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Chlorooxoishwarone and 2,6-Dimethoxybenzoic Acid

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Abstract. The simple direct method for solving projections of centrosymmetric crystals [Swaminathan & Lessinger, *Cryst.* (1973), A29, 717–720; A30, 458] has been found quite effective for the centrosymmetric projections of two non-centrosymmetric crystals: (i) the unique axis projection of chlorooxoishwarone ($P2_1$) and (ii) the *c*-axis projection of 2,6-dimethoxybenzoic acid ($P2_12_12_1$).

Introduction. Orthoveratric acid (space group $P2_1/c$), (±)-2,4,6-trimethylpimelic acid ($P2_1/c$), morpholinium nitrate ($P2_1/c$) and 3,4-dimethoxybenzoic acid ($P\bar{1}$) were recently solved in their short axis projections by a set of very few optimally chosen reflexions (Swaminathan & Lessinger, 1973, 1974; Swaminathan, Vimala & Lessinger, 1975). This simple method is also effective for the centrosymmetric projections of the following two non-centrosymmetric crystal structures.

Chlorooxoishwarone, $C_{15}H_{20}O_2Cl$. This crystallizes in the space group $P2_1$ with $a=9{\cdot}15$, $b=6{\cdot}90$, $c=11{\cdot}86$ Å, $\beta=114{\cdot}4°$ and $Z=2$. Among 39 $E(h0)\geq 1{\cdot}40$ (Table 1) are 61 $\sum_2$ relations (Table 2) with $P_+\geq 0{\cdot}750$. A phase indication is accepted only if it is corroborated by at least another that is consistent with it. A lone contradiction is overlooked if it is overweighed by several opposite but among themselves consistent indications. Phase indications with more than one contradiction or those of alternative possibilities are to be avoided as suspect. Coincidences (Table 3) resulting from the $\sum_2$ relations give on feedback the sign of the reflexion 602, code No. 50, to be positive. The three consistent indications in Table 3 are further reinforced by a $\sum_1$ indication, $S(47)\,S(47)\,S(50)=+1$.

Table 1. $E(h0)\geq 1{\cdot}40$ *in chlorooxoishwarone*

Code number	*h*	*k*	*l*	*E*	Code number	*h*	*k*	*l*	*E*
3	1	0	−11	1·72	30	0	0	−3	1·51
6	5	0	−11	1·78	36	7	0	−3	1·51
7	6	0	−11	2·18	37	8	0	−3	1·78
8	1	0	−10	1·72	40	1	0	−2	1·43
9	8	0	−10	1·47	43	8	0	−1	2·01
10	9	0	−10	1·53	44	5	0	0	1·53
11	1	0	−9	2·00	47	3	0	1	1·40
15	2	0	−8	2·01	48	6	0	1	1·83
16	4	0	−8	1·74	50	6	0	2	2·29
17	7	0	−8	3·02	51	7	0	2	1·44
18	8	0	−8	1·60	53	2	0	3	1·51
19	2	0	−7	1·40	56	6	0	3	1·64
20	5	0	−7	1·47	58	6	0	4	2·17
21	6	0	−7	1·47	60	1	0	5	1·95
22	7	0	−7	1·69	61	5	0	5	1·68
23	10	0	−7	1·72	65	7	0	6	1·46
25	6	0	−6	1·70	67	1	0	8	1·45
26	7	0	−6	2·35	68	5	0	8	1·63
27	8	0	−6	1·59	73	2	0	10	1·53
28	6	0	−5	1·58					

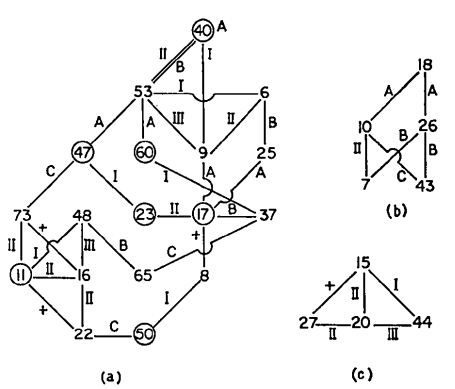

Fig. 1. Graph showing the interdependence of the $\sum_2$ relations for chlorooxoishwarone. Code numbers in circles are for the starting set.

