

space is $g(t) = \exp[-(2\sigma)^{-1}(t_1^2 + t_2^2 + t_3^2)]$. Then the temperature factor is given by

$$T(t) = g(t)[1 + P^{-1}A],$$

where

$$\begin{aligned} A = & i\beta(k_B T)^{-1}t_1t_2t_3 - (\gamma + \frac{2}{5}\delta)(k_B T)^{-1}(t_1^4 + t_2^4 + t_3^4) \\ & - 2(\gamma - \frac{3}{5}\delta)(k_B T)^{-1}(t_1^2t_2^2 + t_1^2t_3^2 + t_2^2t_3^2) \\ & + 10\gamma(k_B T)^{-1}(t_1^2 + t_2^2 + t_3^2)\sigma + [C/(k_B T)^2] \\ & \times \{ -\beta^2[t_1^2t_2^2t_3^2 - (t_1^2t_2^2 + t_1^2t_3^2 + t_2^2t_3^2)\sigma \\ & + (t_1^2 + t_2^2 + t_3^2)\sigma^2] - i2\beta(\gamma + \frac{2}{5}\delta)(t_1^5t_2t_3 + t_1t_2^5t_3 \\ & + t_1t_2t_3^5) + 4\beta(\gamma - \frac{3}{5}\delta)(t_1t_2^3t_3^3 + t_1^3t_2t_3^3 + t_1^3t_2^3t_3) \\ & - \beta[44\gamma - \frac{32}{5}\delta](t_1^3t_2t_3 + t_1t_2^3t_3 + t_1t_2t_3^3)\sigma \\ & + \beta[198\gamma - \frac{144}{5}\delta]t_1t_2t_3\sigma^2\} \\ & + [\gamma^2 + \frac{4}{5}\gamma\delta + \frac{4}{25}\delta^2](t_1^8 + t_2^8 + t_3^8) \\ & + [4\gamma^2 - \frac{4}{5}\gamma\delta - \frac{24}{25}\delta^2] \\ & \times [t_1^6(t_2^2 + t_3^2) + t_2^6(t_1^2 + t_3^2) + t_3^6(t_1^2 + t_2^2)] \\ & + [6\gamma^2 - \frac{16}{5}\gamma\delta + \frac{44}{25}\delta^2](t_1^4t_2^4 + t_1^4t_3^4 + t_2^4t_3^4) \\ & + [12\gamma^2 - \frac{52}{5}\gamma\delta + \frac{48}{25}\delta^2](t_1^4t_2^2t_3^2 + t_1^2t_2^4t_3^2 + t_1^2t_2^2t_3^4) \\ & - [36\gamma^2 + \frac{104}{5}\gamma\delta + \frac{64}{25}\delta^2](t_1^6 + t_2^6 + t_3^6)\sigma \\ & - [108\gamma^2 - \frac{208}{5}\gamma\delta - \frac{48}{25}\delta^2] \\ & \times [t_1^4(t_2^2 + t_3^2) + t_2^4(t_1^2 + t_3^2) + t_3^4(t_1^2 + t_2^2)]\sigma \\ & - [216\gamma^2 - \frac{936}{5}\gamma\delta + \frac{864}{25}\delta^2]t_1^2t_2^2t_3^2\sigma \\ & + [378\gamma^2 + \frac{572}{5}\gamma\delta + \frac{432}{25}\delta^2](t_1^4 + t_2^4 + t_3^4)\sigma^2 \end{aligned}$$

$$\begin{aligned} & + [756\gamma^2 - \frac{1716}{5}\gamma\delta + \frac{144}{5}\delta^2](t_1^2t_2^2 + t_1^2t_3^2 + t_2^2t_3^2)\sigma^2 \\ & - [1260\gamma^2 + \frac{960}{25}\delta^2](t_1^2 + t_2^2 + t_3^2)\sigma^3 \}. \end{aligned}$$

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On the Application of Phase Relationships to Complex Structures. XXV. TRITAN – or Recycled Failure

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Abstract

Even when direct methods fail to give a clear solution, *E* maps from some of the phase sets obtained contain correctly oriented fragments. It is shown that such

information from several phase sets can be amalgamated by an automatic procedure to give estimates of the values of three-phase invariants. These estimates are incorporated into a modified tangent formula which is used in a new run of a multitool direct-methods procedure. Tests of the total process, called *TRITAN*, reveal that it is very effective in determining structures which otherwise would not be found routinely.

