completely overwhelms f_1^V for $q=0$ and 1, thus falls off very rapidly with q. If the cubic or icosahedral p.g. is purely rotational, 432 or 532, then at $q=V/2$ for any polyhedron (or assembly of points) of this symmetry with no vertex (point) on a rotation axis $\frac{1}{2}(1-V)\log 2-(3\log e)/4V+\log k\leq\log R<\frac{1}{2}(1-V)\log 2+\log k$, where $k=9$ for 432 and 15 for 532. The linearity of $\log R$ improves asymptotically as V increases. This expression shows that the effect of symmetry on N tends to vanish even in point groups of high symmetry if V is sufficiently large. For $V=240$ and p.g. 532, for example, $\log R\sim -34{\cdot}80$, which means that $N(A_{120}B_{120})\sim C(240,120)\sim 10^{72}$, so that the effect of symmetry relative to N is completely negligible.

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Use of Negative Quartet Cosine Invariants as a Phasing Figure of Merit: NQEST

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Recent theoretical advances in the identification of those cosine invariants $\cos(\varphi_h+\varphi_k+\varphi_l+\varphi_m)$ which are probably negative suggest algorithms for the calculation of a figure of merit which is sensitive to the integrity of a phase set. The negative quartet figure of merit, NQEST, defined here is of particular utility in conjunction with fast multi-solution tangent formula techniques. Development of the methods and applications to both known and unknown crystal structures are presented.

Introduction

A general methodology of crystal structure determination which has found wide application in one form or another is the multi-solution tangent refinement technique. Although the actual procedures employed within the general framework of the method may vary widely, the use of the tangent formula (Karle & Hauptman, 1956) to extend and refine a number of plausible basis sets of phases is a common feature to all. On one end of the spectrum are those procedures which introduce

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a number of ambiguities at the onset, assign them initial numerical values, and immediately proceed with tangent refinement and extension. These methods are characterized by the small size of the basis set of phases available at the commencement of tangent refinement and the rather large number of plausible phase sets which must be generated to insure that at least one correct phase set is reached. Such methods lend themselves to automation, and excellent program packages such as *MULTAN* (Germain, Main & Woolfson, 1971) which employ this approach are widely used. On the other end of the spectrum are those methods which seek to broaden the basis set of phases, introducing symbolic ambiguities when necessary, before proceeding with tangent refinement. Such methods tend to minimize the number of ambiguities by minimizing the number of 'conflicts' in phase assignment, such as in the symbolic addition procedure (Zachariasen, 1952; Karle & Karle, 1966). These methods do not lend themselves as easily to automation.

Both methods eventually produce a number of plausible phase sets which then must be tested for correctness. If only a small number of phase sets need be tested, then an inspection of the resulting E maps poses no great problem. If, however, a large number of phase sets must be tested, the calculation and inspection of the resulting E maps may present a real problem in terms of computing time and possible inspection errors. Ideally one would like to know *a priori* whether a plausible phase set is likely to yield a solution without calculating and inspecting its resulting E map. Various figures of merit, such as the 'absolute figure of merit' (Germain, Main & Woolfson, 1971), the Ψ_0 test (Cochran & Douglas, 1955), and the residual R_K (Karle & Karle, 1966) have been proposed to rank phase sets in the order of their plausibility. However it has been found by experience that none of these figures of merit consistently discriminates against hopelessly incorrect phase sets, nor can they be depended upon to indicate the presence of a correct phase set. Declerq, Germain, Main & Woolfson (1973), recognizing the poor performance of these figures of merit, have incorporated a fast Fourier transform program into the most recent *MULTAN* package which automatically calculates E maps for all phase sets and displays them in an easily usable form. Nevertheless, it would be clearly desirable to construct a figure of merit which is reliable, absolute, and easily calculated. Recently secured estimates for the cosine invariants, $\cos(\varphi_h+\varphi_k+\varphi_l+\varphi_m)$, make it possible to propose such a figure of merit, NQEST.

Method

The quartets are the four-phase cosine invariants $\cos(\varphi_h+\varphi_k+\varphi_l+\varphi_m)$ where $h+k+l+m=0$. Hauptman (1974*a*,*b*) has shown, for sufficiently large $B=(2/N)\,|E_hE_kE_lE_m|$, where N is the number of assumed identical atoms in the unit cell, that

$$\cos(\varphi_h+\varphi_k+\varphi_l+\varphi_m)\simeq\begin{cases}+1 \text{ if } |E_{h+k}|,|E_{h+l}|,|E_{h+m}| \text{ are all large} & (1a)\\ -1 \text{ if } |E_{h+k}|,|E_{h+l}|,|E_{h+m}| \text{ are all small.} & (1b)\end{cases}$$

We define a PQ (positive quartet) to be a quartet with 'cross terms' $\{|E_{h+k}|,|E_{h+l}|,|E_{h+m}|\}$ all large and a NQ (negative quartet) to be one with cross terms all small. Note that a PQ is not necessarily positive nor is a NQ necessarily negative.

We will restrict our subsequent attention to the NQ because they form the basis of the required figure of merit, but it should be apparent that the PQ are equally important in their own right. The PQ are not, however, suitable as the basis for the required figure of merit because they are insensitive to the integrity of a phase set derived from tangent formula procedures. The reason for this is that tangent procedures generally insure that cosine invariants $\cos(\varphi_h+\varphi_k+\varphi_{-h-k})\simeq+1$, for large $A=(2/N^{1/2})\,|E_hE_kE_{-h-k}|$, that is, the strongest phase relationships are generally not violated by the tangent formula procedure. It can be easily shown that, for a given quartet invariant, if any one of the conditions:

$$\{\cos(\varphi_h+\varphi_k+\varphi_{-h-k})=+1 \text{ and } \cos(\varphi_l+\varphi_m+\varphi_{h+k})=+1\},$$

or

$$\{\cos(\varphi_h+\varphi_l+\varphi_{-h-l})=+1 \text{ and } \cos(\varphi_k+\varphi_m+\varphi_{h+l})=+1\},$$

or

$$\{\cos(\varphi_h+\varphi_m+\varphi_{-h-m})=+1 \text{ and } \cos(\varphi_k+\varphi_l+\varphi_{h+m})=+1\} \quad (2)$$

is fulfilled, then necessarily $\cos(\varphi_h+\varphi_k+\varphi_l+\varphi_m)=+1$.

The cosine invariants of equation (2) are the six cosine triples associated with each quartet; *i.e.*, the associated triples. For PQ the A values of the associated triples are large, by equation (1*a*), and for NQ the A values of the associated triples are small. Therefore we expect the phase sets generated by tangent formula procedures to identify the PQ well, regardless of the correctness of the set. However, the tangent refinement procedure is ordinarily designed to avoid the associated triples of the NQ and therefore to avoid biasing the proposed figure of merit.

For some specific values of $B_{\min}$ and E_{cross},* construct n quartets such that $B\geq B_{\min}$ and $\{|E_{h+k}|, |E_{h+l}|,|E_{h+m}|\}\leq E_{\text{cross}}$. In addition, for a specific value of E_{main}, insure that only quartets of interest will be constructed by imposing the condition that the 'main terms' satisfy $\{|E_h|,|E_k|,|E_l|,|E_m|\}\geq E_{\text{main}}$.* This latter condition limits the quartets generated to those with each main term greater than or equal to E_{main}, the

* E_{cross} is defined as the least upper bound of the cross terms and E_{main} as the greatest lower bound of the main terms.

smallest normalized structure factor phased in the tangent refinement procedure. Then an estimate, NQEST, of the integrity of the phase set with respect to the NQ is defined by

$$\text{NQEST} = \sum_{h,k,l}^{n} B \cos(\varphi_h + \varphi_k + \varphi_l + \varphi_m) / \sum_{h,k,l}^{n} B .$$

Clearly, NQEST ranges from -1 to $+1$ and, in view of equation (1*b*), is expected to be negative for a correct set of phases provided that E_{cross} is sufficiently small and B_{min} is sufficiently large.

