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Rubrofusarin: A Structure Determination Using Direct Phase Calculation

By George H. Stout

Department of Chemistry, University of Washington, Seattle 5, Washington, U.S.A.

and Lyle H. Jensen

Department of Anatomy, University of Washington, Seattle 5, Washington, U.S.A.

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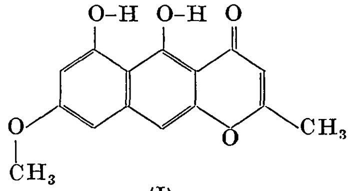
The molecular and crystal structure of the mold metabolite rubrofusarin, $C_{15}H_{12}O_5$, has been determined by application of the relationship $S_{hkl}S_{h'k'l'} \sim S_{h+h',\,k+k',\,l+l'}$ followed by conventional refinement. One hundred twenty-three of the 132 strongest reflections were assigned phases by repeated application of the relationship and eighteen of the twenty atoms were found on Fourier syntheses computed using these. The final two atoms were located during the refinement.

Subsequent examination showed that, using the requirement that a reflection be indicated at least twice as strongly toward one sign rather than the alternative, phases could be determined for 198 of the 221 strongest reflections. Comparison with signs calculated on the final structure showed that all of these choices were correct.

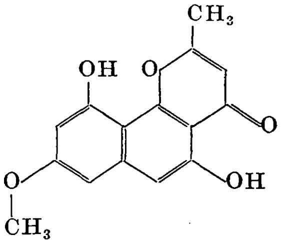
Introduction

Rubrofusarin is a red crystalline substance which was first isolated from the mycelium of strains of the mold *Fusarium culmorum* by Ashley, Hobbs & Raistrick (1937). It was assigned the formula $C_{15}H_{12}O_5$ and a number of derivatives were prepared, but no structure was proposed. Later Mull & Nord (1944) suggested two possible structures on spectral grounds that were subsequently considered by Lund, Robertson & Whalley (1953) to be insufficient.

Our chemical investigations (Stout, Dreyer & Jensen, 1961) contradicted the suggestions of earlier workers and led us to propose that rubrofusarin should have one of the structures (I) or (II).



(I)



(II)

The evidence which we had was strongly suggestive but not conclusive and certainly did not distinguish between these two chemically very similar structures. Due to the small amount of material available, we felt that it would be difficult to decide between them chemically and so turned to X-ray methods.

Experimental

Rubrofusarin crystallizes from chloroform as well formed monoclinic needles elongated along *c*. From rotation and Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) on a crystal rotated about the needle axis, the unit cell parameters were found to be

$$a = 7{\cdot}52,\ b = 23{\cdot}14,\ c = 7{\cdot}20\ \text{Å};\ \beta = 98{\cdot}2^\circ.$$

Systematic absences were $h0l$ for l odd, $0k0$ for k odd and the space group was therefore $P2_1/c$. The density as determined by flotation in carbon tetrachloride-hexane mixtures was 1·473 g.cm.$^{-3}$ and led to four molecular weight (275·3) units per unit cell. Molecular weight calculated for $C_{15}H_{12}O_5$ is 272·7.

Three-dimensional integrated equi-inclination Weissenberg data were collected on a Nonius camera set to integrate in one direction only. The resulting unidimensionally integrated reflections were scanned photometrically at right angles to the direction of the first integration, and the area under the recorder tracing, as determined by a planimeter, was taken as proportional to the integrated intensity. Since the purpose of this investigation was to determine the molecular structure of rubrofusarin rather than to study exhaustively its crystal structure, the diffraction data were collected in groups of varying completeness. One hundred twenty-one $hk0$ and 164 $0kl$ reflections (including those unobserved) were collected. Three-dimensional data were compiled in a short deck of 358 of the strongest reflections sampled throughout the Cu $K\alpha$ sphere, and a long deck of 1835 reflection (63·5% of 2890 possible) consisting of complete data for $l=1, 3, 4, 5, 6$ and partial data for $l=0$ and 2.

Structure determination

Because of uncertainty about the structure of rubrofusarin, it was felt that a direct solution would be most desirable if it could be achieved. Sayre (1952), Cochran (1952) and Zachariasen (1952) have all put forth arguments leading to the conclusion that, for reflections of suitably large unitary structure factors (U) in centrosymmetric space groups,

$$U_{hkl}U_{h'k'l'}U_{h+h',\ k+k',\ l+l'} = \text{a positive quantity}$$

or

$$S_{hkl}S_{h'k'l'} = S_{h+h',\ k+k',\ l+l'},$$

where S_{hkl} is the sign of U_{hkl}. For convenience, we have referred to these as 'phase-determining equations' (PDE). The diffraction data indicated the presence of a subcell, presumably corresponding to the repetitious nature of the ring system. This encouraged us to attempt a direct determination of enough phases to obtain recognizable electron density maps.

As pointed out by Harker & Kasper (1948) and discussed at some length by Karle & Hauptman (1953) and by Lonsdale & Grenville-Wells (1954), with certain restrictions two signs may be chosen arbitrarily for zonal and three for general data. By choosing three appropriate signs and without applying inequalities, we hoped to determine signs in a way similar to that described by Zachariasen (1952).

The first attempt was carried through on $0kl$ data by hand adjustments of the signs of the strongest reflections so as to maximize the number of agreements in the PDE. This led to 34 reflections either determined absolutely or in terms of S_{022}. Fourier projections were calculated for S_{022} both (+) and (−) and showed similar electron density, a positive ridge lying at an angle across the c axis. With $S_{022}(+)$, the molecules lay across symmetry centers. Since the molecule was not expected to be centrosymmetric this sign was rejected. With $S_{022}(-)$, however, the molecules lay in reasonable positions between symmetry centers. Because of overlap, attempts to refine the projection at this stage led to no clearcut results.

Since the isolation by hand of the PDE from all possible combinations of a large number of reflections was both laborious and subject to error, a program was written for the IBM 650 which determined for a given set of monoclinic indices all the relationships in which the indices for two members of a set added to give those of a third.

Application of the program to the $hk0$ data and solution of the resulting set of PDE as simultaneous equations (with the reservation that not all of them need be true) led to the determination of 31 signs, about half being determined absolutely, the rest in terms of S_{280}. F_o projections with $S_{280}(+)$ and (−) showed similar patterns of electron density with obvious six-membered rings, the two choices again differing mainly by a shift along an axis, the b axis, and of magnitude about half the width of a ring.

