	0	4	24	0	-5	27	0	-3	4.54	27	6	-65.0	-1	-1.00
12	3	0	2	18	3	-8	3	-3	12	3.19	36	7	-63.8	-1	-0.93
13	3	0	2	15	2	-8	6	-2	12	2.98	38	9	-61.9	-1	-0.99
14	21	0	4	2	0	-3	5	0	-1	5.41	42	8	-60.3	-1	-1.00
15	21	0	4	10	4	-10	7	-4	-12	4.17	23	6	-59.9	-1	-0.99
16	21	0	4	20	0	-9	17	0	-11	3.95	24	6	-57.9	-1	-1.00
17*	3	5	-12	8	-5	-10	5	0	2	5.60	24	7	-57.6	-1	-1.00
18*	5	0	16	3	1	2	2	-1	14	5.56	9	7	56.5	+1	0.99
19	21	0	4	3	5	-11	6	-5	-9	3.11	21	6	56.1	+1	0.98
20	8	5	-10	13	-1	13	11	-4	-1	3.10	25	7	54.7	+1	0.99
21	21	0	4	10	4	-10	13	-4	-8	3.99	25	7	-54.3	-1	-1.00
22	3	0	2	16	4	-9	5	-4	13	3.03	31	6	-54.1	-1	-1.00
23	21	0	4	17	4	-7	14	-4	-9	4.23	22	6	-52.2	-1	-0.99
24	21	0	4	17	3	0	14	-3	-2	3.43	27	6	51.2	+1	0.99
25	21	0	4	16	4	-9	19	-4	-7	3.78	19	6	-50.9	-1	-0.99
26	21	0	4	1	5	-11	2	-5	13	3.32	21	6	-50.7	-1	-0.77
27	21	0	4	9	4	-9	6	-4	-11	2.71	24	6	-50.7	-1	-1.00
28	21	0	4	13	1	13	10	-1	11	2.75	27	7	49.9	+1	0.98
29	21	0	4	14	4	-8	11	-4	-10	3.13	23	7	-49.1	-1	-1.00
30	21	0	4	12	5	-8	9	-5	-10	3.12	22	7	46.4	+1	0.69
31	3	0	2	5	0	-1	16	0	5	3.09	43	9	-43.5	-1	-1.00
32	21	0	4	10	5	-11	7	-5	-13	3.97	18	6	43.2	+1	1.00
33	8	1	11	5	0	2	19	-1	-11	3.10	34	6	42.4	+1	-0.58
34*	8	1	11	5	0	2	13	-1	13	4.43	16	7	-41.8	-1	-0.91
35	17	2	-9	9	-7	1	2	5	14	3.21	18	6	-41.8	-1	-0.97
36*	3	5	-12	5	0	2	2	-5	14	3.97	17	7	40.7	+1	1.00
37	21	0	4	18	3	-7	15	-3	-9	3.50	22	6	40.3	+1	0.99
38	21	0	4	12	4	-10	15	-4	-8	3.11	21	7	-39.8	-1	-0.93
39	8	1	11	2	-5	14	16	4	1	2.63	22	7	-39.4	-1	-0.94
40	21	0	4	16	4	-9	13	-4	-11	3.47	15	6	-39.2	-1	-0.96
41	3	0	2	18	0	-12	3	0	16	2.63	29	6	-38.9	-1	-1.00
42	21	0	4	4	4	-12	1	-4	-14	2.73	15	6	-38.6	-1	-1.00
43	21	0	4	4	5	-10	7	-5	-8	3.02	21	6	37.9	+1	0.95
44	3	0	2	8	0	14	13	0	-10	2.69	35	8	-37.6	-1	-1.00
45	21	0	4	14	4	-9	11	-4	-11	3.31	22	7	-37.5	-1	-0.94
46	8	1	11	8	-5	-10	6	4	-3	3.46	26	8	37.4	+1	0.95
47	21	0	4	24	1	-6	27	-1	-4	3.15	27	6	36.4	+1	0.98
48	3	5	-12	3	-1	9	16	-4	1	2.68	27	7	36.3	+1	0.95
49	3	5	-12	9	-7	1	22	2	-7	4.09	19	7	35.3	+1	0.98
50	21	0	4	22	3	-3	19	-3	-5	2.89	24	6	35.3	+1	0.98