Applications

A preliminary analysis of the negative quartet cosine invariants for an artificial 29 equal-atom structure in $P1$ suggested the simple form of a figure of merit based on the NQ. An inspection, Fig. 1, of the observed conditional average cosine

$$\langle \cos \Phi_4 \rangle \equiv \langle \cos(\varphi_h + \varphi_k + \varphi_l + \varphi_m) \mid \{|E_{h+k}|, |E_{h+l}|, |E_{h+m}|\} \leq E_{\text{cross}} \rangle_{h,k,l}$$

for various small values of E_{cross} as a function of B indicates that $\langle \cos \Phi_4 \rangle$ is everywhere negative and approaches -1 in the limit of large B. Additionally, the standard deviation of the cosine, $\sigma(\cos \Phi_4)$, decreases as B increases, indicating that the estimate for $\cos(\varphi_h + \varphi_k + \varphi_l + \varphi_m)$ given in equation (1*b*) becomes increasingly reliable at large B values. These results suggest that, for a cross term cutoff which is small, say $E_{\text{cross}} \leq 0{\cdot}85$, a simple average cosine weighted on B would be sensitive to the correctness of a phase set. NQEST, by definition, is normalized to lie in the range $\{-1, +1\}$, thereby eliminating the dependence of the figure of merit on the number of NQ generated.

In order to determine the effect of varying B_{min} and E_{cross} on NQEST, negative quartet cosine invariants were constructed for the known structure *d*-(+)-biotin (DeTitta, Edmonds, Stallings & Donohue, 1975). NQEST was calculated using the refined ($R = 0{\cdot}055$) phases and the criteria in Table 1. In each case NQEST is negative. As the restrictions on E_{cross} and B_{min} are relaxed; *i.e.*, as E_{cross} increases or B_{min} decreases, the total number of NQ increases and NQEST becomes less negative. In actuality, these variations are in complete accord with the theoretical predictions which state that, for fixed small values of $|E_{h+k}|, |E_{h+l}|, |E_{h+m}|$, the larger the value of B the more negative the cosine is likely to be and that, for a fixed value of B, the smaller the values of $|E_{h+k}|, |E_{h+l}|, |E_{h+m}|$, the more negative the cosine will be. Qualitatively we observe that $E_{\text{cross}} > 1{\cdot}0$ is too large to be considered 'small' for normal values of B_{min}, and $B_{\text{min}} < 0{\cdot}25$ is too small to be considered 'sufficiently large' for the conditions in equation (1*b*) to hold. In practice we have found $E_{\text{cross}} \sim 0{\cdot}7$ to be a good starting value with B_{min} chosen such that a sufficient number ($\sim$100–300) of NQ are constructed. An alternative method might employ a sliding scale for E_{cross} as a function of B_{min} in an attempt to make NQEST uniform for all ranges of B considered.

Table 1. *Variation of NQEST with B_{min} and E_{cross} for d-biotin*

The number in brackets refers to the total number of NQ

E_{cross} / B_{min}	0·50	0·75	1·00
0·25	−0·47 [717]	−0·33 [3519]	[⩾3519]*
0·50	−0·69 [39]	−0·54 [137]	−0·29 [421]
0·75	−0·99 [3]	−0·83 [10]	−0·71 [17]

* The NQEST value for $B_{\text{min}} = 0{\cdot}25$, $E_{\text{cross}} = 1{\cdot}00$ could not be readily calculated because of insufficient computer storage. We estimate the number of NQ for this particular set of B_{min} and E_{cross} values to be in excess of 40000.

The total number of NQ generated for specific B_{min}, E_{main}, and E_{cross} seems to be strongly structure dependent. Negative quartet invariants were generated using the criteria of Table 2 for the refined crystal structures prostaglandin A_1: monoclinic form (PGA_1M DeTitta, Edmonds & Duax, 1975), and orthorhombic form (PGA_1O, Duax & Edmonds, 1973; Edmonds & Duax, 1975), prostaglandin E_2 (PGE_2, Edmonds & Duax, 1975), indomethacin (INDOM, Kistenmacher

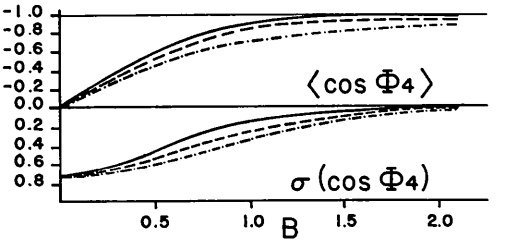

Fig. 1. Plots of $\langle \cos \Phi_4 \rangle \equiv \langle \cos(\varphi_h + \varphi_k + \varphi_l + \varphi_m) \{|E_{h+k}|, |E_{h+l}|, |E_{h+m}|\} \leq E_{\text{cross}} \rangle_{h,k,l}$ and $\sigma(\cos \Phi_4)$ as functions of B at values of $E_{\text{cross}} = 0{\cdot}35$ (———), 0·50 (– – – –) and 0·85 (–·–·–) for a 29 equal-atom artificial structure in $P1$.

Table 2. *Variation of NQEST with structure*

See text for explanation of the abbreviations.

Structure	Space group	N	$\langle(\lvert E\rvert^2 - 1)^2\rangle$	E_{main}	B_{min}	E_{cross}	#NQ	NQEST
Biotin	$P2_12_12_1$	64	1·115	1·5	0·5	0·7	137	−0·55
CLACM	$P2_1$	54	1·360	1·5	0·5	0·7	961	−0·41
PGA_1O	$P2_12_12_1$	96	1·627	1·5	0·5	0·7	84	−0·36
PGE_2	$P1$	25	1·893	1·5	0·5	0·7	154	−0·35
PGA_1M	$P2_1$	48	2·485	1·75	1·0	0·7	123	−0·64
INDOM	$P\bar{1}$	50	2·969	1·75	1·0	0·7	280	−0·66

& Marsh, 1972), *cis*-lactam of digitoxigenin, monoclinic form (CLACM, Rohrer, Duax & Wolff, 1974) and *d*-(+)-biotin. In the cases of PGA_1M and INDOM it was not feasible to use the less restrictive B_{min} and E_{main} criteria employed for the remaining four structures due to the very large number of NQ which would have been generated. Dependence of NQEST on the Patterson overlap function (Hauptman, 1964) $\langle(|E|^2-1)^2\rangle$ is inferred weakly but appears to be a second-order effect. In each case the calculated NQEST using the refined phases is decidedly negative. Applications to unknown crystal structures have been made: PGA_1M, CLACM and INDOM (in this context treated as unknown) having been solved in this laboratory using NQEST in conjunction with *MULTAN*. The multi-solution tangent refinement program of Main, Germain & Woolfson was chosen because it is efficient, is being used by a large number of investigators, and already incorporates a number of figures of merit which are useful for comparison with NQEST.

I. PGA_1M

MULTAN was permitted to generate 16 phase sets and phase extension was carried out to $|E|=1{\cdot}43$. NQ were generated with $B_{min}=1{\cdot}0$, $E_{main}=1{\cdot}75$, $E_{cross}=0.7$, and NQEST calculated over the 123 NQ for each of the 16 sets, Table 3. All 16 E maps were calculated and inspected in order of increasing NQEST: *i.e.* from most negative to most positive. Phase sets 16 and 12, having the most favorable values of NQEST, immediately revealed the structure, with the strongest 19 peaks in each map corresponding to correct atomic positions. The two solutions are related by a trivial translation along the polar axis. Phase sets 8 and 4, having the next most favorable values of NQEST and also related to each other by a translation along b, revealed essentially a complete molecular structure misplaced along the direction of the C(1)–C(8) hydrocarbon chain of the prostaglandin molecule (see DeTitta, Edmonds & Duax, 1975). The remaining 12 phase sets revealed only the direction of the hydrocarbon chain which can continuously across the cell in each map.