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Introduction

It is sometimes claimed that one of the strengths of direct methods is that no prior knowledge of the structure is required for a solution to be found. Indeed, from time to time the structure revealed by a direct-methods approach is unexpected and different from what was supposed; in such circumstances a method which relied on knowledge of the structure would suffer a positive handicap.

Nevertheless, not too much should be made of this 'strength'. There are many cases where direct methods have been totally unsuccessful and where a sophisticated Patterson-search technique has triumphed. Actually a number of workers have made use of structural information in the application of direct methods - for example, Hauptman (1964), Oda, Naya & Nitta (1967), Kroon & Krabbendam (1970) and Thiessen & Busing (1974). The most systematic approach has been that of Main (1976) who has shown that knowledge of a correctly oriented structural fragment modifies the Cochran distribution for a three-phase invariant. From the fragment can be found a complex quantity

$$Q(\mathbf{h}, \mathbf{k}) = |Q(\mathbf{h}, \mathbf{k})| \exp \{iq(\mathbf{h}, \mathbf{k})\} \quad (1)$$

such that the structure invariant

$$\varphi_3(\mathbf{h}, \mathbf{k}) = \varphi(\mathbf{h}) - \varphi(\mathbf{k}) - \varphi(\mathbf{h} - \mathbf{k}) \quad (2)$$

has a probability distribution

$$P[\varphi_3(\mathbf{h}, \mathbf{k})] = \frac{\exp \{K'(\mathbf{h}, \mathbf{k}) \cos [\varphi_3(\mathbf{h}, \mathbf{k}) - q(\mathbf{h}, \mathbf{k})]\}}{2\pi I_0[K'(\mathbf{h}, \mathbf{k})]} \quad (3)$$

where

$$K'(\mathbf{h}, \mathbf{k}) = 2|Q(\mathbf{h}, \mathbf{k})E(\mathbf{h})E(\mathbf{k})E(\mathbf{h} - \mathbf{k})|. \quad (4)$$

A run of a direct-methods procedure, e.g. *MULTAN*, using a modified tangent formula which incorporates $|Q(\mathbf{h}, \mathbf{k})|$ and $q(\mathbf{h}, \mathbf{k})$ often solves the structure when a straightforward approach would not do so.

Experience has shown that E maps from phase sets generated by *MULTAN* or other direct-methods procedures, even when they do not show the structure, reveal in *post hoc* examination the presence of correctly oriented structural fragments. We wish to report a simple and automatic procedure for using this concealed partial structure information without the need specifically to look at E maps.

The TRITAN procedure

The scenario that we are presenting is that there have been runs of, say, *MULTAN87* (Debaerdemaeker, Tate & Woolfson, 1988) in all its possible modes but that no correct solution has been found. Entering the

TRITAN procedure initiates the following sequence of calculations.

(1) For each of n (usually six to ten) 'best' phase sets, as judged by the combined figure of merit CFOM, the E map is calculated and the largest chemically sensible fragment is automatically found with the *SEARCH* routine of *MULTAN*.

(2) For each of the fragments partial structure factors are calculated,

$$S_j(\mathbf{h}) = |S_j(\mathbf{h})| \exp [i\psi_j(\mathbf{h})] \quad (j = 1 \text{ to } n), \quad (5)$$

for \mathbf{h} corresponding to the set of large $E(\mathbf{h})$ for which phases are required.