Application of the program to the most intense general hkl reflections and solution of the PDE in the usual manner led to striking results, 63 signs being determined absolutely or as before in terms of S_{022} Among the signs determined was S_{280} which appeared unambiguously to be (−). Since projection along [100] had suggested that the molecules were planar and that half of them lay approximately parallel to (011) (the other half, because of the glide reflection, being parallel to $(0\bar{1}1)$), it was felt clarity of interpretation would be gained in the early stages by making electron density calculations in the plane of the molecule. In the absence of a general plane program, the cell was transformed to a triclinic one with (100) → (100)*, (010 → (010)*, and (011) → (001)*. Half the molecules were now nearly parallel to the plane (001)*, and only two or three sections parallel to this were needed to include an entire molecule. These showed clear atomic peaks corresponding to three rings joined as in (I). Nineteen atoms were placed and corresponded to those in the three rings and the 5 atoms directly connected to them. For the short deck, calculation of the structure factors with N atom scattering factors gave $R=46·3\%$. An F_o synthesis based on the calculated phases showed the location of the remaining atom, indicated some considerable shifts and indicated which atoms were, in fact, oxygen. Recalculation of the structure factors based on 15 C and 5 O atoms reduced R to 29·6%. The structure appeared to be correct, but several cycles of three-dimensional ΔF syntheses reduced R only to 22·9% and certain reflections remained much in error. Most important of these were 660, 5,12,0, and 5,17,0, which were among the group signed statistically. Even use of the long deck three-dimensional data in ΔF syntheses did not greatly improve matters although coordinate shifts averaged 0·06 Å in the direction of the final structure.

At this point it was felt that the chemical structure (I) for rubrofusarin indicated by these Fourier syntheses was probably correct, but that the molecule was incorrectly located in the cell. Accordingly the phase determining procedure for the general hkl data was systematically reexamined. Approximate values of U were calculated for all reflections, taking into account the variation in the atomic scattering factors due to finite size of the atoms but omitting that due to thermal motion. This procedure restricts the possible U's of significant magnitude to a finite number while not neglecting the reflections at high Bragg angle. The reflections were arranged in order of decreasing U, the maximum being about 0·3, and comparison with the signs originally determined showed that almost all reflections with $U>0·17$ had been signed correctly. However, those reflections with large discrepancies in the F_c calculation (e.g. F_{660}) were just the ones whose signs rested on the least evidence, one or two PDE.

Signs which were deduced from four or more agreeing PDE were accepted as correct and used as input to a new program which computed $(S_{hkl})(S_{h'k'l'})$ and assigned the product to $U_{h+h',\,k+k',\,l+l'}$ if of unknown sign. With this program and the requirement of a least four agreeing PDE, it was possible to determine signs for all reflections of $U > 0{\cdot}17$ *except* those which had given trouble before. Incorporation of the newly determined signs and repetition of the method extended the list to include most reflections of $U > 0{\cdot}15$. All reflections for which a number of PDE were obtained showed high consistency in their PDE.

Those reflections for which few or no relationships could be found were classed as undetermined. Examination of this group revealed that combinations of two of its members could be related in PDE with one reflection of known sign, i.e. they formed a subgroup only weakly connected with the main body of strong reflections. On this basis it was possible to determine the signs of all reflections in the subgroup in terms of S_{660}. Using this sign as a variable, the calculations were extended to $U \sim 0{\cdot}12$. At this point 103 signs had been determined absolutely, and an additional 20 in terms of S_{660}.

Sections from the reindexed triclinic cell were calculated for $S_{660}(+)$ and $(-)$. Both choices showed essentially the same pattern of electron density; small displacements of the atomic centers were the only differences. The atomic positions implied by the sections with $S_{660}(-)$ were virtually identical to those found in the earlier work. This was not surprising since the original choice of phases had included $S_{660}(-)$ and a few other related phases based on this value.

Evidence that the proper choice for S_{660} was $(+)$ came with the calculation of F_{hk0}. Eighteen maxima could definitely be located in the sections from either of the above three-dimensional F_o syntheses and were taken as C atoms (nos. 1–18). For $S_{660}(+)$, $R = 40{\cdot}9\%$, $R' = 47{\cdot}7\%$ (R' is the residual index with unobserved reflections taken as half the minimum observable value), while for $S_{660}(-)$. $R = 45{\cdot}9\%$, $R' = 54{\cdot}9\%$. An F_o synthesis projected along [001] with $S_{660}(+)$ allowed the identification of atoms 19 and 20 from among several possible peaks on the sections and suggested that atoms 1, 8, 13 and 18 were oxygen. With these additions and changes and a temperature factor of 2·5 instead of 2·0, R dropped to 23·5% ($R' = 25{\cdot}6\%$). Three cycles of ΔF syntheses along [001] and two along [100] showed atom 14 to be oxygen and reduced R_{hk0} to 13·6% ($R' = 15{\cdot}6\%$) and R_{0kl} to 13·2% ($R' = 15{\cdot}5\%$). R_{hkl} was 11·3% for the short deck three-dimensional data. Fig. 1 shows a composite molecule as viewed down [001] on the basis of an F_o synthesis calculated at this point using the short hkl deck. The electron density around the individual atomic centers is plotted from sections taken through the three dimensional atom at the point of greatest density.

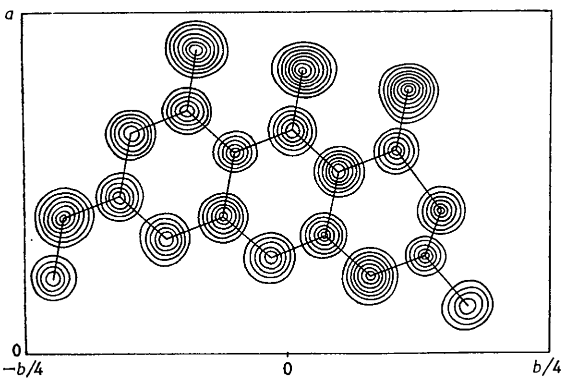


Fig. 1. Composite projection on (001). Section contours ca. 1 e.Å^{-3} starting at 2 e.Å^{-3}.