Table 3. *Figures of merit for* PGA_1M

Set #	ABSFOM	Ψ_0	RESID	NQEST
1	1·035	1·87*10⁴	41·04	+0·674
2	1·049	1·03	38·98	+0·648
3	1·055	1·04	30·82	+0·602
4	0·967	0·98	40·64	−0·499
5	1·030	1·02	39·74	+0·591
6	1·047	1·03	40·42	+0·669
7	1·039	1·03	40·65	+0·670
8	0·959	0·98	40·55	−0·507
9	1·085	1·05	37·34	+0·674
10	1·087	1·05	37·44	+0·675
11	1·082	1·05	37·15	+0·671
12	0·969	0·98	40·15	−0·527
13	1·066	1·05	36·93	+0·657
14	1·090	1·05	37·45	+0·675
15	1·088	1·05	37·42	+0·675
16	0·978	0·98	39·68	−0·533

The 123 NQ generated for PGA_1M along with $\cos(\varphi_h+\varphi_k+\varphi_l+\varphi_m)_{calc}$ for the refined set of phases ($R=0{\cdot}08$) are given in Table 4. For comparison the

Table 4. *The 123 NQ for* PGA_1M

Columns marked h,k,l,m are the indices of the structure invariant, $\varphi_h+\varphi_k+\varphi_l+\varphi_m$ where $h+k+l+m=0$. E_{CT} are the cross term magnitudes, from left to right $|E_{h+k}|, |E_{h+l}|, |E_{h+m}|$. B is the magnitude $(2/N)\,.\,|E_h\,.\,E_k\,.\,E_l\,.\,E_m|$ and C is the cosine invariant $\cos(\varphi_h+\varphi_k+\varphi_l+\varphi_m)$ calculated with the refined ($R=0{\cdot}08$) phases.