(3) It is now required to find the fragment that bears probably the greatest resemblance to the complete structure. This is done by finding for each fragment a correlation coefficient

$$r_j = \frac{\langle |S_j(\mathbf{h})E(\mathbf{h})| \rangle_{\mathbf{h}} - \langle |S_j(\mathbf{h})| \rangle_{\mathbf{h}} \langle |E(\mathbf{h})| \rangle_{\mathbf{h}}}{\sigma_j^s \sigma_E} \quad (6)$$

where

$$\sigma_j^s = [\langle |S_j(\mathbf{h})|^2 \rangle_{\mathbf{h}} - \langle |S_j(\mathbf{h})| \rangle_{\mathbf{h}}^2]^{1/2} \quad (7a)$$

and

$$\sigma_E = [\langle |E(\mathbf{h})|^2 \rangle - \langle |E(\mathbf{h})| \rangle^2]^{1/2}. \quad (7b)$$

The assumption made here is that the greater the resemblance between the fragment and the complete structure the closer will be the partial-structure magnitudes to a scaled version of the complete-structure magnitudes. If the partial set was exactly a scaled version of the complete set then the value of r_j would have the maximum possible value for a linear correlation coefficient, unity, and the less its value the less valid is the scaling assumption. If the largest value of r_j is for $j = i$ then the first estimates of the three-phase invariants are obtained from

$$\varphi_{3,e}^1(\mathbf{h}, \mathbf{k}) = \psi_i(\mathbf{h}) - \psi_i(\mathbf{k}) - \psi_i(\mathbf{h} - \mathbf{k}). \quad (8)$$

(4) For each other fragment ($j \neq i$) there are calculated

$$R_j = [\langle \sin \varphi_{3,e}^1(\mathbf{h}, \mathbf{k}) \sin \psi_{3,j}(\mathbf{h}, \mathbf{k}) \rangle_{\mathbf{h}, \mathbf{k}} - \langle \sin \varphi_{3,e}^1(\mathbf{h}, \mathbf{k}) \rangle_{\mathbf{h}, \mathbf{k}} \langle \sin \psi_{3,j}(\mathbf{h}, \mathbf{k}) \rangle_{\mathbf{h}, \mathbf{k}}] / \mu_e \mu_j \quad (9)$$

where

$$\psi_{3,j}(\mathbf{h}, \mathbf{k}) = \psi_j(\mathbf{h}) - \psi_j(\mathbf{k}) - \psi_j(\mathbf{h} - \mathbf{k}) \quad (10)$$

and μ_e and μ_j are the standard deviations of the quantities $\sin \varphi_{3,e}^1(\mathbf{h}, \mathbf{k})$ and $\sin \psi_{3,j}(\mathbf{h}, \mathbf{k})$ respectively.

The value of R_j , which is a linear correlation coefficient, is theoretically constrained by the form of (9) to be in the range

$$-1 \leq R_j \leq 1. \quad (11)$$

If $R_j = 1$ then it indicates perfect positive correlation of the quantities $\sin \varphi_{3,e}^1(\mathbf{h}, \mathbf{k})$ and $\sin \psi_{3,j}(\mathbf{h}, \mathbf{k})$ so

Table 1. Comparison of TRITAN-estimated three-phase invariants with true values

True (°)	Positive triples		True (°)	Negative triples	
	Estimated (°)	$K^n(\mathbf{h}, \mathbf{k})$		Estimated (°)	$K^n(\mathbf{h}, \mathbf{k})$
26	4	35.2	262	56	21.7
354	8	23.4	137	265	2.7
346	349	45.0	209	86	3.7
26	7	12.3	265	336	21.1
357	344	8.9	90	31	6.5
342	2	27.9	130	65	2.5
2	353	27.2	182	98	2.9
15	23	9.7	187	260	1.4
314	0	7.4	223	64	3.2
12	340	2.0	270	237	3.4
344	331	4.0	199	267	3.9
338	339	5.0	237	119	3.4
45	348	5.3	248	324	2.7
341	357	13.4	171	205	3.2
352	346	28.8	97	73	1.8
356	18	29.8	195	248	2.5
339	352	17.7	210	213	2.5
315	340	7.5	233	194	1.5
357	350	4.4	258	289	2.9
47	339	4.2	126	179	3.2
7	357	20.4	240	295	4.6
325	356	17.2	201	120	3.2
8	355	5.8	227	207	0.5
323	13	4.2	267	9	2.3
25	9	10.1	222	277	2.3
355	294	1.9	240	7	1.0
324	343	27.1	180	258	3.2
7	347	7.9	238	140	3.2
47	4	8.1	216	258	4.0
344	340	14.5	92	274	1.2
52	32	1.9	262	314	2.7
326	349	23.1	170	93	1.7
7	13	4.1	253	119	3.8
16	330	4.6	113	90	4.5
47	91	2.1	212	134	1.8
2	340	8.0	254	294	1.2
13	271	0.8	169	97	5.9
67	6	5.1	236	194	0.7
299	297	1.3	204	175	2.1
326	307	7.2	204	257	3.5
1	349	9.5	260	340	4.8
312	355	6.9	113	60	2.3
19	33	3.5	270	291	3.2
29	13	1.9	224	345	1.4
328	1	3.1	247	227	3.4
350	350	4.0	268	323	3.7
342	9	2.3	211	297	5.5
32	353	3.9	267	24	0.5
27	9	4.6	123	28	2.8
311	337	12.3	95	350	3.4

