ΔR is usually much smaller than Δy, a reasonable weighting scheme will be obtained by setting $w_i = [1-(\lambda\zeta_i)^2]^{-3/2}$. w_i increases rapidly if $\lambda\zeta_i$ is not small enough. Practically, however, the tilted axis method is more frequently used for $\lambda\zeta_i \gtrsim 0\cdot3$. Although general treatment for this case is complicated, a rough estimation may be given by considering the simplest case in which (1) the cylindrical film (radius R) is used with its axis normal to both the incident beam and fiber axis and (2) the fiber axis is tilted so that the meridional point of the layer line in question lies on the reflexion sphere. Starting from $\zeta = 2\sin\theta/\lambda$, $2\theta = y/R$, where y is the height of the reflexion (this should be on the meridian of the photograph) and neglecting ΔR again, we get

$$w_i' = [1-(\lambda\zeta/2)^2]^{-1/2}\,.$$

The variation of w_i' is not appreciable within the range, $\zeta\lambda = 0 \sim 1\cdot0$, which is practically important. Non-systematic factors such as the diffuseness of individual reflexions may be more important in deciding w_i's.

Extinction rules for a multistrand coiled coil

The fact that coiled coil structures are very likely to occur as a multistrand rope (Crick, 1953*b*) must be taken into account for assigning (p,q,s,m). Let us consider the simplest case in which each strand is related by a rotational symmetry only. Using the revised formula of Fraser, MacRae & Miller (1964), it is easy to get the extinction rule that only the layer lines with $q-p-d=kN$ $(k=0, \pm1, \ldots)$ appear for the N strand coiled coil structure (Mitsui, 1968). If d is set to 0 as in the previous section, we have $q-p=kN$. Similar considerations for the simple helix have already been made by Klug, Crick & Wyckoff (1958).

The author wishes to express his sincere gratitude to Professor Y. Iitaka of the University of Tokyo, and Professor G. N. Ramachandran of the University of Madras for valuable discussions.

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Application of the Symbolic Addition Procedure in Neutron Diffraction for Non-centrosymmetric Crystals

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(*Received* 30 *December* 1969)

For non-centrosymmetric crystals containing both positive and negative scatterers of neutrons, the symbolic addition procedure has been tested as a means of obtaining phases of neutron reflexions. Test calculations were done for two structures, α-resorcinol and methyl GAG.2HCl.H_2O, which have already been studied by neutron diffraction using conventional methods. It is found that this procedure yields the phase angles with reasonable accuracy. The average error in phases for α-resorcinol was 14° and the F_o Fourier synthesis with these phases revealed the position of all the positive scatterers and three out of six hydrogen atoms. The average error in methyl GAG.2HCl.H_2O was 40° and only 10 positively scattering atoms out of 16 could be clearly seen in the Fourier map. For both the structures an F_o map was found to be superior to an E map. When the contribution of the negative scatterers to the total neutron scattering is less than 25%, it has been shown that the symbolic addition method will apply for crystals containing up to 100 atoms per unit cell.

Introduction

In an earlier paper (Sikka, 1969) the author has shown that in centrosymmetric crystals, the application of the symbolic addition procedure (Karle & Karle, 1966) determines correctly the signs of about 95% of the neutron structure factors (with $|E_{\mathbf{h}}| \geq 1\cdot5$) when the contribution of the negatively scattering atoms to the total neutron scattering is less than 25%. In this paper, we report the application of this procedure for obtaining the phases of the neutron reflexions in non-centrosymmetric crystals. First we show that large values of normalized structure factors (E_h) of a structure are associated with large values of the normalized structure factors (V_h) for the corresponding squared structure, a condition which is necessary for the validity of the symbolic addition procedure and then we describe the application of this procedure for determining the phase angles for two structures already studied by neutron diffraction: α-resorcinol (Jude, 1969) and methyl GAG.2HCl.H_2O* (Hamilton & La Placa, 1968). In the last section the limit on the maximum number of atoms in the unit cell for which this procedure can be applied is determined.