Table 2 (*cont.*)

Serial	Seminvariant Triple h_1	k_1	ℓ_1	h_2	k_2	ℓ_2	h_3	k_3	ℓ_3	A	No. of Quintets	No. of Cross Terms	Discr.	Calc Cos	True Cos
51	21	0	4	12	0	-12	15	2	-12	3.13	16	7	-34.6	-1	-1.00
52*	5	0	2	9	4	-10	14	-4	-8	4.02	28	7	33.7	+1	0.73
53*	8	1	11	5	0	2	3	-1	9	3.70	30	7	-33.6	-1	-1.00
54	21	0	4	2	5	-11	1	-5	13	2.87	22	6	-33.4	-1	-0.85
55*	5	0	2	9	4	-10	4	-4	-12	3.87	28	7	32.1	+1	0.92
56	3	0	2	5	5	-12	2	-5	14	2.64	26	8	32.0	+1	0.93
57	8	1	11	11	4	-1	13	-5	-8	2.65	26	8	31.7	+1	0.67
58	3	5	-12	13	-1	13	6	-4	-3	2.99	26	7	31.6	+1	0.99
59*	3	0	2	10	4	-10	7	-4	-12	3.74	28	7	29.9	+1	0.99
60*	3	0	2	10	4	-10	13	-4	-8	3.58	28	7	28.3	+1	1.00
61*	21	0	4	2	1	14	19	-1	-10	4.66	11	6	28.0	+1	0.99
62	5	0	2	10	5	-11	1	-5	-11	3.63	28	8	-28.0	-1	-0.21
63	18	3	-9	14	4	-8	14	-7	3	3.10	17	7	-27.6	-1	-0.43
64	8	5	-10	17	2	-9	19	-7	5	2.63	15	6	27.3	+1	0.82
65	2	0	-3	5	0	-1	5	0	-2	3.47	47	10	-27.1	-1	-1.00
66	1	6	10	12	-7	3	3	1	9	3.91	20	7	-27.0	-1	-0.99
67	9	0	-15	5	0	2	4	0	-7	4.76	39	8	26.8	+1	1.00
68*	8	5	-10	5	0	2	13	-5	-8	3.08	24	7	-26.7	-1	-0.84
69	12	5	-9	9	-7	1	3	2	14	4.38	20	7	-25.8	-1	0.95
70*	3	5	-12	8	-1	11	11	-4	-1	4.83	18	6	25.1	+1	0.97
71	9	7	1	12	-5	-8	15	-2	-11	2.62	20	10	-24.1	-1	-1.00
72*	3	0	2	17	4	-7	14	-4	-9	3.79	28	7	23.7	+1	0.99
73	3	5	-12	14	-4	-8	1	-1	0	3.24	28	8	23.5	+1	0.70
74	9	4	-10	14	-7	3	13	3	-11	2.71	20	6	-23.2	-1	-0.90
75	9	7	1	14	-4	-8	13	-3	-11	2.96	20	7	-23.1	-1	-0.57
76	8	1	11	5	0	2	9	-1	-15	3.77	36	10	22.6	+1	0.77
77	9	0	-15	5	0	2	2	0	-7	4.55	39	8	-22.3	-1	-1.00
78	3	1	2	5	0	2	2	-1	14	4.68	40	6	-22.1	-1	-0.99
79	18	3	-9	5	-7	8	5	4	-3	3.44	20	6	-22.0	-1	-0.97
80	4	0	-7	7	0	-5	5	0	-2	3.54	45	10	-21.3	-1	-1.00
81*	3	1	2	12	3	-10	15	-4	-8	3.04	27	9	21.2	+1	0.89
82	5	0	16	3	5	-12	8	-5	-10	6.65	19	6	20.7	+1	1.00
83	10	7	10	14	-4	-8	14	-3	-2	2.98	19	6	-20.7	-1	-0.47
84*	3	0	2	16	4	-9	19	-4	-7	3.40	26	7	20.5	+1	0.99
85*	3	5	-12	3	0	2	0	-5	14	4.70	17	6	20.3	+1	0.97
86	5	0	2	12	4	-10	13	-4	-8	2.72	32	8	20.3	+1	0.93
87*	8	1	11	3	-1	2	5	0	9	3.41	28	9	-20.0	-1	-1.00
88*	21	0	4	8	1	11	13	-1	-7	3.72	15	6	19.8	+1	1.00
89*	3	1	2	6	-1	-7	9	0	-5	3.44	37	9	19.7	+1	0.91
90	18	3	-9	7	0	-5	17	-3	0	3.87	32	6	-19.4	-1	-1.00
91*	3	1	2	12	-3	-10	15	2	-8	3.41	29	9	19.1	+1	0.97
92*	5	0	2	14	1	-12	19	-1	-10	3.84	26	7	-19.0	-1	-1.00
93*	5	0	2	17	2	-9	22	-2	-7	3.55	20	7	19.0	+1	0.91
94*	8	1	11	8	5	-10	16	-6	1	3.00	12	6	18.6	+1	0.88
95	1	6	10	12	-7	3	19	1	-11	3.27	18	7	18.5	+1	-0.67
96*	3	0	2	16	4	-9	13	-4	-11	3.12	28	7	18.5	+1	0.96
97	5	0	2	17	4	-7	15	-4	-9	3.92	30	8	18.3	+1	0.99
98	3	0	2	12	5	-9	17	-5	-11	4.44	28	8	18.1	+1	0.70
99*	3	1	2	18	-3	-9	21	2	-7	3.49	25	9	18.1	+1	1.00
100*	3	1	2	18	-3	-9	15	2	-11	3.45	26	9	-17.9	-1	-0.98