Table 1. *Final atomic coordinates and isotropic temperature factors for rubrofusarin*

	x/a	y/b	z/c	B (Å^2)
O1	0·4077	−0·2113	0·4669	3·134
O8	0·8971	−0·0892	0·4270	3·189
O13	0·8370	0·0173	0·3059	2·519
O14	0·2318	0·0778	0·1098	2·124
O18	0·7682	0·1172	0·1820	2·860
C2	0·4582	−0·1573	0·4158	2·298
C3	0·3377	−0·1153	0·3423	2·439
C4	0·4053	−0·0606	0·2922	1·855
C5	0·5989	−0·0496	0·3214	1·502
C6	0·7113	−0·0962	0·3948	2·290
C7	0·6448	−0·1494	0·4403	2·417
C9	0·2866	−0·0167	0·2198	1·955
C10	0·3548	0·0368	0·1786	1·946
C11	0·5402	0·0492	0·2055	1·831
C12	0·6580	0·0061	0·2780	1·612
C15	0·2936	0·1315	0·0701	2·691
C16	0·4630	0·1479	0·0912	2·687
C17	0·6040	0·1053	0·1580	2·248
C19	0·1335	0·1721	0·0008	3·925
C20	0·2211	−0·2220	0·4616	3·400

Further refinement was obtained on an IBM 709 using the full matrix least squares program of Busing & Levy (1959). Three cycles with individual isotropic temperature factors reduced R to 8·2% for the short deck. At this point the standard errors in coordinates were calculated to be ±0·016 Å for oxygen and ±0·025 Å for carbon. Starting from these coordinates, one cycle reduced R for the long deck to 11·4% ($R' = 15{\cdot}0\%$) and gave the coordinates and isotropic temperature factors listed in Table 1. Of the 60 positional parameters varied in this last refinement, 52 (87%) shifted less than their previously estimated standard errors and of the remaining 8 none changed by more than twice the standard error. Thus the assumptions made as to the accuracy of the intensity data used appear to be justified. Structure factor