The origin in projection is defined by reflexions $70\bar{8}$, code No. 17, and 301, code No. 47, through symbols I and II. Reflexion $10,0,\bar{7}$, code No. 23, is related to them by a $\sum_2$ relation and pending corroboration is given the symbol III. Three reflexions, code Nos. 40, 60 and 11, are assigned the symbols *A*, *B* and *C* respectively. The interdependence of the $\sum_2$ relations is best seen graphically (Fig. 1). In the graph, each line connecting the code numbers of a pair of reflexions is marked with the symbol of a third reflexion belonging to the starting set and with which the first two form a $\sum_2$ relation. If along any closed path in the graph the symbols occur in pairs, the $\sum_2$

Table 2. $\sum_2$ *Relations in chlorooxoishwarone*

Serial number	Code numbers of reflexions			Serial number	Code numbers of reflexions		
1	3	7	44	32	15	36	61
2	3	17	56	33	16	22	47
3	3	22	58	34	16	23	48
4	3	25	61	35	16	29	53
5	6	9	47	36	16	50	73
6	6	17	53	37	17	23	47
7	6	25	60	38	17	25	40
8	7	10	47	39	17	37	60
9	7	18	53	40	18	26	40
10	7	26	60	41	19	22	44
11	7	36	67	42	19	27	48
12	7	43	73	43	19	37	58
13	8	17	50	44	19	47	67
14	8	18	51	45	20	23	44
15	8	22	56	46	20	27	47
16	8	26	58	47	20	48	67
17	8	29	61	48	22	29	40
18	9	23	53	49	25	37	53
19	9	17	40	50	25	51	67
20	10	11	43	51	26	30	36
21	10	18	40	52	26	43	60
22	10	19	36	53	27	30	37
23	11	16	47	54	30	48	58
24	11	17	48	55	30	60	67
25	11	22	50	56	30	61	68
26	11	26	56	57	40	47	53
27	11	37	65	58	40	51	58
28	11	47	73	59	40	53	60
29	15	17	44	60	40	56	61
30	15	20	47	61	48	60	65
31	15	27	50				

Table 3. *Coincidences and phase indications from the* $\sum_2$ *relations in chlorooxoishwarone*

Code numbers (1)	(2)	(3)	Coincidence relationships	Phases obtained from coincidences		
11	16	47				
11	47	73	16=73	16	50	73 → 50+
11	16	47				
16	22	47	11=22	11	22	50 → 50+
9	17	40				
17	25	40	9=25			
10	18	40				
18	26	40	10=26			
15	20	47	15=23			
20	23	47	15=27	15	27	50 → 50+
20	27	47	23=27			
7	26	60				
26	43	60	7=43	7	43	73 → 73+
19	22	40				
22	29	40	19=29			
40	47	53				
40	53	60	47=60			

relations involved are consistent with each other; if they do not occur in pairs, relations between the symbols are obtained. There are at least six indications that III=I×II. There are indications that *B* is II (which can be chosen arbitrarily) and also that it is positive. From the graph in Fig. 1(*a*), 18 phases are obtained through the three symbols *A*, *B* and *C*. The origin-defining symbols, I and II, are both assumed negative. Of eight maps that were made the best was

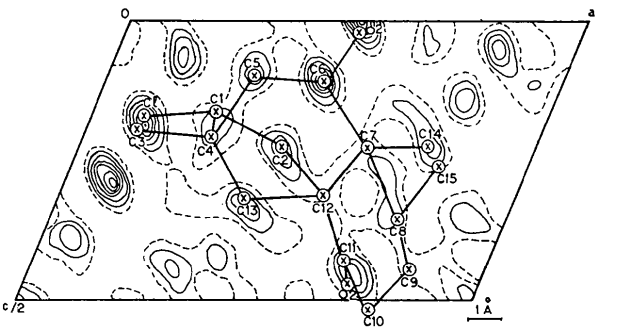

Fig. 2. (010) electron density projection of chlorooxoishwarone. Terms used: *A*−; *B*+; *C*−.