h	k	l	m	E_{CT}	B	C
1 1 -2	-5 1 9	12 0 -2	-8 -2 -5	0.461 0.697 0.270	2.062	-0.966
1 1 -2	-5 -1 9	-8 0 -5	12 0 -2	0.391 0.270 0.697	1.369	-0.960
1 1 -2	-3 0 -8	12 -1 -2	-10 0 12	0.679 0.601 0.312	1.713	0.957
1 1 -2	7 -1 -11	4 1 3	-12 -1 10	0.513 0.455 0.257	1.875	0.640
1 1 -2	7 -1 -11	4 -1 3	-12 1 10	0.513 0.687 0.679	1.875	0.878
1 1 -2	7 -1 -11	3 0 7	-11 0 6	0.513 0.603 0.649	1.641	-0.854
1 1 -2	-6 1 1	15 -2 -1	-10 0 12	0.455 0.482 0.542	1.437	-0.831
1 1 -2	-6 -1 1	15 0 1	-10 0 0	0.687 0.482 0.542	1.641	-0.981
1 1 -2	4 1 3	9 0 -9	-14 -2 8	0.455 0.422 0.278	1.536	-0.690
1 1 -2	4 -1 3	9 -2 -9	-14 2 8	0.687 0.422 0.360	1.377	-0.502
1 1 -2	9 0 -9	4 3 3	-14 -4 8	0.422 0.421 0.360	1.260	-0.461
1 1 -2	9 0 -9	4 -3 3	-14 4 8	0.422 0.455 0.360	1.223	-0.672
1 1 -2	-5 -3 9	12 0 -2	-8 2 -5	0.461 0.697 0.347	1.529	-0.597
1 1 -2	12 2 -3	-3 -3 5	-10 0 0	0.345 0.659 0.542	1.217	-0.132
1 1 -2	12 2 -3	-9 0 -5	-4 -3 10	0.345 0.318 0.631	1.207	-0.284
1 1 -2	-3 -2 -8	12 1 -2	-10 0 12	0.679 0.250 0.312	1.329	0.979
1 1 -2	-3 0 -8	-10 0 12	2 2 11	0.472 0.312 0.568	1.213	0.995
1 1 -2	6 -3 -9	-10 0 0	3 2 11	0.393 0.542 0.370	1.059	-0.019
1 1 -2	9 -2 -9	4 3 3	-14 -2 8	0.422 0.421 0.278	1.095	-0.826
10 0 -8	3 2 5	-3 3 5	-10 -5 -2	0.271 0.384 0.480	1.103	-0.993
7 0 -3	7 0 -3	-10 -1 9	-4 1 -3	0.343 0.185 0.185	3.870	-0.983
7 0 -3	7 0 -3	-3 0 -5	-11 0 11	0.343 0.557 0.557	3.406	-0.999
7 0 -3	7 0 -3	-10 -3 9	-4 3 -3	0.343 0.222 0.222	2.490	-0.963
7 0 -3	7 0 -3	-11 -2 11	-3 2 -5	0.343 0.666 0.666	2.459	-0.769
7 0 -3	7 2 -3	-10 1 9	-4 -3 -3	0.370 0.185 0.222	2.529	-0.951
7 0 -3	7 2 -3	-10 -1 9	-4 -1 -3	0.370 0.185 0.185	3.177	-0.875
7 0 -3	7 2 -3	-3 0 -5	-11 -2 11	0.370 0.557 0.666	2.644	-0.978
7 0 -3	7 2 -3	-4 1 -3	-10 -3 9	0.370 0.185 0.222	2.567	-0.989
7 0 -3	7 2 -3	-11 0 11	-3 -2 -5	0.370 0.557 0.666	2.132	-0.884
7 0 -3	-10 -1 9	-3 0 -5	6 1 -1	0.185 0.557 0.697	2.992	-0.956
7 0 -3	-10 -1 9	-3 -1 -5	-3 2 -5	0.185 0.697 0.666	2.282	-0.895
7 0 -3	-10 -1 9	-3 -2 -4	6 3 -2	0.185 0.461 0.345	1.868	-0.190
7 0 -3	-10 -1 9	7 4 -3	-4 -3 -3	0.185 0.476 0.222	1.664	-0.649
7 0 -3	6 1 -1	-10 -3 9	-3 2 -5	0.697 0.222 0.666	1.865	-0.990
7 0 -3	-5 -4 12	-3 -2 -5	1 6 -4	0.351 0.666 0.392	1.600	-0.999
7 0 -3	8 1 5	0 0 -4	-12 2 2	0.509 0.391 0.687	1.686	-0.999
7 0 -3	-4 -1 -3	-10 -3 9	7 4 -3	0.185 0.222 0.476	1.690	-0.714
7 0 -3	-10 -3 9	-3 0 -4	6 3 -2	0.222 0.391 0.345	1.516	-0.813
7 0 -3	-7 -1 13	-3 -2 -5	3 3 -5	0.472 0.666 0.294	1.265	0.022
7 0 -3	-11 -2 13	-6 4 -3	-3 -2 -5	0.666 0.476 0.666	1.375	-0.975
7 0 -3	1 6 -4	-4 -3 -3	-6 -3 10	0.392 0.222 0.416	1.001	-0.985
7 1 -9	-10 1 7	1 -1 -4	2 -1 6	0.482 0.513 0.166	1.269	-0.957
7 1 -9	-10 -1 7	1 -1 -4	2 1 6	0.247 0.513 0.157	1.269	-0.990
7 1 -9	0 3 8	-8 -3 5	1 -1 -4	0.317 0.261 0.513	1.146	-0.986
0 2 -9	9 11 -2	-3 -2 8	-10 2 0	0.523 0.241 0.405	1.582	-0.793
10 0 1	-1 -1-12	-8 -5 7	-1 6 4	0.399 0.340 0.519	1.502	-0.789
10 0 1	-12 0 7	1 6 -4	1 -6 -4	0.355 0.421 0.421	1.220	-0.999
2 0 8	9 1 -6	-8 -1 5	-3 0 -7	0.213 0.560 0.241	2.024	-0.990
2 0 8	9 1 -6	-8 -4 5	-12 2 2	0.318 0.568 0.405	1.137	-0.999
12 0 6	-7 -2 3	-6 -1 2	1 3-11	0.376 0.676 0.345	1.477	-0.950
5 1 -9	0 1 8	-4 -1 -3	-1 -1 4	0.639 0.468 0.120	1.500	-0.842
5 1 -9	0 1 8	-4 -3 -3	-1 1 4	0.639 0.499 0.583	1.194	-0.830
5 1 -9	0 -1 8	-4 1 -3	-1 -1 4	0.215 0.499 0.120	1.200	-0.960
5 1 -9	0 -1 8	-4 -1 -3	-1 1 4	0.215 0.468 0.583	1.500	-0.999
5 1 -9	-4 1 -3	0 -3 8	-1 1 4	0.499 0.639 0.583	1.161	-0.759
11 1 -2	-6 1 1	-1 2 -8	-4 -4 9	0.639 0.405 0.347	1.215	-0.601
11 1 -2	-3 -7 5	0 3 -8	-8 3 5	0.383 0.506 0.648	1.339	-0.300
11 1 -2	-8 1 5	-3 -5 5	0 4 -8	0.671 0.196 0.506	1.449	-0.977
7 2 -3	7 2 -3	-10 -1 9	-4 -3 -3	0.476 0.185 0.185	2.076	-0.607
7 2 -3	7 2 -3	-4 -1 -3	-10 -3 9	0.476 0.185 0.185	2.108	-0.675
7 2 -3	7 2 -3	-11 -2 11	-3 -2 -5	0.476 0.557 0.557	1.657	-0.961
7 2 -3	7 -2 -3	-10 1 9	-4 -1 -3	0.343 0.222 0.185	2.608	-0.994
7 2 -3	7 -2 -3	-3 0 -5	-11 0 11	0.343 0.666 0.666	2.294	-0.999
7 2 -3	7 -2 -3	-10 3 9	-4 -3 -3	0.343 0.182 0.185	1.677	-0.999
7 2 -3	7 -2 -3	-11 2 11	-3 -2 -5	0.343 0.500 0.557	1.657	-0.769
7 2 -3	7 -2 -3	-4 0 -5	-10 0 0	0.343 0.671 0.671	1.282	-0.999
7 2 -3	-10 1 9	-3 0 -5	6 3 -1	0.222 0.666 0.697	1.651	-0.831
7 2 -3	-10 1 9	6 -1 -1	-3 -2 -5	0.222 0.697 0.557	1.874	-0.995
7 2 -3	-10 1 9	-4 1 -3	7 -4 -3	0.222 0.222 0.370	1.717	-0.743
7 2 -3	-10 1 9	6 1 -2	-3 -4 -4	0.222 0.345 0.461	1.328	-0.051
7 2 -3	-10 -1 9	-3 0 -5	6 3 -1	0.185 0.666 0.697	2.455	-0.999
7 2 -3	-10 -1 9	-3 -2 -4	6 1 -2	0.185 0.391 0.345	1.520	-0.709
7 2 -3	-10 -1 9	7 -4 -3	-4 3 -3	0.185 0.370 0.182	1.365	-0.856
7 2 -3	-10 -1 9	6 3 -2	-3 -4 -4	0.185 0.481 0.461	1.339	-0.059
7 2 -3	-10 -1 9	-3 2 -5	6 3 -1	0.185 0.500 0.697	1.760	-0.892
7 2 -3	3 0 8	3 -3 -5	-10 0 0	0.206 0.233 0.671	1.177	0.038
7 2 -3	-3 0 -5	-7 1 13	3 -3 -5	0.666 0.684 0.233	1.361	-0.177
7 2 -3	-3 0 -5	-11 2 11	7 -4 -3	0.666 0.500 0.370	1.429	-0.965
7 2 -3	6 -1 -1	-10 -3 9	-3 3 -3	0.697 0.185 0.500	1.449	-0.990
7 2 -3	-4 -1 -3	-10 3 9	7 -4 -3	0.185 0.182 0.370	1.387	-0.931
7 2 -3	-4 -1 -3	3 -5 -5	-6 4 11	0.185 0.294 0.338	1.384	-0.916
7 2 -3	-10 3 9	-3 -2 -5	6 -3 -1	0.182 0.557 0.697	1.019	-0.909
7 2 -3	-10 -3 9	-3 0 -4	6 1 -2	0.185 0.461 0.345	1.238	-0.999
7 2 -3	-10 -3 9	-3 -2 -4	6 3 -1	0.185 0.391 0.481	1.239	-0.494
7 2 -3	-10 -3 9	-3 -2 -5	6 3 -1	0.185 0.557 0.455	1.019	-0.438
7 2 -3	3 -5 -5	-7 1 13	-3 2 -5	0.294 0.684 0.500	1.190	0.085
7 2 -3	3 -5 -5	0 3 8	-10 0 0	0.294 0.336 0.671	1.044	-0.212
7 2 -3	3 -5 -5	-6 3 2	-4 3 6	0.294 0.427 0.671	1.026	-0.913
7 2 -3	-11 0 11	7 -4 -3	-3 2 -5	0.666 0.370 0.500	1.151	-0.908
7 2 -3	-3 0 -4	-12 0 2	8 -2 5	0.461 0.455 0.509	1.111	-0.934
7 2 -3	-7 -1 13	-3 2 -5	3 -3 -5	0.472 0.500 0.233	1.038	0.789
6 0-10	3 0 4	3 0 4	-12 0 2	0.570 0.570 0.296	1.210	-0.999
6 0-10	3 0 4	3 -2 4	-12 0 2	0.147 0.147 0.296	1.200	-0.999
9 1 -6	3 0 8	-8 -1 5	-4 0 -7	0.273 0.241 0.517	1.802	-0.990
9 1 -6	2 2 8	-8 -1 5	-3 -2 -7	0.682 0.241 0.560	1.687	-0.785
9 1 -6	-14 4 7	4 1 3	1 -6 -4	0.472 0.271 0.537	1.421	-0.999
9 1 -6	-3 -7 5	4 -1 3	-10 5 -2	0.654 0.271 0.338	1.318	-0.907
9 1 -6	-8 -1 5	-4 -2 -7	3 2 8	0.241 0.517 0.333	1.411	-0.829
9 1 -6	4 -1 3	-3 -5 5	-10 5 -2	0.587 0.568 0.338	1.154	-0.935
10 2 1	3 -7 -5	-12 0 2	-1 5 2	0.455 0.659 0.436	1.232	0.019
1 3 -2	6 -2-10	-1 5 2	-6 1 10	0.481 0.233 0.436	1.238	0.503
1 3 -2	7 -3-11	4 1 3	-12 -1 10	0.513 0.421 0.679	1.194	-0.026
1 3 -2	7 -3-11	4 -2 7	-12 2 6	0.513 0.369 0.328	1.222	-0.114
1 3 -2	-15 -2 8	6 -4-10	8 3 4	0.355 0.481 0.399	1.190	0.378
1 3 -2	6 -4-10	-6 -4 10	-1 5 2	0.481 0.120 0.233	1.262	0.531
10 1 -9	3 2 4	-7 -4 3	-6 3 1	0.697 0.222 0.500	1.087	-0.969
10 1 -9	4 -1 3	-7 4 3	-7 -4 3	0.343 0.182 0.222	1.130	-0.994
10 1 -9	3 2 4	-7 -4 3	-6 1 2	0.345 0.222 0.461	1.001	-0.893
3 0 8	-3 0 -5	-12 0 3	12 0 -6	0.149 0.408 0.509	1.499	-0.999
3 0 8	-12 0 3	8 1 -7	1 -1 -4	0.408 0.191 0.473	1.263	-0.910
6 2-10	3 0 4	3 -2 4	-12 0 2	0.147 0.570 0.336	1.078	-0.655
0 1 8	-2 -1-12	-8 -1 5	10 1 -1	0.519 0.513 0.504	1.249	-0.975
0 1 8	9 -2 -7	-8 2 -5	-1 -1 4	0.099 0.537 0.468	1.026	0.938
0 1 8	-11 3 2	8 -1 -5	3 -5 -5	0.506 0.273 0.648	1.404	0.573
0 1 8	-11 3 2	8 -1 -5	3 -3 -5	0.506 0.281 0.671	1.225	0.908
0 1 8	-4 1 -3	5 -3 -9	-1 1 4	0.583 0.639 0.499	1.114	-0.314
3 0 5	-3 -5 5	7 1-13	-7 4 3	0.480 0.233 0.500	1.026	-0.586
0 4 0	0 4 0	14 -4 -7	-14 -4 7	0.233 0.368 0.368	1.874	-0.995
8 1 -9	-9 -3 6	-3 -2 -4	4 4 7	0.481 0.517 0.396	1.018	0.317
14 4 -7	-4 +1 -3	-9 3 6	-1 -6 4	0.405 0.605 0.271	1.055	-0.956
5 4-12	-8 1 5	4 1 3	-1 -6 4	0.680 0.453 0.666	1.111	-0.992
12 0 -7	-8 0 -5	-7 0 5	3 0 7	0.438 0.094 0.429	1.059	-0.999
15 2 -8	-4 1 -3	-10 3 7	-1 -6 4	0.539 0.472 0.444	1.001	0.245