Table 2. *Observed and calculated structure factors*

h	k	F_o	F_c
$\ell = 0$			
0	2 *	841	1155
0	4 *	548	-635
0	6	-43	-43
0	8	217	267
0	10	153	148
0	12	110	-68
0	14	196	161
0	16	251	-223
0	18 *	201	185
1	0 *	988	-1454
1	1	-31	27
1	2	238	-232
1	3 *	455	-511
1	4	206	169
1	5	272	220
1	6	149	-182
1	7	119	-68
1	8	69	48
1	9 *	394	378
1	10 *	423	455
1	11 *	707	765
1	12 *	407	403
1	13	-72	3
1	14	139	-130
1	15	-79	-59
1	16	-83	37
1	17	-85	27
1	18 *	200	-218
1	19 *	432	451
1	20 *	290	-299
1	21 *	315	306
2	0 *	663	-701
2	1	347	-387
2	2	293	-351
2	3	140	-135
2	4	-48	59
2	5	-51	-50
2	6	194	181
2	7	270	281
2	8 *	531	-522
2	9 *	621	646
2	10 *	503	-493
2	11	-68	5
2	12	-72	-45
2	13	126	-99
2	14	-79	4
2	15	-83	10
2	16	-85	-100
2	17	-88	47
2	18	-91	76
2	19	171	-173
2	20 *	288	277
3	0	123	56
3	1	-56	73
3	2	176	186
3	3	-58	77
3	4	94	-52
3	5	146	152
3	6	-63	-44
3	7	-65	-57
3	8 *	277	244
3	9 *	330	-297
3	10	-73	119
3	11	-76	-100
3	12	171	-174
3	13	150	-147
4	0	292	-268
4	1 *	401	-370
4	2	209	-153
4	3	200	-154
4	4	226	-190
4	5	111	-82
4	6	123	-127
4	7	-75	36
4	8	135	103
4	9	-80	-2
4	10	-82	-49
4	11	143	-100
4	12	-85	15
4	13	-88	61
4	14	-90	92
4	15	-91	-47
4	16	-92	38
4	17	151	146
5	0	133	112
5	1	160	148
5	2	-81	-48
5	3	-82	-70
5	4	183	169
5	5	-84	-43
5	6	163	-153
5	7	136	168
5	8	158	-166
5	9	-88	95
5	10	-89	-51
5	11	-91	-64
5	12 *	226	-199
5	13	127	-108
5	14	-93	50
5	15	124	-120
5	16	-92	43
5	17 *	211	-218
5	18	126	146
6	0	93	-132
6	1	166	154
6	2	-90	69
6	3	-90	-1
6	4 *	153	121
6	5 *	162	-172
6	6 *	373	345
6	7 *	299	-300
6	8 *	183	210
6	9	130	-125
6	10	-93	-29
6	11	110	109
7	0	-93	13
7	1	-93	-16
7	2	-93	13
7	3 *	143	116
7	4	-92	37
7	5 *	131	115
$\ell = 1$			
0	2	165	-143
0	1	83	-149
0	3	78	104
0	4	185	-214
0	5	273	-317
0	6	112	110
0	7	460	417
0	8	228	-214
0	9 *	339	-347
0	10	279	-320
0	11	-39	3
0	12	235	-223
0	13	185	-198
0	14	-45	11
0	15	94	100
0	16 *	68	-57
0	17	183	178
0	18	108	-110
0	19 *	257	-239
0	20	-56	45
0	21	-57	-41
0	22	-56	68
0	23	-55	11
0	24	-53	50
0	25	-50	50
0	26	-46	-7
0	27	-42	45
0	28	-36	-74
0	29	-29	87
1	1	174	177
1	2	222	-241
1	3	299	-295
1	4	404	379
1	5	280	289
1	6	521	-516
1	7	232	211
1	8	68	-104
1	9	137	170
1	10	83	-110
1	11	116	117
1	12	276	248
1	13	-44	-49
1	14	-46	36
1	15	-49	-25
1	16	179	-159
1	17	163	142
1	18 *	245	-263
1	19 *	297	278
1	20	218	-196
1	21	-57	22
1	22	159	149
1	23	-55	1
1	24	-53	33
1	25	-50	18
1	26	-45	1
1	27	-41	-36
1	28	-35	9
1	29	-26	-27
-1	1	231	-236
-1	2	207	167
-1	3 *	463	-444
-1	4	370	-303
-1	5	478	466
-1	6	331	311
-1	7	281	-312
-1	8	70	-44
-1	9 *	406	-439
-1	10	172	128
-1	11	282	-266
-1	12	142	-130
-1	13	151	119
-1	14	-46	-1
-1	15	90	114
-1	16	83	59
-1	17	-53	-24
-1	18	-54	45
-1	19	-56	-24
-1	20	-56	-86
-1	21 *	240	-222
-1	22	200	-194
-1	23	-55	-23
-1	24	-53	11
-1	25	-50	48
-1	26	-46	-14
-1	27	-41	20
-1	28	-35	36
-1	29	-28	18
2	1	122	75
2	2	261	321
2	3	44	97
2	4	223	125
2	5	197	213
2	6	103	-82
2	7	176	146
2	8	331	-318
2	9	133	157
2	10	105	93
2	11	96	-111
2	12	71	-52
2	13	88	-65
2	14	115	-125
2	15	132	-130
2	16	181	170
2	17	-54	-79
2	18	-56	62
2	19	-56	-60
2	20	-57	20
2	21	-56	-72
2	22	177	-185
2	23	131	-122
2	24	93	-101
2	25	115	-118
2	26	84	64
2	27	-38	-6
2	28	-31	6
-2	1	465	-487
-2	2	139	111
-2	3	46	41
-2	4	-29	78
-2	5	127	90
-2	6	60	-81
-2	7	-34	-33
-2	8	240	220
-2	9	-38	47
-2	10	196	-161
-2	11	-42	10
-2	12	-44	10
-2	13	-46	47
-2	14	-48	36
-2	15	118	-111
-2	16	68	-49
-2	17	66	79
-2	18	197	182
-2	19	198	236
-2	20	-57	44
-2	21 *	260	295
-2	22	-56	-13
-2	23	-54	50
-2	24	-51	-42
-2	25	94	-74
-2	26	-44	-7
-2	27	99	64
-2	28	-33	29
3	1	132	116
3	2 *	321	315
3	3 *	499	477
3	4 *	617	571
3	5	120	128
3	6	-40	-37
3	7	135	-130
3	8	123	-109
3	9	106	82
3	10	-45	4
3	11	-47	46
3	12	-49	-6
3	13	-51	38
3	14	-52	40
3	15	-54	-41
3	16	78	66
3	17	65	-68
3	18	143	123
3	19	90	-98
3	20	65	-34
3	21	-55	42
3	22	78	58
3	23	74	93
3	24	-47	52
3	25	-43	-16
3	26	-38	24
3	27	81	-65
3	28	-19	70
-3	1 *	347	-311
-3	2	246	-218
-3	3	49	-56
-3	4	261	-223
-3	5	79	68
-3	6	84	77
-3	7	80	94
-3	8	247	251
-3	9	128	134
-3	10	205	218
-3	11	148	-132
-3	12	144	123
-3	13	101	-104
-3	14	-51	-44
-3	15	-53	-2
-3	16	-54	2
-3	17	-56	20
-3	18	-56	13