h	*k*	*l*	*E*	*h*	*k*	*l*	*E*
5	0	−11	−1·78	1	0	−2	−1·43
1	0	−9	−2·00	6	0	2	+2·29
7	0	−7	−1·63	7	0	6	+1·46
8	0	−3	−1·78	8	0	−10	+1·47
6	0	1	+1·83	7	0	−8	−3·02
1	0	5	+1·95	6	0	−6	−1·70
1	0	−10	−1·72	3	0	1	−1·40
4	0	−8	+1·74	2	0	3	+1·51
10	0	−7	+1·72	2	0	10	+1·53

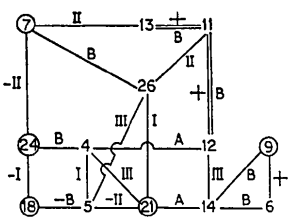

Fig. 3. Interdependence of $\sum_2$ relations in 2,6-dimethoxybenzoic acid. Reflexions of the starting set are circled.

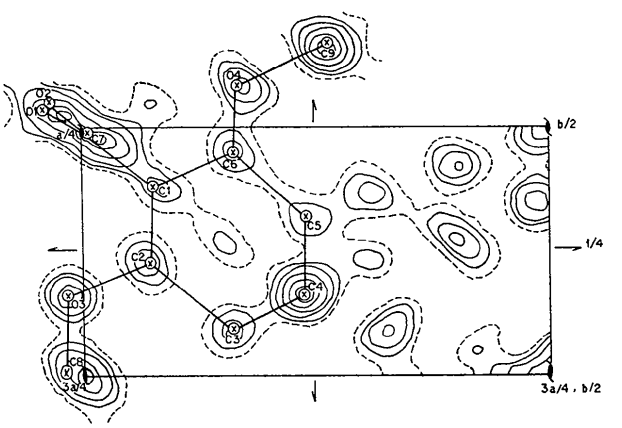

Fig. 4. (001) electron density projection of 2,6-dimethoxybenzoic acid. Terms used: *A*+; *B*+. (Phases correspond to origin shifted by **a**/4.)

h	*k*	*l*	*E*	*h*	*k*	*l*	*E*
0	4	0	+1·64	3	3	0	−1·64
2	2	0	+1·85	5	8	0	−2·42
3	1	0	+1·79	8	7	0	−1·35
4	2	0	+1·61	1	12	0	+1·71
7	5	0	−1·67	2	6	0	+2·31
1	9	0	−2·01	3	5	0	+1·64
2	3	0	−1·68	6	4	0	+2·30

easily chosen, and shows (Fig. 2) the main features of the molecule. In this case a model was fitted to the map. Even if a complete model is not available for lack of the chemical structure, fragments of known configuration may often be inferred from spectrochemical evidence, and the fragments may be recognized in the map or fitted to it. The structure analysis and refinement in three dimensions are complete with $R=0{\cdot}120$ using individual isotropic temperature factors for the eighteen (non-hydrogen) atoms.

2,6-Dimethoxybenzoic acid. In contrast to two other isomers [orthoveratric acid and 3,4-dimethoxybenzoic acid (Swaminathan & Lessinger, 1973, 1974; Swaminathan, Vimala & Lessinger, 1975)], 2,6-dimethoxybenzoic acid crystallizes in the non-centrosymmetric space group $P2_12_12_1$ with $a=7{\cdot}21$, $b=13{\cdot}95$, $c=8{\cdot}98$ Å and $Z=4$. The crystals grow as needles along the c axis. $E(hk0)$ were obtained from a Wilson plot for only the zonal reflexions. There are 26 reflexions (Table 4) with $E(hk0)\geq 1{\cdot}35$, among them 56 $\sum_2$ relations (Table 5) with $P_+\geq 0{\cdot}750$. Coincidences resulting from the $\sum_2$ relations show contradictions involving code numbers 8, 10, 15, 20, 22 and 25. These reflexions were left out of consideration, along with the $\sum_2$ relations in which they occur. 20 reflexions, with 27 $\sum_2$ relations among them, remain. The accepted coincidences consistently show that reflexion 040, code No. 1, is positive. (There are no contrary indications from the rejected coincidences that it is otherwise.) Three $\sum_1$ relations, $S(1)S(6)S(6)=+1$, $S(1)S(14)S(14)=+1$ and $S(1)S(20)S(20)=+1$, support this phase.