121 PQ with $B \geq 4{\cdot}4$, $E_{\text{main}} = 1{\cdot}75$ and $E_{\text{cross}} \geq 1{\cdot}75$ are given in Table 5. It is worth while to note that of the 123 cosine invariants predicted to be negative only 19 are actually positive and, of these 19, five are only marginally positive. This may be contrasted with the results for the PQ, wherein all of the cosine invariants predicted to be positive were in fact positive. However, it is impossible to make a direct comparison of the PQ and NQ results because the B_{min} and E_{cross} conditions are completely different.

Table 5. *The* 121 *PQ for* PGA_1M

Columns marked h, k, l, m are the indices of the structure invariant, $\varphi_h + \varphi_k + \varphi_l + \varphi_m$ where $h+k+l+m=0$. E_{CT} are the cross term magnitudes, from left to right $|E_{h+k}|, |E_{h+l}|, |E_{h+m}|$. B is the magnitude $(2/N) \cdot |E_h \cdot E_k \cdot E_l \cdot E_m|$ and C is the cosine invariant cos $(\varphi_h + \varphi_k + \varphi_l + \varphi_m)$ calculated with the refined ($R = 0{\cdot}08$) phases.

h	k	l	m	E_{CT}	B	C
0 0 9	0 2 0	0 2 0	0 -4 -9	3.538 3.538 2.636	6.111	0.935
0 0 9	0 2 0	-1 1 7	1 -3-11	3.538 1.838 2.849	5.704	0.948
0 0 9	0 2 0	-1 -1 2	1 -1-11	3.538 1.838 3.945	5.690	0.965
0 0 9	0 2 0	10 0 -8	-10 -2 -1	3.538 3.462 3.355	8.825	0.962
0 0 9	0 2 0	-7 0 3	7 -2-12	3.538 2.506 3.133	6.677	0.917
0 0 9	0 2 0	0 2 -9	0 -4 0	3.538 4.404 1.767	7.319	0.972
0 0 9	0 2 0	-10 0 -1	10 -2 -8	3.538 3.884 2.894	9.120	0.974
0 0 9	0 2 0	10 2 -8	-10 -4 -1	3.538 2.894 2.076	5.680	0.951
0 0 9	0 2 0	-7 -2 3	7 0-12	3.538 2.228 3.611	6.186	0.986
0 0 9	0 2 0	9 1 -6	-9 -3 -3	3.538 2.908 2.255	4.939	0.934
0 0 9	0 2 0	9 -1 -6	-9 -1 -3	3.538 2.908 3.033	6.928	0.997
0 0 9	0 2 0	-9 1 -3	9 -3 -6	3.538 3.033 2.073	5.149	0.908
0 0 9	0 2 0	-10 2 -1	10 -4 -8	3.538 3.355 2.157	4.716	0.976
0 0 9	-1 -1 2	10 0 -8	-9 -1 -3	1.838 3.462 3.033	7.946	0.980
0 0 9	-1 -1 2	10 2 -8	-9 -1 -3	1.838 2.894 3.033	6.862	0.932
0 0 9	-1 -1 2	10 -2 -8	-9 3 -3	1.838 2.894 2.255	4.892	0.786
0 0 9	-1 -1 2	9 0 -7	-8 1 -4	1.838 2.282 2.419	4.508	0.997
0 0 9	10 2 -8	-9 1 -3	-1 -3 2	2.894 3.033 1.862	4.956	0.945
0 0 9	10 2 -8	-10 2 -1	0 -4 0	2.894 3.355 1.767	5.560	0.850
0 2 0	0 2 0	1 1 -2	-1 -5 2	2.636 2.849 2.849	6.074	0.999
0 2 0	0 2 0	1 -1 -2	-1 -3 2	2.636 3.945 3.945	8.722	0.999
0 2 0	0 2 0	10 0 -8	-10 -4 8	2.636 3.355 3.355	6.256	0.882
0 2 0	0 2 0	7 0 -3	-7 -4 3	2.636 3.133 3.133	6.109	0.962
0 2 0	0 2 0	7 -1 -9	-7 -3 9	2.636 3.636 3.636	7.458	0.986
0 2 0	0 2 0	0 -2 -9	0 -2 -9	2.636 4.456 4.456	9.711	0.934
0 2 0	0 2 0	6 -1 -9	-6 -3 9	2.636 3.506 3.506	5.736	0.998
0 2 0	0 2 0	10 0 1	-10 -4 -1	2.636 2.894 2.894	5.795	0.857
0 2 0	0 2 0	10 -2 -8	-10 -2 8	2.636 3.884 3.884	8.732	0.898
0 2 0	0 2 0	9 0 -7	-9 -4 7	2.636 2.618 2.618	4.532	0.915
0 2 0	0 2 0	5 -1 -9	-5 -3 9	2.636 3.151 3.151	5.722	0.479
0 2 0	0 2 0	11 -1 -2	-11 -3 2	2.636 3.136 3.136	5.909	0.878
0 2 0	0 2 0	7 -2 -3	-7 -2 3	2.636 3.817 3.817	7.618	0.946
0 2 0	0 2 0	6 0-10	-6 -4 10	2.636 2.780 2.780	5.701	0.783
0 2 0	0 2 0	9 -1 -6	-9 -3 6	2.636 3.033 3.033	5.307	0.976
0 2 0	0 2 0	9 -1 3	-9 -3 -3	2.636 2.908 2.908	4.680	0.956
0 2 0	0 2 0	10 -2 1	-10 -2 -1	2.636 3.462 3.462	6.498	0.855
0 2 0	0 2 0	10 -1 -9	-10 -3 9	2.636 2.804 2.804	4.933	0.949
0 2 0	0 2 0	6 -2-10	-6 -2 10	2.636 3.111 3.111	5.994	0.870
0 2 0	0 2 0	7 -1-11	-7 -3 11	2.636 2.770 2.770	5.249	0.054
0 2 0	0 2 0	2 -2 8	-2 -2 -8	2.636 3.314 3.314	5.468	0.825
0 2 0	0 2 0	9 -2 -7	-9 -2 7	2.636 3.235 3.235	5.317	0.855
0 2 0	0 2 0	10 -1 -7	-10 -3 7	2.636 2.609 2.609	4.718	0.576
0 2 0	0 2 0	8 -1 -7	-8 -3 7	2.636 2.447 2.447	4.444	0.552
0 2 0	0 2 0	15 -2 -8	-15 -2 8	2.636 2.330 2.330	4.401	0.934
0 2 0	1 1 -2	-1 1 2	0 -4 0	2.849 2.849 4.404	7.225	0.985
0 2 0	1 1 -2	-10 0 8	-9 -3 6	2.849 3.355 3.033	6.088	0.972
0 2 0	1 1 -2	7 0 -3	-8 -3 5	2.849 3.133 2.419	5.367	0.911
0 2 0	1 1 -2	-7 0 3	6 -3 -1	2.849 3.133 2.631	4.699	0.876
0 2 0	1 1 -2	0 -2 -9	-1 -1 11	2.849 4.456 1.838	4.519	0.090
0 2 0	1 1 -2	-10 0 -1	9 -3 3	2.849 2.894 2.908	4.991	0.988
0 2 0	1 1 -2	-10 -2 8	9 -1 -6	2.849 3.884 3.033	7.072	0.905
0 2 0	1 1 -2	9 0 -7	-10 -3 9	2.849 2.618 2.804	5.095	0.964