-3	19	-57	-45
-3	20 *	241	236
-3	21	124	-117
-3	22	108	103
-3	23	-52	-42
-3	24	-48	-20
-3	25	-44	6
-3	26	-40	-2
-3	27	-34	-15
-3	28	-25	-20
4	1	130	98
4	2	56	-63
4	3	243	-203
4	4	236	-241
4	5	226	-197
4	6	269	234
4	7	181	-168
4	8	-48	44
4	9	-50	-39
4	10	-51	43
4	11	64	87
4	12	165	157
4	13 *	353	365
4	14 *	428	475
4	15 *	266	243
4	16	204	203
4	17	180	-153
4	18	108	-106
4	19	-55	10
4	20	-54	44
4	21	-52	51
4	22	-49	60
4	23	-45	4
4	24	-41	24
4	25	-35	41
4	26	64	-56
-4	1 *	549	516
-4	2 *	570	-520
-4	3	174	184
-4	4	-43	10
-4	5	143	-134
-4	6	-44	-28
-4	7	61	79
-4	8	252	231
-4	9	161	147
-4	10 *	218	253
-4	11	161	-184
-4	12 *	316	336
-4	13 *	220	-209
-4	14	-55	-17
-4	15	139	112
-4	16	95	-72
-4	17	-57	-16
-4	18	116	112
-4	19	-56	-55
-4	20	-55	-30
-4	21	-53	-43
-4	22	-50	14
-4	23	-47	-19
-4	24	-43	21
-4	25	-38	24
-4	26	-32	-4
5	1	-50	-37
5	2	193	-205
5	3	-51	-11
5	4	-51	49
5	5 *	513	-514
5	6	219	214
5	7	194	-168
5	8	151	13
5	9	-55	7
5	10	-55	12
5	11	-56	82
5	12	-56	-43
5	13 *	297	-299
5	14 *	294	-284
5	15	206	-206
5	16	173	-185
5	17	-55	42
5	18	75	52
5	19	-51	0
5	20	-48	-0
5	21	-45	44
5	22	-41	-7
5	23	-36	19
5	24	103	97
5	25	-19	91
-5	1	144	138
-5	2	-49	-4
-5	3	173	158
-5	4	171	-178
-5	5	144	-123
-5	6	117	139
-5	7	73	109
-5	8	119	123
-5	9	75	69
-5	10	135	-149
-5	11 *	443	433
-5	12 *	506	-519
-5	13 *	321	326
-5	14	116	-109
-5	15	-57	-11
-5	16	89	82
-5	17	109	-117
-5	18	115	-117
-5	19	-53	-51
-5	20	-50	-31
-5	21	-47	32
-5	22	-44	39
-5	23	84	-86
-5	24	-34	14
-5	25	-26	-6
6	1	-56	-20
6	2	94	105
6	3	112	-106
6	4 *	261	-271
6	5	148	138
6	6 *	407	-437
6	7	-57	84
6	8	-57	67
6	9	-57	58
6	10	-57	-18
6	11	-56	-50
6	12	-56	-49
6	13	-55	14
6	14	83	-75
6	15	-53	11
6	16	104	-72
6	17	-48	-14
6	18	-45	-6
6	19	-43	55
6	20	-39	16
6	21	-34	-0
6	22	-27	-27
-6	1	-54	-42
-6	2	-54	-47
-6	3	-55	72
-6	4	95	82
-6	5	-55	59
-6	6	133	-104
-6	7 *	374	-386
-6	8 *	417	-422
-6	9	122	-118
-6	10	-57	-45
-6	11	-57	-63
-6	12	101	92
-6	13	-56	-37
-6	14	-55	-8
-6	15	-54	-51
-6	16	-53	-44
-6	17	-51	-62
-6	18	-48	-4
-6	19	-45	11
-6	20	-45	-46
-6	21	85	53
-6	22	143	-115
-6	23	151	139
7	1	-56	-8
7	2	-56	-34
7	3	92	75
7	4	61	87
7	5	164	163
7	6	172	208
7	7	-55	53
7	8	-54	-48
7	9	-53	-42
7	10	-52	-35
7	11	-51	-21
7	12	-50	4
7	13	92	108
7	15	112	96
7	16	-40	31
7	17	58	49
-7	1	-57	-40
-7	2	178	178
-7	3 *	232	-265
-7	4	141	148
-7	5	127	-100
-7	6	-56	-49
-7	7	168	172
-7	8	-56	81
-7	9	-55	50
-7	10	-54	36
-7	11	72	-77
-7	12	79	74
-7	13	55	-52
-7	14	-49	59
-7	15	-46	-70
-7	16	-44	-16
-7	17	-41	21
8	1	-49	33
8	2	-49	-7
8	3	-49	-52
8	4	-48	27
8	5	-48	-60
8	6	-46	27
8	7	-45	-45
8	8	-44	34
8	9	-43	-12
8	10	-41	-20
8	11	-39	38
8	12	-36	-36
8	13	70	-53
8	14	54	30
8	15	-31	-140
-8	1	-52	24
-8	2	-52	-70
-8	3	-52	43
-8	4	-51	-62
-8	5	-51	53
-8	6	-50	42
-8	7	-49	4
-8	8	-48	43
-8	9	-46	15
-8	10	-45	3
-8	11	-43	60
-8	12	-41	-51
-8	13	-39	36
-8	14	-39	-66
-8	15	94	75
-8	16	72	56
9	1	48	27
9	2	69	-63
9	3	92	71
9	4	115	-120
9	5	49	38
9	6	75	-88
$\ell = 2$			
0	1 *	1168	-1187
0	2 *	1197	-1359
0	3 *	1088	-1291
0	4 *	575	-581
0	7 *	454	429
0	8 *	318	-242
0	12	181	174
0	13	199	191
0	14 *	279	267
0	16 *	323	-332
0	17 *	254	273
1	1	183	217
1	3	413	-380
1	6	317	-284
1	7	306	302
1	9	165	131
1	12 *	279	-273
1	14 *	342	-347
1	16 *	246	264
1	17 *	362	-386
1	18 *	404	402
-1	0 *	792	870
-1	1 *	830	832
-1	2 *	1098	1167
-1	3 *	1110	1116
-1	4	221	196
-1	5	373	-336
-1	6	219	-240
-1	7	265	228
-1	8 *	425	-387
-1	9 *	566	542
-1	12 *	379	366
-1	18 *	175	-159
-1	21 *	238	276
-1	22 *	249	248
2	3	324	358
2	6 *	557	537
2	7 *	662	-608
2	8 *	334	298
-2	0 *	374	376
-2	1	202	302
-2	2	238	175
-2	3	173	139
-2	7 *	307	-278
-2	8	275	257
-2	9 *	353	-364
-2	10 *	539	552
-2	11 *	249	234
-2	12	180	198
-2	21 *	249	-270
-2	22 *	235	-251
-2	23	192	-202
3	3	188	-191
3	6	168	-165
-3	8	149	155
-3	9	229	-228
-3	10	102	-163
-3	11 *	464	-478
-3	12 *	253	-247
4	0	189	-209
4	1	140	-164
4	2	179	206
4	4	242	225
4	5	176	162
4	7	134	132
4	15 *	198	-234
-4	2	184	183
-4	3	161	-134
-4	19	186	-60
5	4 *	334	342
5	5 *	193	-242
5	6 *	260	242
5	13 *	173	172
-5	0 *	265	-247
-5	2	222	-206
-5	3	155	154
-5	10 *	182	181
6	1	160	162
6	3 *	161	145
6	4 *	258	-264