Relation between E_h and V_h

Both α-resorcinol and methyl GAG.2HCl.H_2O belong to the space group $Pna2_1$. The values of σ, the mean relative contribution† of the hydrogen atoms to the total mean neutron scattering in these two structures are 0·21 and 0·16 respectively. The values of $|V_h|$, φ_0 the true phase angle for the normal structure, and φ_V the phase angle for V_h were computed from the published atomic parameters and the $|E_h|$ was evaluated from the observed structure factors $|F_h|$ using the expression

$$|E_h|^2=\frac{|F_h|^2\exp\{2B\sin^2\theta/\lambda^2\}}{\varepsilon\sum\limits_{j=1}^{N}b_j^2} \qquad (1)$$

Here ε is a number which corrects certain reflexions for space group absences and B is the overall temperature factor. Tables 1 and 2 list some values of $|E_h|$, $|V_h|$, φ_0 and φ_V for α-resorcinol and methyl GAG. 2HCl.H_2O respectively. It can be concluded from these that

(*a*) large $|E_h|$ values are associated with large $|V_h|$ values,

(*b*) the phases φ_0 and φ_V agree well with each other. The average deviation $\langle|\varphi_0-\varphi_V|\rangle$ up to $|E_h|\geq 1{\cdot}3$ for α-resorcinol was 21° and for methyl GAG.2HCl.H_2O it was 12° up to $|E_h|\geq 1{\cdot}4$. In Fig. 1(*a*) and (*b*), we have plotted the average deviation $\langle|\varphi_0-\varphi_V|\rangle$ for different ranges of $|E_h|$ values for the two structures. As expected, the deviation is higher for smaller $|E_h|$'s but still reasonably low. It is relevant to mention here that Srinivasan (1961) has shown that a Fourier synthesis with the phases from one structure and amplitudes from another will reproduce the former, though with incorrect peak heights.

Applications

Test calculations were done for both α-resorcinol and methyl GAG.2HCl.H_2O in order to determine the phases by the symbolic addition procedure. The procedure given by Karle & Karle (1966) was followed. '$\sum_2$' listings were generated by a computer program and used to choose reflexions for fixing the origin in the space group $Pna2_1$ in conjunction with the rules given by Hauptman & Karle (1956). The values of phases of these chosen reflexions were taken to be the same as those given by the final structures.* For α-resorcinol, three more reflexions were given symbolic phases. These are listed in Table 3. Using the '$\sum_2$' listings and the relation

$$\varphi_{\mathbf{h}}\simeq\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}} \qquad (2)$$

the phases of 75 more reflexions in α-resorcinol were determined in terms of 0, π, *a*, *b*, and *c*. It became apparent during the analysis that the symbol $a=0$ and $c=\pi$. For methyl GAG.2HCl.H_2O, starting from three reflexions given in Table 3, the phases of another 49 reflexions were determined in terms of 0, π and

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* Methylglyoxal bisguanylhydrazine dihydrochloride monohydrate, $C_5N_8H_{12}.2HCl.H_2O$.

† $\sigma=\sum_{j=1}^{Q}b_j{}^2/\sum_{j=1}^{N}b_j{}^2$ where b_j is the neutron scattering factor for the jth atom, Q is the number of hydrogen atoms and N is the total number of atoms in the unit cell.

* As in Sikka (1969), this facilitates the comparison of the phases determined by this procedure with those from the final structures.

Table 1. *Comparison of* E_h *and* V_h *for α-resorcinol*

All $|E_h|$'s $\geq 2{\cdot}0$.

h	k	l	$\lvert E_h\rvert$	$\lvert V_h\rvert$	φ_0	φ_V
3	9	0	3·32	3·03	0°	0°
4	7	0	3·25	2·51	0	0
6	6	0	3·10	3·02	0	0
11	5	0	2·80	1·40	0	0
9	2	2	2·62	1·55	174	171
6	2	6	2·58	3·11	21	25
6	10	1	2·44	1·93	315	298
10	2	1	2·44	1·51	371	342
9	3	1	2·34	1·74	360	359
8	4	1	2·26	1·63	186	173
10	2	0	2·26	1·62	180	180
4	6	3	2·24	1·30	69	79
9	1	2	2·22	1·00	317°	261°
4	5	4	2·19	1·89	273	292
5	3	4	2·18	1·46	233	286
11	4	1	2·16	1·78	190	212
5	3	4	2·15	1·46	369	353
6	6	2	2·07	1·76	239	151
6	5	1	2·06	1·85	180	195
4	3	4	2·06	1·15	150	106
8	2	2	2·05	1·86	252	240
5	9	3	2·04	1·81	204	184
1	4	4	2·02	1·62	75	97
4	7	2	2·01	0·93	181	250