that one set is just a scaled version of the other with a positive scaling factor. On the other hand $R_j = -1$ indicates a perfect negative correlation which can be transformed into a perfect positive correlation by taking the enantiomorph of the j th fragment which reverses all the values of $\psi_j(\mathbf{h})$ and hence of $\psi_{3,j}(\mathbf{h}, \mathbf{k})$.

(5) For the largest value of $|R_j|$ calculate a second estimate of each invariant from

$$\tan \varphi_{3,e}^2(\mathbf{h}, \mathbf{k}) = \frac{K^1(\mathbf{h}, \mathbf{k}) \sin \varphi_{3,e}^1(\mathbf{h}, \mathbf{k}) + s_j |R_j|^{1/2} K_j(\mathbf{h}, \mathbf{k}) \sin \psi_{3,j}(\mathbf{h}, \mathbf{k})}{K^1(\mathbf{h}, \mathbf{k}) \cos \varphi_{3,e}^1(\mathbf{h}, \mathbf{k}) + |R_j|^{1/2} K_j(\mathbf{h}, \mathbf{k}) \cos \psi_{3,j}(\mathbf{h}, \mathbf{k})} = T^1(\mathbf{h}, \mathbf{k}) / B^1(\mathbf{h}, \mathbf{k}), \quad (12)$$

where

$$K^1(\mathbf{h}, \mathbf{k}) = 2\sigma_3\sigma_2^{-3/2} |S_i(\mathbf{h})S_i(\mathbf{k})S_i(\mathbf{h}-\mathbf{k})| \quad (13a)$$

$$K_j(\mathbf{h}, \mathbf{k}) = 2\sigma_3\sigma_2^{-3/2} |S_j(\mathbf{h})S_j(\mathbf{k})S_j(\mathbf{h}-\mathbf{k})|. \quad (13b)$$

$\sigma_n = \sum_{j=1}^N z_j^n$ (z_j is the atomic number of the j th atom) and s_j is the sign of R_j .

Equation (12) is a tangent-formula combination of two estimates of the three-phase invariants. The presence of s_j ensures that the estimates are from the same enantiomorph and $|R_j|^{1/2}$ is an arbitrary, but empirically effective, way of influencing the degree to which the new estimate should modify the previous one. The K values for these second estimates of the three-phase invariants are derived from

$$K^2(\mathbf{h}, \mathbf{k}) = [T^1(\mathbf{h}, \mathbf{k})^2 + B^1(\mathbf{h}, \mathbf{k})^2]^{1/2}. \quad (14)$$

(6) A chain process is now entered in which at each stage triple-phase estimates from each residual fragment are compared with the current combined estimates to yield values of R_j , as indicated in (9), followed by the estimates corresponding to the largest $|R_j|$ being combined with the current estimate as shown by (12). The weights $K^m(\mathbf{h}, \mathbf{k})$ associated with the invariants increase in general as m increases; thus at each successive stage of the chain process the effect of the estimates from the latest fragment, with weights $|R_j|^{1/2} K_j(\mathbf{h}, \mathbf{k})$, make less and less difference to the overall estimate. When all the fragments have been used there exists for each three-phase invariant an estimate $\varphi_{3,e}^n(\mathbf{h}, \mathbf{k})$ with weights $K^n(\mathbf{h}, \mathbf{k})$.