0 2 0	1 1 -2	-9 0 7	8 -3 -5	2.849 2.618 2.419	4.568	0.863
0 2 0	1 1 -2	-7 -2 3	-8 -1 5	2.849 3.817 2.631	4.267	0.931
0 2 0	1 1 -2	-7 -2 3	6 -1 -1	2.849 3.817 2.631	5.732	0.879
0 2 0	1 1 -2	9 -1 3	-10 -2 -1	2.849 2.908 3.462	5.850	0.937
0 2 0	1 1 -2	-10 -1 9	9 -2 -7	2.849 2.804 3.235	5.102	0.983
0 2 0	1 1 -2	-9 -2 7	8 -1 -5	2.849 3.235 2.419	4.401	0.801
0 2 0	1 -1 -2	-10 0 8	9 -3 -6	3.945 3.355 3.033	8.191	0.966
0 2 0	1 -1 -2	7 0 -3	-8 -1 5	3.945 3.133 2.419	6.418	0.965
0 2 0	1 -1 -2	-7 0 3	6 -1 -1	3.945 3.133 2.631	6.982	0.925
0 2 0	1 -1 -2	0 2 -9	-1 -3 11	3.945 1.767 1.838	4.527	0.744
0 2 0	1 -1 -2	0 -2 -9	-1 1 11	3.945 4.456 1.842	4.519	0.707
0 2 0	1 -1 -2	-10 0 -1	9 -1 3	3.945 2.894 2.908	7.000	0.990
0 2 0	1 -1 -2	-10 2 8	9 -3 -6	3.945 2.076 3.033	5.256	0.998
0 2 0	1 -1 -2	-10 -2 8	9 1 -6	3.945 3.884 2.255	7.072	0.954
0 2 0	1 -1 -2	9 0 -7	-10 -1 9	3.945 2.618 2.804	4.305	0.948
0 2 0	1 -1 -2	-9 0 7	8 -1 -5	3.945 2.618 2.419	5.437	0.918
0 2 0	1 -1 -2	7 2 -3	-8 -3 5	3.945 2.063 2.419	4.406	0.950
0 2 0	1 -1 -2	7 -2 -3	-8 1 5	3.945 3.817 2.023	5.267	0.971
0 2 0	1 -1 -2	-7 -2 3	6 -1 -1	3.945 3.817 2.631	5.732	0.993
0 2 0	1 -1 -2	9 1 3	-10 -2 -1	3.945 2.073 3.462	5.850	0.890
0 2 0	1 -1 -2	-9 -1 -3	8 0 5	3.945 2.908 1.950	4.906	0.999
0 2 0	1 -1 -2	-1 3 2	0 -4 0	3.945 1.984 4.404	5.220	0.955
0 2 0	1 -1 -2	-10 1 9	9 -2 -7	3.945 2.267 3.235	5.102	0.983
0 2 0	1 -1 -2	-3 -1 -9	-6 0 11	3.945 2.762 1.917	4.689	0.970
0 2 0	1 -1 -2	-9 -2 7	8 1 -5	3.945 3.235 2.023	4.401	0.974
0 2 0	10 0 -8	0 2 9	-10 -4 -1	3.355 1.767 2.894	5.222	0.936
0 2 0	10 0 -8	0 -2 9	-10 0 -1	3.355 4.456 2.894	8.385	0.983
0 2 0	10 0 -8	-10 2 8	0 -4 -4	3.355 2.076 4.404	6.052	0.960
0 2 0	10 0 -8	-9 1 6	-1 -3 2	3.355 2.255 3.945	5.916	0.999
0 2 0	7 0 -3	0 -2 -9	-7 0 12	3.133 4.456 2.228	5.965	0.983
0 2 0	7 0 -3	-10 0 -1	3 -2 4	3.133 2.894 2.139	4.963	0.826
0 2 0	7 0 -3	-7 2 3	0 -4 0	3.133 2.063 4.404	5.535	0.976
0 2 0	7 0 -3	1 -3 -2	8 1 5	3.133 3.945 2.023	4.636	0.999
0 2 0	7 0 -3	-1 -3 7	-6 1 1	3.133 3.945 1.770	5.045	0.992
0 2 0	7 0 -3	-7 -1 11	0 -1 -8	3.133 2.770 2.704	5.039	0.897
0 2 0	7 0 -3	0 1 -8	-7 -3 11	3.133 2.092 2.770	4.440	0.488
0 2 0	7 1 -9	-7 1 8	0 -4 0	2.644 2.644 4.404	6.138	0.999
0 2 0	7 1 -9	-11 -1 2	4 -2 7	2.644 3.136 2.200	4.461	0.803
0 2 0	7 -1 -9	-11 1 2	4 -2 7	3.636 2.428 2.200	4.461	0.999
0 2 0	7 -1 -9	-11 -1 2	4 0 7	3.636 3.136 2.221	4.419	0.999
0 2 0	0 0 9	-10 0 -1	10 -4 -8	1.767 2.894 3.355	4.480	0.953
0 2 0	0 2 9	10 -2 -8	-10 -2 -1	1.767 3.884 3.462	6.050	0.949
0 2 0	0 -2 9	10 2 -8	-10 -2 -1	4.456 2.076 3.462	6.050	0.974
0 2 0	0 -2 9	10 -2 -8	-10 2 -1	4.456 3.884 2.157	6.050	0.990
0 2 0	0 -2 9	9 1 -6	-9 -1 -3	4.456 2.255 2.908	5.300	0.998
0 2 0	0 -2 9	9 -1 -6	-9 1 -3	4.456 3.033 2.908	5.500	0.830
0 2 0	6 1 -9	-6 1 9	0 -4 0	2.109 2.109 4.404	5.706	0.995
0 2 0	10 0 1	-9 1 -3	-1 -3 2	2.894 2.073 3.945	5.057	0.991
0 2 0	10 0 1	-10 2 -1	0 -4 0	2.894 2.157 4.404	4.652	0.947
0 2 0	10 2 -8	-9 -1 6	-1 -3 2	2.076 3.033 3.945	5.109	0.951
0 2 0	2 0 8	4 -1 -9	-6 -2 7	2.655 2.972 2.631	4.565	0.896
0 2 0	9 0 -7	1 -3 -2	-10 1 9	2.618 3.945 2.267	4.555	0.948
0 2 0	5 1 -9	-5 1 9	0 -4 0	2.340 2.340 4.404	4.612	0.923
0 2 0	11 1 -2	-11 1 2	0 -4 0	2.428 2.428 4.404	4.565	0.924
1 1 -2	-1 1 2	7 0 -3	-7 -2 3	4.404 2.419 2.631	7.447	0.924
1 1 -2	-1 1 2	8 0 -7	-9 -2 7	4.404 2.804 2.419	5.272	0.869
1 1 -2	-1 1 2	9 -1 3	-9 -1 -3	4.404 3.462 2.427	5.267	0.986
1 1 -2	-1 1 2	-9 -1 -3	9 -1 3	4.404 2.427 3.462	5.267	0.986
1 1 -2	-1 1 2	10 -1 -9	-10 -1 9	4.404 2.201 3.235	4.897	0.997
1 1 -2	-1 1 2	-10 -1 9	10 -1 -9	4.404 3.235 2.201	4.897	0.997
1 1 -2	-10 0 8	0 2 -9	9 -3 3	3.033 1.842 2.894	4.498	0.944
1 1 -2	-10 0 8	0 -2 -9	9 1 3	3.033 1.838 2.894	6.309	0.947
1 1 -2	7 0 -3	-7 2 3	-1 -3 2	2.419 1.770 4.404	5.381	0.972
1 1 -2	-7 0 3	7 -2 -3	-1 -3 2	2.631 2.023 4.404	5.381	0.972
1 1 -2	0 2 -9	-10 -2 8	9 -1 3	1.842 3.033 3.462	5.447	0.991
1 1 -2	0 -2 -9	-10 2 8	9 -1 3	1.838 2.255 3.462	5.447	0.999
1 1 -2	7 -2 -3	-7 -2 3	-1 3 2	2.419 2.631 2.636	4.416	0.811
1 1 -2	-7 -2 3	7 -2 -3	-1 3 2	2.631 2.419 2.636	4.416	0.811
10 0 -8	0 2 9	-9 1 -3	-1 -3 2	2.894 1.838 2.255	4.558	0.998