6	5 *	224	242
-6	0 *	232	-197
-6	8 *	249	-243
-6	10 *	339	-347
-7	8 *	143	157
$\ell = 3$			
0	1	85	-76
0	2	220	235
0	3	251	258
0	4	102	-134
0	5	111	131
0	6	88	90
0	7	250	269
0	8	150	-148
0	9	236	-231
0	10	135	119
0	11	147	172
0	12	123	156
0	13	87	55
0	14 *	241	209
0	15	93	77
0	16	124	-95
0	17 *	207	183
0	18 *	258	-226
1	1	-27	-20
1	2	88	-114
1	3	-30	-23
1	4	439	448
1	5	121	101
1	6	-36	-17
1	7	-38	25
1	8	131	128
1	9	-42	-67
1	10	111	-111
1	11	110	120
1	12	49	35
1	13	125	-100
1	14	92	116
1	15 *	287	-277
1	16 *	222	225
1	17 *	213	-214
1	18	134	135
1	19	-61	57
1	20	128	-104
1	21	-59	61
1	22	-56	31
1	23	107	-82
1	24	-50	-44
1	25	103	-104
1	26	-40	-49
-1	1	231	256
-1	2	205	228
-1	3	145	-155
-1	4	40	-47
-1	5 *	394	416
-1	6	173	-186
-1	7	76	67
-1	8 *	295	-314
-1	9	184	160
-1	10	71	76
-1	11	145	-127
-1	12	63	49
-1	13	-50	23
-1	14	89	-82
-1	15	-55	70
-1	16	89	-117
-1	17	-59	-25
-1	18	-60	26
-1	19	-61	-31
-1	20	-60	-8
-1	21	400	-122
-1	22	-56	15
-1	23	86	77
-1	24	131	118
-1	25	-47	64
-1	26	-42	-30
-1	27	67	71
2	1	90	88
2	2	65	71
2	3	145	-145
2	4	237	228
2	5	90	-95
2	6	228	235
2	7	76	-84
2	8	118	-104
2	9	94	81
2	10	-49	-29
2	11	-51	-17
2	12	-53	30
2	13	-55	48
2	14	-56	41
2	15	-58	53
2	16	166	169
2	17	-60	25
2	18	-61	-15
2	19	-60	-8
2	20	-59	9
2	21	-56	-17
2	22	-54	-9
2	23	110	102
2	24	86	73
2	25	84	101
2	26	119	120
-2	1	-29	2
-2	2	120	119
-2	3	103	102
-2	4	-32	-23
-2	5	74	-86
-2	6	73	-82
-2	7	-39	-35
-2	8	231	202
-2	9	115	-80
-2	10	199	-212
-2	11	57	-101
-2	12	117	-123
-2	13	-52	-9
-2	14	-54	-43
-2	15	-56	-22
-2	16	-58	-0
-2	17	78	59
-2	18	94	137
-2	19	116	-117
-2	20	-60	-38
-2	21	77	-132
-2	22 *	167	-170
-2	23	123	-135
-2	24	111	-122
-2	25	66	-49
-2	26	-40	32
3	1	82	79
3	2	-45	3
3	3	109	-111
3	4	-46	-32
3	5 *	566	-525
3	6 *	254	-254
3	7 *	282	-286
3	8	90	-4
3	9	-53	89
3	10	-54	49
3	11	-55	-7
3	12	-57	-5
3	13	-58	37
3	14	-60	68
3	15	171	159
3	16	94	81
3	17	145	157
3	18	74	36
3	19	58	-60
3	20	-56	-23
3	21	-53	1
3	22	63	34
3	23	60	75
3	24	65	-71
3	25	58	61
3	26	-24	-76
-3	1	119	-129
-3	2	-38	-2
-3	3	77	-83
-3	4	105	-90
-3	5	68	60
-3	6	88	92
-3	7	93	76
-3	8	102	-91
-3	9	90	74
-3	10 *	215	-233
-3	11	78	-117
-3	12	64	-78
-3	13	96	-83
-3	14	-57	-10
-3	15	-58	34
-3	16	-60	-7
-3	17	82	102
-3	18 *	182	-189
-3	19 *	213	222
-3	20	-59	-48
-3	21	-56	83
-3	22	-54	31
-3	23	-50	4
-3	24	-46	7
-3	25	-41	28
4	1	-52	19
4	2	-52	7
4	3	134	-138
4	4	70	-59
4	5	-54	3
4	6	63	17
4	7	79	-78
4	8	83	-89
4	9	-37	3
4	10	-59	81
4	11	-60	16
4	12	64	-43
4	13	72	78
4	14 *	260	-251
4	15 *	194	-192
4	16 *	388	-368
4	17 *	346	-332
4	18	132	-135
4	19	-53	44
4	20	-50	52
4	21	-47	57
4	22	-42	-17
-4	1 *	517	-530
-4	2 *	393	-349
-4	3	-46	21
-4	4	-47	-8
-4	5	-48	-32
-4	6	-49	0
-4	7	-50	24
-4	8	98	80
-4	9	90	67
-4	10	126	-112
-4	11	-56	-7
-4	12	-57	-0
-4	13	136	-126
-4	14	-60	-8
-4	15	-60	59
-4	16	72	-57
-4	17	-60	-23
-4	18	89	80
-4	19	79	-51
-4	20	-55	26
-4	21	72	51
-4	22	56	57
-4	23	-45	31
5	1	-58	-78
5	2 *	228	-209
5	3 *	411	430
5	4 *	343	-301
5	5	197	161
5	6	-60	-40
5	7	-60	48
5	8	-61	42
5	9	-61	-35
5	10	-61	-30
5	11	85	97
5	12	93	-87
5	13	-59	-48
5	14	-57	-3
5	15	-56	75
5	16	77	92
5	17	105	113
5	18	-49	62
5	19	-45	-28
-5	1	110	97
-5	2	83	74
-5	3	-54	8
-5	4	133	-134
-5	5	-55	-42
-5	6	-55	59
-5	7	-56	-22
-5	8 *	211	209
-5	9 *	416	-420
-5	10 *	532	526
-5	11 *	237	-220
-5	12	68	82
-5	13	116	109
-5	14	79	-71
-5	15	-60	29
-5	17	78	-76
-5	18	-55	57
-5	19	69	12
-5	20	80	92
-5	21	-46	73
-5	22	-41	-8
-5	23	-36	-30
6	1	-61	75
6	2	79	66
6	3 *	179	-187
6	4	140	142
6	5	-60	11
6	6	114	103
6	7 *	208	196
6	8 *	196	205
6	9	76	74
6	10	68	-61
6	11	55	-56
6	12	54	-14
6	13	52	2
6	14	50	39
6	15	47	33
6	16	68	60
6	17	55	21
6	18	89	73
-6	1	142	141
-6	2	-59	8
-6	3	-60	56
-6	4	-60	50
-6	5	-60	-27
-6	6	-60	-22
-6	7	99	-115
-6	8	61	-12
-6	9 *	459	467
-6	10	61	46
-6	11 *	316	322
-6	12	-60	-12
-6	13	-58	11
-6	14	-57	-9
-6	15	-55	-29
-6	16	-53	19
-6	17	-50	22
-6	18	-48	55
-6	19	137	-58
-6	20	177	82
7	1	-54	-20
7	2	-54	50
7	3	-54	-9
7	4	-53	2
7	5	-53	-24
7	6	-52	-18
7	7	90	-106
7	8	84	-97
7	9	-48	-25
7	10	-46	19
7	11	68	-38
7	12	107	105
7	13	68	-53
7	14	61	18
-7	1 *	242	246
-7	2	155	-138
-7	3	-60	-20
-7	4	-60	62