$n = 1$. These identify those structure seminvariants approximately equal to 0 or π and give the most reliable estimates (± 1) for cos T_0, column headed Calc. Cos. in Table 1.

For valinomycin the 496 phases corresponding to the (experimentally determined) $|E|$'s >1.727 were used to generate the 30 000 three-phase structure seminvariants having the largest values of A (4.1). The discriminants Δ were calculated, arranged in decreasing order of $|\Delta|$, and the first 100 listed in Table 2 together with the corresponding seminvariants T_0 and the estimates (± 1) for cos T_0, column headed Calc. Cos. in Table 2.

In Tables 1 and 2 the columns headed No. of Quintets show the number of quintets Q_j in which the three-phase seminvariants T_j were embedded, *i.e.* the number of extensions of the T_j's actually used in the calculation.

Although calculations were made with the number of contributors n to the average in (3.19) equal to 1, 2, 3, 4 and 5, these all led to essentially the same Tables 1 and 2 with only minor changes in the order in which the seminvariants T_0 appeared. Therefore Tables 1 and 2 show only the case that $n = 1$, *i.e.* for each T_0 only that extension having the maximum value of $r_1\, r_2\, r_3|(R_j^2 - 1)\Delta_{K_j}|$ was used in (3.19). The columns headed No. of Cross Terms show the number of cross-terms actually observed in the quintet having the maximum value of $r_1\, r_2\, r_3|(R_j^2 - 1)\Delta_{K_j}|$. Since the formulae for the quintet discriminants, (3.2), (3.7), (3.11) and (3.15) require the

presence of the full complement of ten cross-terms, the missing cross-terms, provided there were no more than four of them, were replaced by unity, the average value of $|E|^2$, a procedure not difficult to justify. (See, *e.g.* Heinerman, 1978, who appears to have been the first to make this observation for quartets; but see also Heinerman, Krabbendam & Kroon, 1977.) In this way many more structure seminvariants T_0 could be reliably estimated than would otherwise have been the case, as inspection of the columns headed No. of Cross Terms in Tables 1 and 2 shows.