Table 2. *Comparison of* E_h *and* V_h *for methyl* GAG.2HCl.H$_2$O

All $|E_h|$'s ≥ 2·0.

h	k	l	$\|E_h\|$	$\|V_h\|$	φ_0	φ_V	h	k	l	E_h	V_h	φ_0	φ_V
2	2	6	4·06	3·96	68°	70°	10	4	4	2·24	1·34	275°	265°
14	1	3	3·90	3·69	183	192	5	10	2	2·19	2·81	323	316
1	9	3	3·56	3·58	164	156	2	5	6	2·18	2·45	192	186
14	3	3	3·54	3·61	349	342	2	4	6	2·17	1·53	243	236
7	5	5	3·41	3·15	296	288	1	13	0	2·17	2·00	180	180
12	4	3	3·22	3·07	159	163	3	4	4	2·17	2·16	12	17
5	11	2	2·94	3·54	313	317	13	9	0	2·16	1·89	180	180
3	11	0	2·94	1·72	0	0	7	11	1	2·16	1·72	161	184
6	7	5	2·92	4·49	6	7	1	13	3	2·16	1·67	168	163
5	8	2	2·89	1·88	222	214	13	8	0	2·15	2·92	180	180
10	2	4	2·87	2·95	83	89	8	10	5	2·15	2·29	317	300
12	2	3	2·78	3·33	360	357	9	9	1	2·13	1·94	142	136
7	11	5	2·67	2·96	142	134	1	8	3	2·13	1·50	216	192
3	8	4	2·63	1·81	39	7	4	7	2	2·13	1·97	23	23
3	5	4	2·51	1·97	154	145	14	1	0	2·12	2·56	0	0
10	10	0	2·48	2·17	180	180	6	2	5	2·11	2·57	85	86
3	10	4	2·48	3·07	226	231	10	9	1	2·09	1·41	261	269
10	5	4	2·45	2·28	174	179	3	11	4	2·08	2·23	320	329
2	6	6	2·46	2·11	85	82	2	6	7	2·08	2·08	248	232
2	9	3	2·45	2·56	224	223	12	7	0	2·07	2·22	0	0
1	7	3	2·44	1·66	328	331	6	11	1	2·06	1·34	92	114
6	5	5	2·44	1·19	204	211	6	12	1	2·06	2·22	289	307
4	8	5	2·38	2·33	97	103	7	13	1	2·06	3·02	31	22
6	3	5	2·37	2·45	344	350	10	4	3	2·06	1·46	292	296
2	4	4	2·35	1·74	81	86	4	11	0	2·04	1·91	180	180
8	3	2	2·32	2·21	291	287	5	2	5	2·03	0·88	118	25
13	5	0	2·31	2·61	180	180	4	11	1	2·03	1·23	296	281
14	5	3	2·31	2·04	191	184	2	11	1	2·03	1·01	64	40
1	11	3	2·31	3·01	320	338	7	7	5	2·02	1·99	112	106
13	3	0	2·30	2·14	0	0	6	4	5	2·02	1·23	265	263
4	1	1	2·28	3·07	270	263	3	8	3	2·02	1·84	323	316
10	3	4	2·27	2·13	359	366	2	0	1	2·01	1·69	227	203
14	4	3	2·27	2·22	279	286	1	1	5	2·00	0·98	201	206
11	7	0	2·26	1·42	180	180	1	1	5	2·00	0·98	201	206

$\pm\pi/2$.* The next step for both the structures was the refinement of the phases already determined and determination of additional phases by the use of the tangent formula (Karle & Hauptman, 1956),

$$\tan \varphi_{\mathbf{h}} = \frac{\sum_{\mathbf{k}} |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \sin (\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})}{\sum_{\mathbf{k}} |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \cos (\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})} \cdot \quad (3)$$

This part of the calculations was programmed by the author for the CDC 3600 computer. In this program the rapid cycling procedure, in which the freshly determined phase is used for the determination of the subsequent phases (Weinzierl, Eisenberg & Dickerson, 1969), was employed. If for given **h**, the number of interactions was less than 4 and also if normalized $|E_{\mathbf{h}}|_c$.† was less than 0·4 $|E_{\mathbf{h}}|$, it was omitted from the basic deck of reflexions.