F_o and F_c 10 times absolute values. $-F_o$ indicates reflection less than minimum observable. * marks reflections whose phases can be determined from the PDE.

calculations for the long deck *hkl* reflections are shown in Table 2. The reflections whose phases could be determined from the PDE (see below) are starred.

The structure

The molecular structure as shown in Figs. 1 and 2 confirms completely the chemical suggestion of structure (I). Within the limits of experimental error, the atoms in the two aromatic rings and those joined directly to them are co-planar. The standard deviation of these atoms from the least squares plane is 0·021 Å, maximum deviation is 0·037 Å. The heterocyclic ring does not appear to be planar since atoms 15, 16 and 19 are −0·051, −0·077 and −0·107 Å out of the plane calculated for the rest of the molecule.

Table 2 (*cont.*)

h	k		F_o	F_c
-7	5		-62	-30
-7	6		-50	48
-7	7		-58	71
-7	8		57	-87
-7	9		118	-119
-7	10	*	251	-235
-7	11		-54	-58
-7	12		77	-69
-7	13		58	39
-7	14		-47	16
-7	15		76	-54
$l = 4$				
0	1		257	-280
0	2		145	-86
0	3		233	212
0	4	*	627	-632
0	5	*	251	235
0	6	*	323	324
0	7		-41	-19
0	8		-43	-37
0	9		-46	-14
0	10		-49	3
0	11		-52	45
0	12		-54	-69
0	13		143	-187
0	14		93	68
0	15	*	659	-647
0	16		-69	-90
0	17	*	239	-199
0	18		86	111
0	19		-63	24
0	21		-59	-58
0	22		-56	25
0	23		-58	-59
0	20		-61	-24
0	24		-51	3
0	25		-45	-43
0	26		81	-93
1	0		-33	-85
1	1		172	172
1	2		58	15
1	3		-57	-199
1	4	*	458	457
1	5		189	-142
1	6	*	414	396
1	7		44	-12
1	8		-48	6
1	9		-55	-1
1	10		92	-64
1	11		-54	-58
1	12		75	44
1	13		-58	-38
1	14		-63	-70
1	15	*	438	416
1	16		173	-155
1	17		126	143
1	18		-63	18
1	19		-62	-16
1	20		-61	-13
1	21		-58	22
1	22		-54	-5
1	23		-51	-6
1	24		-45	-27
1	25		-39	2
1	26		-30	-1
-1	0		-16	194
-1	1		76	-76
-1	2		210	-169
-1	3	*	674	-537
-1	4	*	1024	-1000
-1	5	*	872	-780
-1	6	*	254	-233
-1	7		95	-55
-1	8		186	155
-1	9		159	154
-1	10		86	-67
-1	11		73	-73
-1	12		-54	41
-1	13		-57	-47
-1	14		123	-153
-1	15		-61	-13
-1	16		-62	31
-1	17		-63	-33
-1	18		-63	-5
-1	19		-63	-1
-1	20		-61	23
-1	21		-59	45
-1	22		-57	-43
-1	23		102	-115
-1	24		49	-42
-1	25		97	-115
-1	26		62	63
2	0		-43	71
2	1		65	-91
2	2		73	43
2	3		143	120
2	4	*	295	-279
2	5	*	275	274
2	6	*	237	-213
2	7		80	-78
2	8		-52	12
2	9		-54	-2
2	10		-56	-16
2	11		-58	16
2	12		-59	-28
2	13		-61	34
2	14		-62	4
2	15		-63	29
2	16		97	105
2	17		-63	61
2	18		-62	-7
2	19		-60	17
2	20		-58	-36
2	21		-55	-27
2	22		51	-64
2	23		90	78
2	24		86	-102
2	25		-121	6
-2	0		-30	69
-2	1		40	61
-2	2		99	97
-2	3		-34	-3
-2	4		54	31
-2	5	*	412	372
-2	6	*	383	-374
-2	7	*	355	356
-2	8	*	330	-309
-2	9		-49	51
-2	10		156	133
-2	11		-53	-22
-2	12		-55	-12
-2	13		58	-57
-2	14		60	-43
-2	15		72	71
-2	16		-62	-39
-2	17		63	82
-2	18		63	-61
-2	19		-62	51
-2	20		-61	-13
-2	21		-58	-0
-2	22		81	101
-2	23	*	171	184
-2	24	*	215	221
-2	25	*	168	176
-2	26		-31	44
3	0		-52	23
3	1		-52	-11
3	2		-52	-4
3	3		-53	-41
3	4		-54	45
3	5		-54	129
3	6		150	142
3	7		184	135
3	8		-38	71
3	9		-59	70
3	10		-61	-10
3	11		-62	45
3	12		-62	-30
3	13		-63	-74
3	14		114	124
3	15		-63	-41
3	16		-62	54
3	17		-61	-74
3	18		-59	-37
3	19		-57	-23
3	20		-53	-13
3	21		-50	19
3	22		-45	-29
3	23		-39	-41
3	24		102	112
-3	0		94	-69
-3	1		173	114
-3	2		131	122
-3	3		274	155
-3	4		147	135
-3	5		80	84
-3	6		-48	31
-3	7		-50	-23
-3	8		-51	-18
-3	9		-53	-21
-3	10		-55	-17
-3	11		-57	20
-3	12	*	255	251
-3	13	*	308	277
-3	14		141	201
-3	15		131	111
-3	16		-53	-25
-3	17		-53	-20
-3	18		-62	-53
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-7	12		102	100

F_o and F_c 10 times absolute values. $-F_o$ indicates reflection less than minimum observable. * marks reflections whose phase can te determined from the PDE.

The standard error of the final coordinates given in Table 1 was calculated by the least squares program to be 0·007 Å for the oxygen and 0·01 Å for the carbon atoms. These values suggest that the standard errors for the bond lengths in Table 3 should be 0·01–0·02 Å. On this basis, the chemically most significant bonds are C15–C16 and C17–O18, whose lengths correspond to normal carbon–carbon and carbon–oxygen double bonds respectively. These values serve to further identify the ring with which they are associated as the heterocyclic one and confirm the non-aromatic nature of the pyrone system.

That the bonds C20–O1 and C15–C19 are longer than customary for single bonds of their respective types, is best explained as a result of the omission of hydrogen atoms from the refinement calculations. Failure to

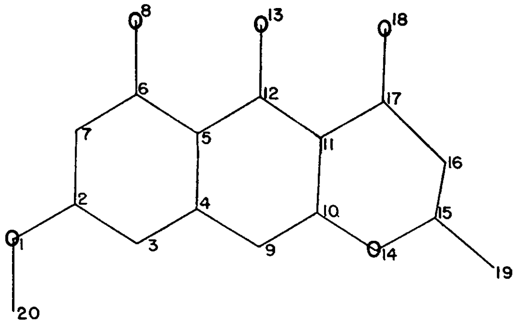

Fig. 2. Molecular structure.

provide sufficient electron density around the two methyl groups has presumably caused the carbon atom to shift outward in an attempt to compensate. No such explanation can be advanced for the abnormal length of C4–C5 and no reasonable alternative has yet presented itself.