The columns headed Discr. list the discriminants Δ (3.19) of the structure seminvariants T_0 arranged in decreasing order of magnitude. Finally the columns headed Calc. Cos. and True Cos. show the calculated values (± 1) of cos T_0, as found from the discriminant Δ, and the true values of cos T_0, respectively.

The asterisks (*) attached to some of the serial numbers in Columns 1 of Tables 1 and 2 identify those structure seminvariants T_0 for which one of the T_j's, $j = 0, 1, 2, 3$, happens to be a structure invariant. These cosine invariants would naturally be expected to have the value +1, approximately, on the basis of the A values alone, which for the most part happen to be sufficiently large (*i.e.* > 3) to justify this estimate. In all such cases (about 20% of the 200 listed in Table 1 and about 25% of the 100 listed in Table 2) the actually estimated values of the cosine seminvariants cos T_0 are in accord with the estimate +1 of the corresponding cosine invariants.

By working through the entries in Table 1, *i.e.* solving the system of linear equations

$$\varphi_{h_1k_1l_1} + \varphi_{h_2k_2l_2} + \varphi_{h_3k_3l_3} = 0 \text{ or } \pi,$$

one may readily confirm that the aldosterone monohydrate structure is solvable *via* the estimated values of the three-phase structure seminvariants alone. More specifically, Table 1 yields the values, with a twofold ambiguity, of 75 phases, which are expanded to 300 *via* the tangent formula. The negative quartet figure of merit, NQEST, (DeTitta, Edmonds, Langs & Hauptman, 1975) is −0·457 and +0·721 for the two solution sets, so that a unique solution (corresponding to NQEST = −0·457) is obtained. The initial E map shows 25 of the 27 nonhydrogen atoms. The interested reader may wish to use Table 2 in the same way to determine for himself the usefulness of the three-phase structure seminvariants alone in limiting the values of the individual phases for valinomycin.

Although the aldosterone monohydrate structure happens to be solvable *via* the three-phase structure seminvariants alone, it should be stressed that in the applications to more difficult structures one would naturally use the results described here to supplement, not replace, other methods and other relationships.

4.1. *The errors*

The average and weighted average of the magnitudes of the errors are given by

$$\langle |\text{Calc. Cos.} - \text{True Cos.}| \rangle \tag{4.2}$$

and

$$\frac{\sum A\,|\text{Calc. Cos.} - \text{True Cos.}|}{\sum A}, \tag{4.3}$$

respectively. Summary tables of the average magnitude of the error are given for aldosterone monohydrate (Table 3) and valinomycin (Table 4) as functions of the discriminant for the 1000 structure seminvariants having the largest values of $|\Delta|$, arranged in descending order of the average value of $|\Delta|$ in groups defined by Columns 2 of these tables. In order to assess the effect of errors in the observed $|E|$'s the calculations were

Table 3. *Average magnitude of the error in estimated values for the three-phase cosine seminvariants,* cos T_0, *for aldosterone monohydrate using (a) exact values of the* $|E|$*'s as calculated from the refined structure and (b) experimentally determined* $|E|$*'s*