In α-resorcinol, the unknown symbol b was assigned values of $+\pi/4$, $+\pi/2$ and $+3\pi/4$‡ and each of the three sets of numerical phases was refined and an

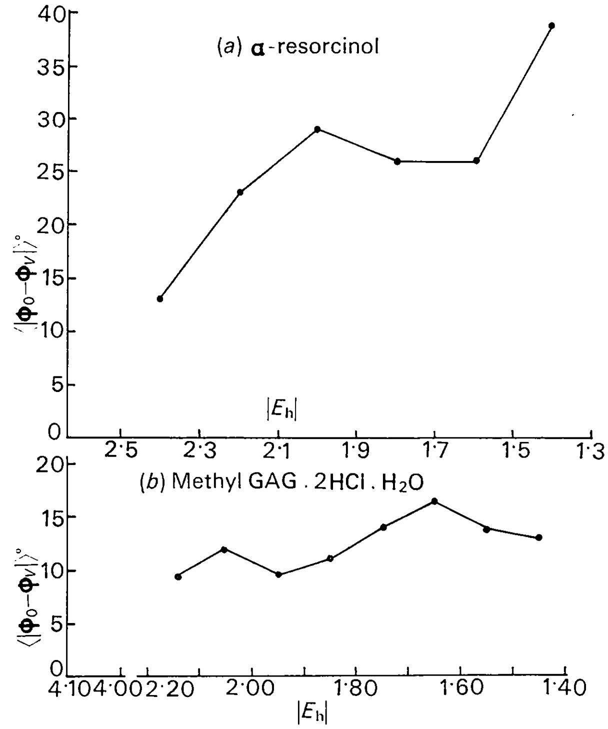

Fig. 1. The average deviation $\langle|\varphi_0-\varphi_V|\rangle$ against E values (*a*) α-resorcinol (*b*) methyl GAG.2HCl.H$_2$O.

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* For those reflexions in methyl GAG.2HCl.H$_2$O, when equation (2) gives values 0 and π using different **k** and **h**−**k** the average was taken.

† $|E_{\mathbf{h}}|_c = |\sum_{\mathbf{k}} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \exp \{i(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})\}|$.

‡ The positive sign fixes the enantiomorph.

additional 42 phases with $|E_{\mathbf{h}}| \geq 1{\cdot}3$ were determined using the tangent formula. At the end of last iteration for each set, a figure of merit

$$C = \sum_{h} \alpha_{\mathbf{h}}$$

was evaluated, where

$$\alpha_{\mathbf{h}} = \frac{2\beta_3}{\beta_2^{3/2}} |E_{\mathbf{h}}| \, |E_{\mathbf{h}}|_c \tag{4}$$

and

$$\beta_n = \sum_{j=1}^{N} b_j^n .$$

Table 3. *Phase assignments for fixing the origin and for implementing equation* (2)

α-resorcinol				Methyl GAG.2HCl.H$_2$O			
h	k	l	φ	h	k	l	φ
4	7	0	0°	13	6	0	0°
3	9	0	0	13	7	0	0
9	3	1	0	4	2	1	0
6	6	0	a				
1	4	4	b				
6	5	1	c				

It turned out that the set with $b = +\pi/2$ had the highest value of C and the corresponding phases were found to be closest to the true phases. For methyl GAG.2HCl.H$_2$O starting from the phases of 49 reflexions determined using equation (2), the phases of 127 ($|E_{\mathbf{h}}| \geq 1{\cdot}4$) additional reflexions were calculated and refined with the use of the tangent formula.