(7) A modified tangent formula, similar to that proposed by Main (1976) and also used by Olthof, Sint & Schenk (1979) and in the program MITHRIL by Gilmore (1984) is used in place of the normal one in a rerun of MULTAN. This tangent formula has the form

$$\varphi(\mathbf{h}) = \text{phase of } \sum_{\mathbf{k}} K^n(\mathbf{h}, \mathbf{k}) \times \exp \{i[\varphi(\mathbf{k}) + \varphi(\mathbf{h}-\mathbf{k}) - \varphi_{3,e}^n(\mathbf{h}, \mathbf{k})]\}. \quad (15)$$

Tests of TRITAN

By their very nature, especially for small structures, the three-phase invariants have values tending to cluster around zero (modulo 2π). An ability to predict those which deviate significantly from zero gives great benefit to any phase-determining process - for example by using the predictions in (15).

In Table 1 are shown predicted values of the three-phase invariants $\varphi_{3,e}^n(\mathbf{h}, \mathbf{k})$ with their weights $K^n(\mathbf{h}, \mathbf{k})$ compared with the true values, $\varphi_3(\mathbf{h}, \mathbf{k})$, for the structure MUCCAR* [Bianchi, Pilati & Simonetta (1978): $C_{13}H_{11}N$, $P1$, $Z=2$]. A random selection of invariants would give very few with true values very

* 11-Methyltricyclo[4.4.1.0⁶]undeca-2,4,7,9-tetraene-11-carbonitrile.

far from zero in value so 50 were randomly chosen from those with $\cos \varphi_3(\mathbf{h}, \mathbf{k})$ positive (*i.e.* within $\pi/2$ of zero) and 50 others from the group with $\cos \varphi_3(\mathbf{h}, \mathbf{k})$ negative. For the 50 positive invariants the r.m.s. phase error of the *TRITAN* estimates is 32.1° whereas the mean phase error from the usual estimate zero is 29.8° , so that the *TRITAN* estimates are slightly worse. However, for the 50 negative invariants the corresponding figures are 82.9 and 130.2° which make the *TRITAN* estimates considerably better. It will also be noted that all the positive invariants are predicted as positive while 25 of the negative invariants are predicted as negative.

It seems that there may be useful information in the *TRITAN* estimates, although it is difficult to tell from the numbers in Table 1 just how helpful such information would be. We now give the results of a series of trials which indicate that the *TRITAN* estimates can be a very powerful aid in the actual process of solving crystal structures.

Some practical trials

The *TRITAN* procedure has been tried on several known structures which can be solved by direct methods but which present difficulties for some direct-methods procedures. In these trials sets of phases were selected which did not individually reveal the structures in order to see whether an amalgamation of information from them would give a solution. The structures are referred to by code names for brevity.

CORTISONE [*Declercq, Germain & Van Meerssche* (1972). $C_{21}H_{28}O_5$, $P2_12_12_1$, $Z = 4$]

Although this structure can be solved by any of the five procedures available in *MULTAN87* there is no perfect solution in 100 trials with *MULTAN80*. None of these sets of phases gave an *E* map showing a five-membered ring although several produced linked six-membered rings.

The ten sets of phases with the highest values of CFOM were subjected to the *TRITAN* procedure. The amalgamated three-phase invariant estimates, used with the modified tangent formula (15), then gave six perfect solutions in 30 trials.

MUCCAR

For this *P1* structure both *MULTAN80* and *MULTAN87* using the statistically weighted tangent formula (SWTF) gave poor results although the *SAYTAN* mode in *MULTAN87* solves it quite easily. *MULTAN80*, with the SWTF, was run for 100 trials. The maps corresponding to the two best CFOMs revealed less than one-half of the structure. Nine phase sets, corresponding to the third to eleventh best CFOMs were input into *TRITAN*. In 30 trials there were found four perfect solutions and three others with only one atom missing.

MUNICH4 [*Szeimes-Seebach, Harnisch, Szeimes, Van Meerssche, Germain & Declercq* (1978). $C_{27}H_{22}O$, *Cc*, $Z = 4$]

With the SWTF no solution was found in 200 trials of *MULTAN80* and 40 trials of *MULTAN87*. The six phase sets with the highest values of CFOM from *MULTAN80* were input into *TRITAN*. In 30 trials there were two perfect maps and four with only one atom missing.