		(*a*) Using exact $\|E\|$'s			(*b*) Using experimental $\|E\|$'s		
Group	Number of seminvariants in group	Avg. |Discr.|	Avg. |Error|	Wt avg. |Error|	Avg. |Discr.|	Avg. |Error|	Wt avg. |Error|
1	50	158·4	0·059	0·062	163·8	0·065	0·068
2	50	78·2	0·108	0·089	86·0	0·101	0·090
3	50	59·0	0·105	0·081	64·2	0·109	0·097
4	50	47·6	0·165	0·136	51·7	0·311	0·341
5	100	37·2	0·165	0·176	40·8	0·185	0·193
6	100	28·7	0·261	0·274	33·2	0·193	0·217
7	200	21·8	0·188	0·180	26·1	0·300	0·329
8	200	16·2	0·330	0·370	20·3	0·398	0·440
9	200	12·8	0·355	0·354	16·6	0·440	0·435
All groups	1000	33·9	0·239	0·233	38·3	0·295	0·298

Table 4. *Average magnitude of the error in estimated values of the three-phase cosine seminvariants,* $\cos T_0$, *for valinomycin using (a) exact values of the* $|E|$*'s as calculated from the refined structure and (b) experimentally determined* $|E|$*'s*

		(*a*) Using exact $\|E\|$'s			(*b*) Using experimental $\|E\|$'s		
Group	Number of seminvariants in group	Avg. |Discr.|	Avg. |Error|	Wt avg. |Error|	Avg. |Discr.|	Avg. |Error|	Wt avg. |Error|
1	50	25·6	0·136	0·126	53·4	0·060	0·053
2	50	11·9	0·059	0·054	24·1	0·177	0·172
3	50	9·3	0·148	0·144	15·8	0·166	0·168
4	50	7·6	0·322	0·322	12·4	0·228	0·249
5	100	6·1	0·200	0·197	9·9	0·314	0·323
6	100	4·9	0·396	0·427	8·2	0·400	0·426
7	200	3·7	0·352	0·375	6·3	0·467	0·472
8	200	2·7	0·529	0·549	4·6	0·580	0·565
9	200	2·1	0·673	0·686	3·6	0·646	0·637
All groups	1000	5·5	0·404	0·410	10·0	0·442	0·435

performed twice, once with experimentally determined $|E|$'s (as for Tables 1 and 2) and then with error-free $|E|$'s calculated from the refined structures. In the columns headed Avg. |Error| and Wt Avg. |Error| of Tables 3 and 4 are listed the values of (4.2) and (4.3), respectively, for aldosterone monohydrate and valinomycin for the groups defined by Columns 2. Also listed in these tables are the average values of $|\Delta|$ (columns headed Avg. |Discr.|) for these groups. Although Table 1 gives estimates for only the first 200 seminvariants and Table 2 for the first 100 seminvariants, Tables 3 and 4 list the average magnitude of the error, in groups, for 1000 seminvariants as a function of the average values of $|\Delta|$. As expected, for each structure the errors tend to increase with decreasing $|\Delta|$, although they are still less than random even when $|\Delta|$ is as small as 3·0. The discriminants for valinomycin are smaller than those for aldosterone monohydrate, a consequence of the greater complexity of valinomycin. Inspection of Tables 3 and 4 shows that the errors are not a function of $|\Delta|$ alone but appear to be structure dependent as well; for fixed $|\Delta|$ the errors are less for valinomycin than for aldosterone monohydrate. Comparison of the columns headed Avg. |Error| and Wt Avg. |Error| shows that the errors are independent of A, a result which is not surprising since A already enters into the definition of Δ [*via* the product $r_1 r_2 r_3$, (3.19)] on which the reliability of the estimate depends. Finally, comparison of Columns 4 and 7 (or 5 and 8) shows that, as expected, the errors tend to increase somewhat when experimentally determined $|E|$'s are used, but the increase is not great; in short the accuracy of the estimates is not overly sensitive to errors in the observed $|E|$'s. It should perhaps be pointed out in conclusion that the accuracy of the observed $|E|$'s as measured by the R factor,

$$R = \frac{\sum ||E|_{\text{obs}} - |E|_{\text{true}}|}{\sum |E|_{\text{obs}}}, \qquad (4.4)$$

is $R = 0{\cdot}187$ for aldosterone monohydrate (2009 reflections) and $R = 0{\cdot}298$ for valinomycin (6189 reflections).