Table 3. *Bond lengths and angles for rubrofusarin*

C20–O$_1$	1·42 Å	C10–C11	1·41 Å
O1 –C2	1·37	C11–C12	1·39
C2 –C3	1·38	C12–C5	1·41
C3 –C4	1·43	C12–O13	1·36
C4 –C5	1·46	C10–O14	1·37
C5 –C6	1·42	O14–C15	1·37
C6 –C7	1·39	C15–C16	1·32
C6 –O8	1·39	C15–C19	1·55
C7 –C2	1·40	C16–C17	1·48
C4 –C9	1·40	C17–C11	1·44
C9 –C10	1·39	C17–O18	1·25
C20–O1 –C2	118°	C10–C11–C12	118°
O1 –C2 –C3	124	C11–C12–C5	122
C2 –C3 –C4	119	C11–C12–O13	119
C3 –C4 –C5	120	C12–C5 –C4	118
C4 –C5 –C6	117	C11–C10–O14	121
C5 –C6 –C7	123	C10–O14–C15	118
C5 –C6 –O8	120	O14–C15–C16	126
C6 –C7 –C2	118	O14–C15–C19	110
C7 –C2 –C3	123	C15–C16–C17	119
C5 –C4 –C9	120	C16–C17–C11	116
C4 –C9 –C10	119	C16–C17–O18	123
C9 –C10–C11	123	C17–C11–C10	120

Discussion

To our knowledge, rubrofusarin represents the largest molecule for which the crystal structure has been solved directly from the relation

$$S_{hkl}S_{h'k'l'} \sim S_{h+h',\ k+k',\ l+l'}.$$

It is probable that the solution was facilitated by the high degree of structure repetition within the molecule. Nonetheless, these results indicate that the method merits wider application, particularly for three-dimensional studies.

Of the 300 PDE used to phase reflections with $U>0\cdot15$, only eight were found to indicate incorrect signs. None of these led to any uncertainty in the sign of a reflection for which four or more PDE were obtained. Extension to include all reflections with $U>0\cdot12$ resulted in a few more disagreements but assignment of phases was still easy and unambiguous.

After the structure of rubrofusarin had been solved, an IBM 709 was programmed to calculate the PDE and the investigation was extended to smaller values of U. As expected from the full Sayre expression, many more cases of disagreement within the set of PDE for any reflection appeared. An arbitrary absolute standard for the acceptance of a phase was devised by requiring that,

$$|n_P-n_m|/(n_P+n_m) \geq 0\cdot35 \quad \text{and} \quad |n_P-n_m| \geq 4\,,$$

where n_P is the number of PDE indicating a plus sign and n_m the number indicating minus. These conditions require a more than 2:1 bias of the PDE and a significant number of agreements for acceptance. Using these criteria the signs of 69 of the 88 reflections with $0\cdot118>U>0\cdot09$ could be determined using the 123 previously found, with S_{660} still as a variable, and some of the missing signs for $U>0\cdot12$ could be found. During these calculations, it became apparent that the internal agreement of the PDE was better with $S_{660}(+)$ and it would have been chosen as the preferred value if Fourier calculations had been begun at this stage. After the acceptable phases had been determined on the bases given above, comparison with those calculated from the final structure showed that all of the 198 judged reliable enough for use were correct. Of the remaining 23 reflections in the range investigated, 19 were correctly indicated by the PDE but had been rejected for ambiguity by the above requirements.

Solving this structure has emphasized the tendency for reflections to cluster in groups with strong intragroup phase relations but only weak inter-group relations. Major groups of this sort are easily identified and cause major molecular shifts when their phases are changed. Minor groups, however, may not appear until late in the sign determining procedure and may be missed entirely unless a systematic effort is made to examine all reflections of magnitude greater than some chosen U. As in rubrofusarin the accidental choice of the wrong sign for such a subgroup may lead to a structure which is incorrectly placed although the internal relationships of the atoms are reasonable, and from which it is difficult or impossible to achieve the true answer by normal methods of refinement. The average atomic shift in going from the false structure to the true was only 0·24 Å (0·1 to 0·38 Å range) and resulted from positive shifts along *a* and *c* and negative shifts along *b*. Despite the apparent closeness of the two structures, refinement of the false coordinates by difference syntheses showed little promise of leading to the true values.

Further studies are in progress on direct structure determination based in the relation

$$S_{hkl}S_{h'k'l'} \sim S_{h+h',\ k+k',\ l+l'}.$$

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Principle of Maximum Superposition. A Method for Determining the Positions of replaceable Atoms in Isomorphous Crystals

By V. Raghupathy Sarma and R. Srinivasan

Department of Physics, University of Madras, Madras-25, India

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This paper describes a new method for the location of replaceable atoms in a pair of isomorphous crystals and is useful when the replaceable atoms are of low atomic number. The method uses what is known as the principle of maximum superposition in the difference-Patterson diagram of the two compounds. The application of the method to an actual case is also given.

1. Introduction

As is well known the use of the technique of isomorphous replacement requires first the determination of the position of the replaceable atoms. The problem is comparatively simple if the replaceable atoms happen to be heavy, since the peaks corresponding to the vectors between them would then stand out prominently in the individual Patterson diagrams. It becomes even easier if the difference Patterson (D.P.) is used. (Kartha & Ramachandran, 1955).

However, the problem becomes rather difficult if the contribution of the replaceable atoms to the intensity is only a small fraction of the total intensity scattered by the whole structure, as, for example, for compounds in which the difference in the scattering factors of the replaceable atoms is of the same order as those of the other atoms in the structure; or the molecule in one crystal may have an atom more than in the other, this additional atom having nearly the same scattering factor as the other atoms in the molecule. An example of the latter type would be the pair morellin ($C_{33}H_{38}O_7$) and its monomethyl ether ($C_{34}H_{39}O_7$) which are at present under investigation in this laboratory.

The determination of the replaceable atom position also becomes difficult when the replaceable atom, although 'heavy', occurs in a structure of high molecular weight, as in the complexes of heavy metals with proteins which are often isomorphous with the free compound. Perutz (1956) has suggested a method for the determination of the replaceable-atom positions in such crystals, making use of the possibility of preparing isomorphous specimens with partial replacement of the heavy atoms. Such a method obviously cannot be used with just a pair of crystals. However, there is a simple and very general method which can be used for the location of the replaceable atom in a pair of isomorphous crystals and the present paper deals essentially with this method, which makes use of what may be called the 'Principle of Maximum Superposition' applied to the difference–Patterson (D.–P.) diagram. The principle is described in the next section and it is applied to an actual case in section 3.

2. The principle of maximum superposition

Let P and Q denote respectively the number of replaceable and the remaining non-replaceable atoms in the unit cell, the total number of atoms being $P+Q=N$. We shall also use indices P and Q to indicate the two types of atoms. Let $f_P^{(1)}$ and $f_P^{(2)}$ be the scattering factors of the replaceable atoms in the two structures and f_Q that of the non-replaceable atoms, which,