CINOBUFAGIN [*Declercq, Germain & King* (1977). $C_{26}H_{27}O_6$, $P2_12_12_1$, $Z = 4$]

This was originally solved with *MULTAN*, using the SWTF, with great difficulty after generating 5000 phase sets. We carried out 200 trials with the SWTF mode of *MULTAN87* but the figures of merit were so poor that we did not even try to use them. Instead we did 50 trials with the *SAYTAN* mode of *MULTAN87*, which readily solves the structure, and input the worst six solutions in terms of CFOM into *TRITAN*. In 30 trials there were six maps produced lacking only one atom.

AZET [*Colens, Declercq, Germain, Putzeys & Van Meerssche* (1974). $C_{21}H_{16}ClNO$, *Pca2_1*, $Z = 8$]

Use of *MULTAN87* in the SWTF mode gave nothing promising but for 50 trials in the *SAYTAN* mode the best map showed one-half of the structure. After amalgamating the information in the five phase sets with the highest CFOMs, in 30 trials *TRITAN* gave one map with four atoms missing and seven maps with eight or nine atoms missing.

Concluding remarks

We are much encouraged by our experiences with *TRITAN* and feel that it has a great deal to offer at the margin where direct methods are not giving a clear solution but merely tantalizing glimpses of the structure. It is known that from a very small fragment the complete structure can often be revealed (Karle, 1968; Yao, 1983) but equally, and not so often reported in the literature, it is possible to spend a great deal of time and effort with a fragment and not end up with the structure. *TRITAN* offers the possibility of strengthening the initial information put into a fragment-development effort even if it does not give a complete, or substantially complete, solution in its own right.

The computer time required to implement the invariant-estimating part of *TRITAN* is very modest - much less than that for an average *MULTAN* run. While we hope to develop *TRITAN* further we feel that even at its present stage of development it is a useful facility to have available and it will certainly be introduced as a standard component of the next version of *MULTAN* - probably *MULTAN89*.

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On the Application of Phase Relationships to Complex Structures. XXVI. Developments of the Sayre-Equation Tangent Formula

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Abstract

The Sayre-equation tangent formula (SETF) develops sets of phases tending to satisfy Sayre's equations for both large and small normalized structure factors. There are two components in the SETF, corresponding to contributions from phase triplets and quartets respectively. The development of objective algorithms for properly weighting these components and for gradually building up the quartet contribution has enabled the SETF, within the procedure SAYTAN, to be incorporated into MULTAN87, the latest version of the package. Examples of tests of MULTAN87 and its use in solving unknown structures are given.

Introduction

In a previous paper Debaerdemaeker, Tate & Woolfson (1985) described the theory of a new tangent formula which had the property of developing phases tending to satisfy a system of Sayre equations. A particular Sayre equation can be written in terms

of normalized structure factors as

$$E(\mathbf{h}) = [f(\mathbf{h})/g(\mathbf{h})V] \sum_{\mathbf{k}} E(\mathbf{k})E(\mathbf{h}-\mathbf{k}) \quad (1)$$

where $f(\mathbf{h})$ and $g(\mathbf{h})$ are the scattering factors for atoms and squared-electron-density atoms respectively and V is the volume of the unit cell.

Phases are sought to achieve minimization of

$$R = \sum_{\mathbf{h}} \left| E(\mathbf{h}) - [K/g(\mathbf{h})] \sum_{\mathbf{k}} E(\mathbf{k})E(\mathbf{h}-\mathbf{k}) \right|^2 \quad (2)$$

where K is an overall scaling factor which compensates for partial data in the \mathbf{k} summations and the $g(\mathbf{h})$ can be determined on theoretical grounds.

The minimization condition is

$$\partial R / \partial \varphi(\mathbf{l}) = 0 \quad \text{for all } \mathbf{l};$$

application of this to (2), followed by some algebraic manipulation, gives the Sayre-equation tangent formula (SETF)

$$\varphi(\mathbf{l}) = \text{phase of } [t(\mathbf{l}) - 2Kq(\mathbf{l})] \quad (3)$$