5. Concluding remarks

The probabilistic theory of the three-phase structure seminvariant T_0 in $P2_1$ has been initiated using the recently introduced extension concept. Employing the discriminant Δ, those seminvariants T_0 whose values are probably 0 or π, approximately, are identified; according as $\Delta \gg 0$ or $\Delta \ll 0$, $T_0 \simeq 0$ or π, respectively. In this work only a suitable 14-magnitude subset of the complete second neighborhood of T_0 has been used. The ability to make use of the full 41-magnitude second neighborhood of T_0 would presumably lead to more reliable estimates of the structure seminvariants in general, but this work still remains to be done.

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Application of Quartet and Quintet Invariants in Phase Determination

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Abstract

Recent derivations of probability expressions for quartet and quintet structure invariants allow the reliable estimation of the phase sums of quartets and quintets in the range 0 to π. A new quartet figure of merit, ENQUAC and a new quintet figure of merit, ENQUIC, based on these estimates are described, which are particularly useful in non-centrosymmetric symmorphic and polar space groups. An adapted tangent-refinement procedure employing selected triplets with a phase sum of 0, together with the quartet and quintet phase estimates, enables enantiomorph-specific phase refinement. The way in which the figures of merit and the refinement technique can be used in various practical procedures is demonstrated and applications to two structures in space group $P1$ are presented.

Introduction

Although more and more structures of moderate complexity (60 to 80 independent atoms) are solved by direct methods, in non-centrosymmetric symmorphic and polar space groups, the application of the triplet relation fails for numerous structures: parts of the phase determination, which are easy to carry out in other space groups, give rise to serious problems, such as:

(i) The enantiomorph definition; in the space groups $P1$, $P2$, $P2_1$, $C2$ and Cc it is a difficult procedure, because it is not possible to select a starting reflection, which is enantiomorph-sensitive ($\Phi \simeq \pm\pi/2$).

(ii) The tangent refinement; occasionally the resulting phases are centrosymmetric, even starting with a correct phase set.

(iii) The various figures of merit, based on triplets; they do not discriminate as consistently between correct and incorrect phase sets as they do in non-symmorphic and non-polar space groups. Some of these difficulties have been dealt with by Schenk (1972), who indicated that they can be ascribed to the influence of the space group symmetry and the properties of the $\sum_2$ relation.

These problems do not exist if the actual values of the phase sums,

$$\Phi_3 = \Phi_H + \Phi_K + \Phi_{-H-K}, \qquad (1)$$

could be used instead of assuming all Φ_3 to be zero. Of course the Φ_3 values cannot be evaluated from $|E|$ magnitudes alone, and in practice only $|\Phi_3|$ values can be calculated, of which the quality is not yet sufficiently good to define reliable enantiomorph-specific procedures (*e.g.* $B_{3,0}$ formula, Karle & Hauptman, 1958; TPROD formula, Hauptman, Fischer, Hancock & Norton, 1969; MDKS formula, Fischer, Hancock & Hauptman, 1970; and the strengthened triplet formula, Giacovazzo, 1977).

Test results of recent expressions for quartets and quintets proved that the absolute values $|\Phi_4|$ and $|\Phi_5|$ of their phase sums,

$$\Phi_4 = \Phi_H + \Phi_K + \Phi_L + \Phi_{-H-K-L} \qquad (2)$$

and

$$\Phi_5 = \Phi_H + \Phi_K + \Phi_L + \Phi_M + \Phi_{-H-K-L-M}, \qquad (3)$$

can be estimated with the required accuracy for enantiomorph-specific procedures. Most of these results are described in papers by Hauptman (1975), van der Putten & Schenk (1976), Schenk & van der Putten (1977), van der Putten & Schenk (1977) and Gilmore (1977). More evidence will be given in this paper.

The main problem left when applying estimated phase sums in structure determination arises from the

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