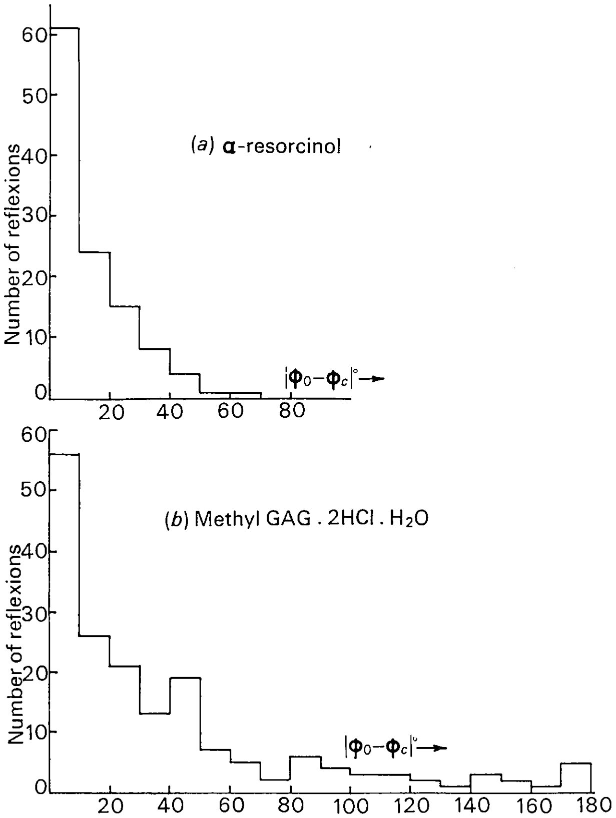

Fig. 2. Frequency distribution of the error $|\varphi_0 - \varphi_c|$ (*a*) α-resorcinol (*b*) methyl GAG.2HCl.H$_2$O.

At the end of the refinements in both the structures the phases determined by the tangent formula (φ_c) and the true phase (φ_0) were compared. Fig. 2 (*a*) and (*b*) displays the frequency distributions of $|\varphi_0 - \varphi_c|$. It can be readily seen that the agreement between φ_0 and φ_c is excellent for α-resorcinol and satisfactory for methyl GAG.2HCl.H$_2$O. For α-resorcinol none of the *hk*0 reflexions (phase 0 or π) had the wrong phase but there were five such cases in methyl GAG.2HCl.H$_2$O. The average values $\langle|\varphi_0 - \varphi_c|\rangle$, $\langle|\varphi_V - \varphi_c|\rangle$ and $\langle|\varphi_0 - \varphi_V|\rangle$ for the two structures are compared in Table 4. It is interesting to note that $\langle|\varphi_0 - \varphi_c|\rangle$ is less than $\langle|\varphi_V - \varphi_c|\rangle$ for the two cases. As the symbolic addition procedure has its basis in the similarity of the structure to the squared structure, one might have expected the reverse to be the case.*

Table 4. *Comparison of* $\langle|\varphi_0 - \varphi_c|\rangle$ *with* $\langle|\varphi_V - \varphi_c|\rangle$ *and* $\langle|\varphi_0 - \varphi_V|\rangle$

	α-Resorcinol	Methyl GAG 2HCl.H$_2$O
$\langle\lvert\varphi_0 - \varphi_c\rvert\rangle$	14°	40°
$\langle\lvert\varphi_V - \varphi_c\rvert\rangle$	24	43
$\langle\lvert\varphi_0 - \varphi_V\rvert\rangle$	21	40

As the errors for methyl GAG.2HCl.H$_2$O are large, an E map was computed to see whether the structure could be obtained with these calculated phases. The map proved to be extremely complicated and could not be interpreted. Next an F_o Fourier map with these phases was calculated. This map contained peaks for all positive scatterers but out of 16 of them, 10 stood out above the spurious peaks. There was negative density at some of the hydrogen atoms positions but these could not have been located without use of chemical considerations. To make a comparison with α-resorcinol for which the phases are more accurately determined, both E and F_o maps were computed. Both the maps contained all the positive scatterers but in the F_o map there were additional sizable negative peaks corresponding to three out of the six hydrogen atoms in the asymmetric unit – thus again confirming that in neutron diffraction, an F_o map with the calculated phases will be more useful.

Maximum number of atoms in the unit cell

Having shown in Sikka (1969) and above that the symbolic addition procedure can be used to determine the phases of neutron reflexions, in this section we have determined the maximum number of atoms in the unit cell for which this procedure can be applied.

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* This observation was made by the referee.