II. *CLACM*

MULTAN was permitted to generate 16 phase sets, and phase extension was carried out to $|E| = 1{\cdot}50$. NQ were generated with $B_{\text{min}} = 0{\cdot}9$, $E_{\text{main}} = 1{\cdot}5$, $E_{\text{cross}} = 0{\cdot}7$, and NQEST calculated over the 83 NQ for each of the 16 sets, Table 6(*a*). E maps were calculated for phase sets 7 and 16, corresponding to the best NQEST $= -0{\cdot}24$. Although the repeating pattern of hexagonal rings indicative of steroid structures was apparent in both maps, it proved too difficult to develop a complete structure from this information. *MULTAN* was then permitted to generate 64 phase sets with the same phase extension, and NQEST was calculated for each phase set, Table 6(*b*). E maps for sets 7 and 8, corresponding to the best NQEST $= -0{\cdot}38$ and related by a trivial translation along **a** by $\frac{1}{2}$, revealed a major portion of the structure.

III. *INDOM*

MULTAN was permitted to generate eight phase sets and phase extension was carried out to $|E| = 1{\cdot}5$. NQ were generated with $B_{\text{min}} = 1{\cdot}0$, $E_{\text{main}} = 1{\cdot}75$, $E_{\text{cross}} = 0{\cdot}7$, and NQEST calculated over the 280 NQ for each of the 8 sets, Table 7(*a*). Discounting the trivial solution, set 1 with all phases zero, E maps were calculated for set 7, with best ABSFOM and RESID and set 5 with best NQEST. No recognizable fragment was located in either map. Similar results were obtained when *MULTAN* was permitted to generate 16 phase sets, Table 6(*b*). However, when *MULTAN* was permitted to generate 32 phase sets, Table 6(*c*), one solution (set 30) appeared to be significantly better than all the others on the basis of NQEST. An E map cal-

Table 6. *Figures of merit for CLACM*

(*a*) 16 Phase sets

Set #	ABSFOM	RESID	NQEST
1	0·96	29·4	−0·15
2	0·97	29·4	−0·15
3	0·97	29·5	−0·19
4	0·97	29·5	−0·19
5	0·97	30·9	−0·04
6	0·97	29·7	−0·03
7	1·00	27·8	−0·24
8	0·97	30·7	−0·02
9	0·94	29·8	−0·22
10	0·94	30·7	0·15
11	0·95	30·2	0·15
12	0·95	29·9	−0·23
13	0·97	29·7	−0·03
14	0·97	30·9	−0·04
15	0·97	30·7	0·02
16	1·00	27·8	−0·24

Table 6 (*cont.*)

(*b*) 64 Phase Sets

Set #	ABSFOM	RESID	NQEST	Set #	ABSFOM	RESID	NQEST	Set #	ABSFOM	RESID	NQEST	Set #	ABSFOM	RESID	NQEST
1	0·02	33·3	0·01	17	0·93	29·8	0·19	33	0·95	29·7	0·16	49	0·94	30·9	0·10
2	0·88	32·0	0·11	18	0·96	32·3	0·12	34	0·97	31·4	0·14	50	0·90	32·6	0·17
3	0·88	31·9	0·06	19	0·06	30·6	0·09	35	0·98	30·7	0·10	51	0·91	32·1	0·14
4	0·92	32·8	0·09	20	0·93	30·3	0·14	36	0·96	29·9	0·15	52	0·97	30·2	0·06
5	0·98	27·5	−0·34	21	0·97	31·6	0·14	37	0·88	34·3	0·31	53	0·95	29·7	0·16
6	0·99	27·5	−0·34	22	0·95	29·7	0·16	38	0·88	34·3	0·31	54	0·97	31·6	0·14
7	0·99	27·2	−0·38	23	0·95	29·9	0·15	39	0·87	34·3	0·30	55	0·98	30·8	0·09
8	0·99	27·2	−0·38	24	0·98	30·8	0·09	40	0·88	34·1	0·25	56	0·95	39·8	0·15
9	0·88	32·0	0·11	25	0·90	32·6	0·17	41	0·97	31·4	0·14	57	0·96	32·2	0·12
10	0·92	33·3	0·01	26	0·94	30·9	0·10	42	0·95	29·7	0·16	58	0·93	29·8	0·19
11	0·92	32·8	0·10	27	0·97	30·2	0·06	43	0·96	29·9	0·15	59	0·93	30·2	0·14
12	0·88	31·9	0·06	28	0·91	32·1	0·14	44	0·98	30·7	0·10	60	0·96	30·6	0·09
13	0·96	30·9	0·05	29	0·99	27·9	−0·29	45	0·93	30·0	0·18	61	0·92	32·0	−0·07
14	0·96	30·9	0·05	30	0·92	32·0	−0·07	46	0·92	29·4	0·19	62	0·99	27·9	−0·29
15	0·97	30·6	0·07	31	0·92	32·6	−0·05	47	0·93	29·7	0·15	63	1·00	27·4	−0·28
16	0·97	30·6	0·07	32	1·01	27·4	−0·28	48	0·94	30·4	0·11	64	0·92	32·6	−0·05

culated for that phase set revealed all but one atomic position, $\frac{24}{25}$ atoms being the strongest peaks in the map.

Results

In the test cases using known crystal structures it has been shown that, if $B_{\min}$ is sufficiently large and E_{cross} sufficiently small, NQEST is always negative. Specifically, if $B_{\min} \simeq 0{\cdot}5$ and $E_{\text{cross}} \simeq 0{\cdot}7$, then NQEST will lie in the range $-0{\cdot}6$ to $-0{\cdot}3$ for the refined set of phases. Confronted with the choice of lowering the $B_{\min}$ cutoff or raising the E_{cross} cutoff to increase the number of NQ generated, the former has been found to be preferable. Although the probability that $\cos(\varphi_h+\varphi_k+\varphi_l+\varphi_m)<0$ is a function of both B and the magnitudes of the cross terms $|E_{h+k}|, |E_{h+l}|, |E_{h+m}|$, the dependence on B is easily taken into account in NQEST while the dependence on the cross terms is much more complicated (Hauptman, 1974*a*). Until additional tests of NQEST on solved crystal structures are made, only plausible conclusions regarding the dependence of NQEST and the total number of NQ generated on the cutoff criteria, $B_{\min}$, E_{cross}, E_{main}, and on the basic characteristics of the structure, such as N, space group and the Patterson overlap function $\langle(|E|^2-1)^2\rangle$, can be made. However, the initial results are encouraging in that they fit the theoretical predictions.

In the test cases using unknown crystal structures the results have been very satisfying. Not only has NQEST performed better than the more traditional figures of merit but the expected independence of NQEST from the tangent refinement procedure has also been borne out. In the case of PGA_1M, ABSFOM and RESID were completely unable to rank the sets in the order of their plausibility. The Ψ_0 test proved more sensitive although it might be argued that the difference of $\Psi_0=0{\cdot}98$ for a correct phase set and $\Psi_0=1{\cdot}02$ for an incorrect phase set is, at best, on the fringe of significance. On the other hand, NQEST proved to be highly sensitive; the four phase sets with NQEST $\simeq -0{\cdot}5$ containing two correct solutions and two correctly oriented but translated solutions, with all other phase sets having NQEST $\geq 0{\cdot}6$.