The origin in projection is defined by reflexions 230, code No. 7, and 508, code No. 18, through symbols I and II which are later both assumed to be negative. Code No. 24 is related to them and is assigned symbol

Table 4. $E(hk0)\geq 1{\cdot}35$ *in 2,6-dimethoxybenzoic acid*

Code number	h	k	l	E	Code number	h	k	l	E
1	0	4	0	1·64	14	4	2	0	1·61
2	0	10	0	1·36	15	4	3	0	1·48
3	0	12	0	2·05	16	4	5	0	1·73
4	1	9	0	2·01	17	4	12	0	1·52
5	1	12	0	1·71	18	5	8	0	2·42
6	2	2	0	1·85	19	5	9	0	1·48
7	2	3	0	1·68	20	6	2	0	1·52
8	2	5	0	1·51	21	6	4	0	2·30
9	2	6	0	2·31	22	6	8	0	1·83
10	2	11	0	1·70	23	6	9	0	1·72
11	3	1	0	1·79	24	7	5	0	1·67
12	3	3	0	1·64	25	8	3	0	1·35
13	3	5	0	1·46	26	8	7	0	1·35

Table 5. $\sum_2$ *Relations in 2,6-dimethoxybenzoic acid*

Serial number	Code numbers of reflexions			Serial number	Code numbers of reflexions		
1	1	6	9	29	7	21	26
2	1	11	13	30	8	12	18
3	1	11	12	31	−8	15	20
4	1	21	22	32	8	15	22
5	1	25	26	33	8	20	25
6	−2	14	17	34	8	20	26
7	2	20	22	35	9	10	16
8	−2	25	26	36	9	12	19
9	3	21	22	37	9	14	21
10	4	5	7	38	9	14	22
11	4	9	12	39	9	15	23
12	4	12	17	40	9	23	25
13	4	21	24	41	10	12	18
14	−5	10	11	42	10	14	23
15	−5	15	19	43	−10	15	22
16	−5	18	21	44	10	21	26
17	5	24	26	45	10	22	25
18	6	7	16	46	11	12	20
19	6	8	15	47	11	12	21
20	6	14	21	48	11	13	21
21	6	23	26	49	11	18	26
22	−7	8	14	50	12	13	20
23	−7	9	15	51	12	13	22
24	7	13	18	52	12	14	24
25	−7	16	20	53	13	18	25
26	7	16	22	54	14	16	25
27	−7	17	23	55	14	16	26
28	−7	18	24	56	−16	17	26

Table 6. *Coincidences and phases from* $\sum_2$ *relations in 2,6-dimethoxybenzoic acid*

$\sum_2$ Relations (serial numbers)	Coincidence reflexions	Phase indication	from	$\sum_2$ Relation (see Table 5)
2 & 3	12=13	20+		(50)
2 & 48	1=21	22+		(4)
3 & 46	1=20			
3 & 47	1=21	22+		(4)
4 & 9	1= 3			
5 & 8	−1= 2			
11 & 12	9=17			
11 & 36	4=19			
18 & 25	6=22			
18 & 26	−6=20			
19 & 31	−6=20			
19 & 32	6=22			
20 & 37	6= 9	1+		(1)
23 & 39	−7=23	17+		(27)
24 & 53	7=25			
24 & 28	−13=24			
25 & 26	−20=22*	2−*		(7)
29 & 44	7=10			
30 & 41	8=10*			
31 & 32	−20=22*	2−*		(7)
31 & 33	−15=25*			
31 & 34	−15=26			
32 & 43	−8=10*			
33 & 34	25=26	1+; 2	−*	(5); (8)
37 & 38	21=22	1+		(4)
39 & 40	15=25*			
43 & 45	−15=25*			
46 & 47	20=21			
46 & 50	11=13	21+		(48)
47 & 48	12=13	20+		(50)
50 & 51	20=22*	2+*		(7)
54 & 55	25=26	1+; 2	−*	(5); (8)
55 & 56	−14=17	2−*		