It is well known that during initial stages of the application of this procedure, only one combination of **k** and **h**−**k** may be available for a given reflexion **h** and in order for a single term to indicate reliably the phase of a new reflexion, Karle & Karle (1966), have recommended the use of probability formulae for centrosymmetric and non-centrosymmetric crystals. The probability formula for the centrosymmetric case, which gives the probability of the sign of $E_{\mathbf{h}}$ being the same as that of $E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}$ (using only one **k**) is

$$P(\mathbf{h})=\tfrac{1}{2}+\tfrac{1}{2}\tanh\left(\beta_3\beta_2^{-3/2}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|\right). \qquad (5)$$

For non-centrosymmetric crystals a possible measure of the correctness of the phase determined using the relation (2), is given in terms of a measure of variance defined by equation (3·33) of Karle & Karle (1966), which in turn depends upon the quantity $\alpha_{\mathbf{h}}$[see equation (4)] which for a single term is

$$\alpha_{\mathbf{h}}=\frac{2\beta_3}{\beta_2^{3/2}}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|. \qquad (6)$$

Karle & Karle (1966) have set the limits as $P(\mathbf{h})\simeq 0{\cdot}97$ and variance $\simeq 0{\cdot}5$ square radians (or $\alpha_{\mathbf{h}}=3$) for the acceptance of any phase indication.

In order to determine the value of $N_{\max}$, we will express $P(\mathbf{h})$ and $\alpha_{\mathbf{h}}$ in terms of N for a C_PH_Q molecule.* Using $b_C=0{\cdot}66$ and $b_H=-0{\cdot}374\times10^{-12}$ cm,

$$\frac{\beta_3}{\beta_2^{3/2}}=\frac{0{\cdot}288P-0{\cdot}052Q}{(0{\cdot}436P+0{\cdot}14Q)^{3/2}}$$
$$=\frac{(1+x)^{1/2}(0{\cdot}288x-0{\cdot}052)}{N^{1/2}(0{\cdot}436x+0{\cdot}14)^{3/2}} \qquad (7)$$

where $x=P/Q$. Setting $P(\mathbf{h})=0{\cdot}97$ we can easily show from (5) and (7) that

$$N=\left[\frac{(1+x)(0{\cdot}288\mathrm{x}-0{\cdot}052)^2}{3{\cdot}3(0{\cdot}436x+0{\cdot}14)^3}\right]\times|E_{\mathbf{h}}\mathrm{E}_{\mathbf{h}}E_{\mathbf{h}-\mathbf{k}}|^2. \qquad (8)$$

The same expression can be derived for the non-centrosymmetric case from (6) by taking $\alpha_{\mathbf{h}}=3{\cdot}5$.† Now, in early stages one usually deals with three E's the magnitude of whose product is about 20 (Germain & Woolfson, 1968). Taking $|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}|=20$ we have plotted N as a function of x (or σ) in Fig. 3. This shows that for each value of x, N reaches a maximum value above which the basic phase relations will introduce enough errors to make the initial steps in the symbolic addition procedure invalid. The value of $N_{\max}$ seems to be around 100. However, as Germain & Woolfson (1968) have pointed out if one can tolerate one error in the first 10 steps or so this number goes up by a factor of almost 2.

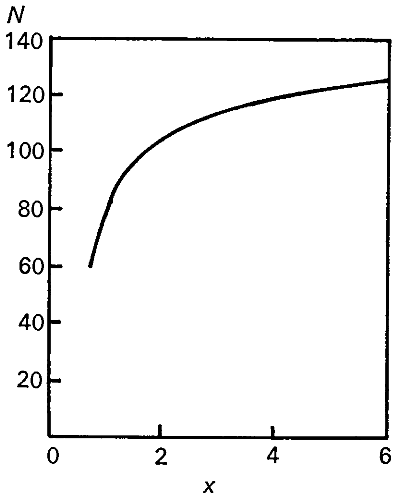

Fig. 3. The plot of N, the maximum number of atoms in the unit cell against x $(=P/Q)$.

The author expresses his thanks to Dr R. Chidambaram for many useful suggestions. Thanks are also due to Mr R. Jude for communicating results on α-resorcinol prior to publication.

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* From neutron scattering length considerations, we can approximately represent any crystal containing positive and negative scatterers by the formula C_PH_Q where P and Q are the number of carbon and hydrogen atoms respectively.

† For $\alpha_h=3{\cdot}5$, the variance calculates to be 0·4 square radians which is close to the limit set by Karle & Karle (1966).