Of perhaps equal significance is the 'absoluteness' of NQEST as an estimate of the correctness of a phase set. By this is meant that NQEST not only points out which of n plausible phase sets is *most* likely to be correct; *i.e.* it is a ranking procedure; but it also decides whether *any* of n phase sets is likely to be correct. For example, in the case of INDOM it is doubtful whether or not any E maps would have been calculated when *MULTAN* was permitted to generate eight and 16 plausible phase sets, Tables 7(*a*) and (*b*), because in these instances the best NQEST values were $+0{\cdot}03$ and $-0{\cdot}03$ respectively. It may be premature to make definitive statements about what value of NQEST implies that a given phase set is correct but it seems safe to conclude that NQEST cannot be positive for a

correct set of phases when calculated with the previously suggested cutoff criteria. Borderline cases, where NQEST is slightly negative (for example, sets 7 and 16 for CLACM, Table 6(*a*), NQEST = −0·24) and partial structure is revealed in the *E* map, point out the need to optimize the cross term, main term, and *B* criteria to insure a clearer indication in these situations.

In terms of computing time, NQEST represents a substantial saving compared with the calculation of all *E* maps, even when a fast Fourier transform program is available. The generation of 154 NQ from a set of 170 normalized structure factors used as 'main terms' for PGE_2 consumes approximately the same computing time as the synthesis of a single *E* map from the same 170 terms in conjunction with a fast Fourier program. The generation of the NQ represents the major portion of the combined NQ/NQEST operation; the time required for the evaluation of NQEST for the phase sets is trivial. Thus the use of NQEST is justified in any situation which suggests that more than one *E* map may have to be calculated in the normal course of multi-solution tangent refinement analysis.

Discussion

Schenk (1973) recognized the utility of the quartet cosine invariants which are negative in a multi-solution symbolic addition procedure and has applied a somewhat analogous figure of merit based upon the special negative quartet invariants where $h=k$ (Schenk & de Jong, 1973) which were developed from the Harker–Kasper inequalities. More recently, Schenk (1974) has discussed the use of negative quartets and explored the strength of the NQ's relative to the $\sum_2$ relation. On the basis of a failure frequency distribution study Schenk has concluded that the number of NQ which are reliably negative (*versus* the number of $\sum_2$ which are reliably positive) is so small as to render the NQ's virtually useless for the evaluation of phases. This pessimism is considered to be unwarranted for the following reasons: (1) it is probably incorrect to expect the estimation of a negative cosine invariant involving four phases, $\cos(\varphi_h+\varphi_k+\varphi_l+\varphi_{-h-k-l}) \simeq -1$, to be directly comparable to the estimation of a positive cosine invariant involving three phases, $\cos(\varphi_h+\varphi_k+\varphi_{-h-k}) \simeq +1$; (2) a comparison of the failure frequency distributions of NQ's and $\sum_2$'s at values of $B=A$ implies that *B* and *A* are comparable quantities whereas recent theoretical results (Hauptman, 1975) imply that the comparable quantities are *A* and 2*B*; (3) the cutoff criterion for the cross terms suggested by Schenk; *i.e.* that the average value of the cross terms be less than a specified value, is not only less restrictive than the condition that all three cross terms be smaller than a specified value, but recent theoretical

Table 7. *Figures of merit for INDOM*

(*a*) 8 Phase sets

Set #	ABSFOM	RESID	NQEST
1	1·16	28·8	1·00
2	0·87	41·3	0·42
3	0·73	44·4	0·15
4	0·91	39·7	0·47
5	0·63	48·0	0·03
6	0·77	45·2	0·24
7	0·92	39·2	0·44
8	0·71	44·8	0·21

(*b*) 16 Phase sets

Set #	ABSFOM	RESID	NQEST
1	1·15	17·1	1·00
2	0·89	29·2	0·35
3	0·70	40·5	0·14
4	0·80	33·6	−0·03
5	0·68	37·3	0·31
6	0·82	33·6	0·49
7	0·84	32·3	0·30
8	0·79	33·7	−0·02
9	0·71	38·3	0·17
10	0·75	35·2	0·27
11	0·91	31·5	0·43
12	0·91	30·1	0·54
13	0·97	29·0	0·39
14	0·91	28·9	0·10
15	0·82	32·4	0·51
16	0·77	34·0	0·25

(*c*) 32 Phase sets

Set #	ABSFOM	RESID	NQEST
1	1·15	17·1	1·00
2	0·91	29·1	−0·15
3	0·71	37·4	−0·15
4	0·69	37·6	0·08
5	0·81	32·0	0·05
6	0·74	33·6	−0·15
7	0·70	37·7	0·09
8	0·67	38·9	0·10
9	0·66	37·3	−0·18
10	0·78	34·3	0·34
11	0·84	31·8	0·16
12	0·84	31·1	−0·13
13	0·71	35·9	−0·14
14	0·82	33·9	0·41
15	0·90	28·0	0·02
16	0·90	31·1	0·46
17	0·80	32·6	−0·11
18	0·74	37·8	0·36
19	0·86	30·3	−0·26
20	0·86	31·1	0·18
21	0·71	36·0	−0·11
22	0·72	38·4	0·24
23	0·91	31·5	0·42
24	0·79	34·8	0·11
25	0·81	32·3	0·25
26	0·79	33·8	0·10
27	0·66	37·9	0·11
28	0·71	37·0	0·16
29	0·97	28·4	0·39
30	0·99	24·1	−0·55
31	0·68	38·4	0·00
32	0·78	32·9	0·53

results (Hauptman, 1975) also show that under certain conditions the expected value of cos $(\varphi_h+\varphi_k+\varphi_l+\varphi_m)$ can be positive if two cross terms are moderately small and the third cross term is moderately large. Additionally it should be emphasized that the identification of even a small number of negative cosine invariants, whether quartets or triples, is extremely helpful in the solution of crystal structures by direct methods.

Schenk (1974) has proposed a practical symbolic addition procedure for symmorphic space groups which employs a figure of merit based on the NQ. As a modification, an analogous scenario for more difficult problems is proposed:

(1) Construct $\sum_2$ and NQ lists. Select origin, enantiomorph, and suitable basis vectors to produce P plausible phase sets. P may well be of the order of 2^{10}.

(2) Initiate tangent refinement and extension for the P plausible phase sets. Stop when phase values have been obtained for some 30 or more NQ; and calculate NQEST over the P plausible phase sets.

(3) Continue tangent extension for, let us say, the $P/2$ plausible phase sets with the best NQEST until phase values have been obtained for an additional 40–50 NQ, and calculate NQEST over these phase sets.

(4) Continue tangent extension for, let us say, the $P/8$ plausible phase sets with the best NQEST until phase values have been obtained for an additional 40–50 NQ.

The threshold values of $P/2$ and $P/8$ in steps 3 and 4 have been arbitrarily selected to indicate that the rejection criteria may become more selective as larger numbers of NQ are reached through the phase extension.

This process is repeated until a specified small number of plausible phase sets is reached and then tangent refinement for these phase sets is completed. This procedure insures that only that specific small fraction of the P plausible basis sets with the best NQEST values will be extended to the limit of the tangent refinement. The initial weeding of the P ambiguities might well be accomplished at a point where the tangent refinement procedure has extended the basis set to as few as 50 phases. Since the time required for successive cycles of tangent refinement increases rapidly, a relatively short time may be spent on steps 2, 3 and 4. This procedure permits the luxury of a large initial basis set, without the attendant expense of a full tangent refinement calculation over all plausible phase sets. Necessarily this procedure is recommended only if less time-consuming procedures such as *MULTAN*/NQEST fail to yield the desired results.

In summary then, experience has shown that the traditional figures of merit often do not discriminate strongly between correct and incorrect phase sets and can even, on occasion, be grossly misleading. NQEST, on the other hand, consistently and accurately discriminates between the two.

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