* Contrary coincidences or indications are also obtained elsewhere in the table.

III. From the reflexions with the largest values for the product of the normalized structure factor with the number of $\sum_2$ relations for a reflexion, code Nos. 9 and 21 are respectively assigned symbols *A* and *B*. The interdependence of the $\sum_2$ relations is shown by the graph in Fig. 3, verifying many times over that III $= -$ I $\times$ II. Fourteen phases are obtained through the two symbols *A* and *B*. The best of four possible maps clearly showed the molecule in projection (Fig. 4). The projection refined easily to $R=0{\cdot}150$ with individual isotropic temperature factors on the thirteen (non-hydrogen) atoms.

Both structures will be published in greater detail.

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(*R*)-7-Ethyl-1,4,5,6,7,8,9,10-octahydro-2*H*-3,7-methanoazacycloundecan[5,4-*b*]indole, (Quebrachamine)

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Abstract. $C_{19}H_{26}N_2$, monoclinic, $P2_1$; $a=15{\cdot}01$ (3), $b=7{\cdot}10$ (2), $c=8{\cdot}25$ (2) Å, $\beta=105{\cdot}8$ (3)°, $V=846{\cdot}2$ Å^3; $Z=2$, $D_m=1{\cdot}114$, $D_x=1{\cdot}108$ g cm^{-3}; μ(Cu $K\alpha$)$=4{\cdot}9$ cm^{-1}, λ(Cu $K\alpha$)$=1{\cdot}5418$ Å, filtered with Ni. The conformation of the eleven-membered ring and the geometry around its N atom are discussed and compared with those of a related alkaloid (cleavamine). A correlation between the slow rate of methylation observed, and the expected positions of the lone pair of N electrons according to the structure obtained, is made.

Introduction. The crude material, extracted from *Aspidosperma* (*Quebracho blanco*), was recrystallized from a saturated methanol solution. On standing, well-developed colourless needles were obtained. They were mounted with the needle axis (*b*) parallel to the goniometer spindle. Preliminary precession photographs taken with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å) gave the cell dimensions with an accuracy of about 3/1000.

From systematic extinctions ($0k0$: $k=2n+1$) as well as from the well known optical activity of the compound, $P2_1$ was inferred to be the correct space group.

Integrated intensity data were gathered by photographic methods. Levels $h0l$ to $h5l$ were taken with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) using equi-inclination Weissenberg techniques, while levels $0kl$ and $hk0$ were recorded with a precession camera, and Mo $K\alpha$ radiation. A total of 1244 reflexions (about 65% of the Cu sphere) were measured with a manual densitometer. Of these, 128 were considered unobserved and given $F_o=0$.

After the usual geometrical corrections were performed, data were cross correlated by the least-squares method of Hamilton, Rollett & Sparks (1965). Absorption corrections were neglected (maximum $\mu R=0{\cdot}5$). A Wilson plot was used to reduce structure amplitudes to an absolute scale and normalized structure factors $|E|$ were calculated.

To solve the phase problem, the multi-solution method described by Germain, Main & Woolfson (1970) and implemented in their program *MULTAN*, was attempted. The origin-defining phases were chosen to be 203, 11,0,$\bar{3}$ and 615 and assigned the value 0. The starting set was completed with three well connected phases: $a=10,4,2$, $b=21\bar{2}$ and $c=13,0,0$.

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