947. *The Crystal Structure of a Calciferol Derivative.*

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The crystal structure of calciferyl 4-iodo-5-nitrobenzoate * has been solved by the heavy-atom method and refined by a least-squares analysis of the three-dimensional diffraction data. The unit cell dimensions are $a = 31{\cdot}2$, $b = 6{\cdot}98$, $c = 15{\cdot}3$ Å, $Z = 4$, space group $P2_12_12_1$. The iodine atoms lie near special positions and the analysis involves the sorting of forty light-atom sites from electron-density distributions which include object and mirror-image peaks. Although it has not been possible to fix the atomic parameters with high precision (the estimated standard deviation of an average bond length is about 0·06 Å), the molecular structure and stereochemistry of calciferol is clearly established.

The X-ray investigation of the crystal structure of calciferyl 4-iodo-5-nitrobenzoate* (I), referred to in interim reports,[1,2] has now been completed by least-squares analysis of the three-dimensional diffraction data. The general course of this investigation has to be

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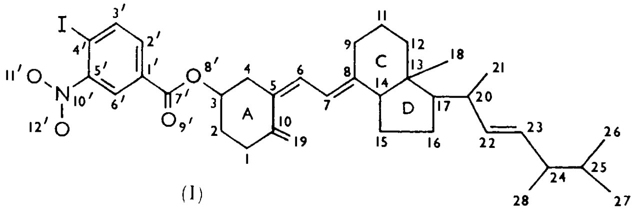
* This compound is more correctly named as the 4-iodo-3-nitrobenzoate. However, to avoid confusion the use of the incorrect name, on which the interim reports [1,2] were based, is continued here.

[1] Crowfoot and Dunitz, *Nature*, 1948, **162**, 608.

[2] Hodgkin, Webster, and Dunitz, *Chem. and Ind.*, 1957, 1148.

considered within the context of the development of crystal-structure analysis, particularly of the steadily increasing power and availability of high-speed electronic computing methods, during the past 16 years. When we began our work in 1947, computing techniques were in their infancy, and derivation of the structure from a study of the *b*-axis projection alone involved desk-calculations of formidable dimensions. Three-dimensional calculations, which now would be done rapidly in initial stages of the analysis, were taken up very slowly, at long intervals of time, as computing techniques improved. Several of these calculations were pilot experiments, on the results of which other analyses have been based. In retrospect it is clear that the most important conclusions of the investigation were those reached comparatively early. Some features of the stereochemical form of the molecule were settled by the initial two-dimensional work, others by the three-dimensional electron-density calculations which followed. The refinement of the crystal structure still presents problems which have not been completely resolved. The difficulties are due to the large number of atoms involved, to the fact that many of them lie near special positions in the unit cell, and to imperfections in the intensity data collected in 1947. If improved intensity measurements can be made in the future it may be worth while to continue this analysis and to derive more exact bond lengths and bond angles in the calciferol molecule than we can calculate at present.



(I)

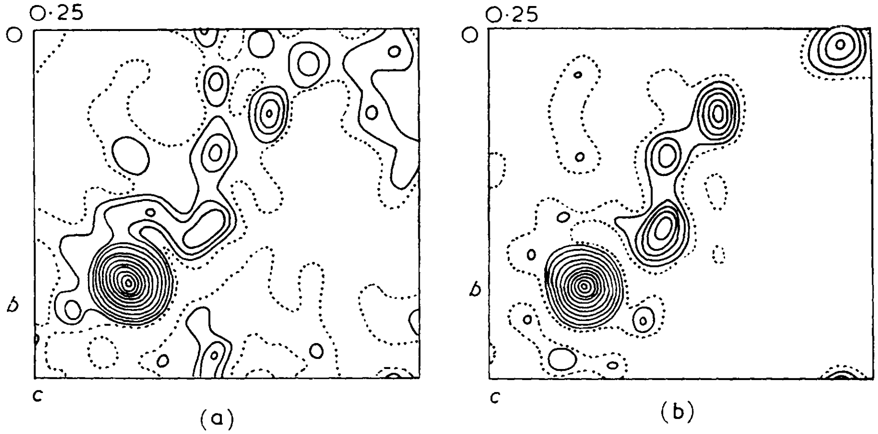
The crystals of calciferyl 4-iodo-5-nitrobenzoate were prepared by Mrs. Rita Cornforth after a search for suitable crystalline heavy-atom derivatives. Experiments by Dr. J. W. Cornforth in 1956 checked that no isomerisation of the molecule had occurred during esterification. The chemical preparation and characterisation of the crystals are decribed in an Appendix to this paper.

STRUCTURE ANALYSIS

Crystals of calciferyl 4-iodo-5-nitrobenzoate, $C_{35}H_{46}INO_4$ (*M*, 671·6), are deep yellow orthorhombic prisms, $a = 31{\cdot}2$, $b = 6{\cdot}98$, $c = 15{\cdot}3$ Å, $Z = 4$, space group $P2_12_12_1$, density calc. = 1·36. Our experimental data consisted of the relative *F* values for 299 *h*0*l*, 369 *h*1*l*, 365 *h*2*l*, 319 *h*3*l*, 198 *h*4*l*, 150 *h*5*l*, and 77 *h*6*l* reflexions (1777 in all). These were derived mostly from visual intensity estimates of the corresponding equi-inclination Weissenberg photographs made with Cu-K_α radiation; the *h*6*l* reflexions were estimated from a supplementary set of oscillation photographs. Data for individual layers were brought to a common scale by correlation with an 0*kl* Weissenberg photograph; the scale factors derived in this way were later adjusted somewhat on the basis of a comparison with calculated *F* values.

The *x* and *z* parameters of the iodine atoms were obtained from the (010) Patterson projection; $x_I = 0{\cdot}010$; $z_I = 0{\cdot}626$. Electron-density projections on (010) then led to the gradual recognition of *x* and *z* parameters for the remaining carbon, oxygen, and nitrogen atoms and eventually to the molecular model described and discussed in our 1948 publication.[1]

The *y* parameter of the iodine atom was estimated from the (100) Patterson projection (along a 31 Å periodicity!) to be about 0·23—0·25. This value was checked by calculating the Harker section ($\frac{1}{2}, y, z$) which led to $y_I = 0{\cdot}24$. With $x \sim 0$ and $y \sim 0{\cdot}25$, the heavy atoms are approximately related by the symmetry operations of the space group *Imma*; a first electron-density distribution phased on their contributions alone might be expected to show the high symmetry of this space group. In the actual first three-dimensional distribution $\rho 1$, calculated at the National Physical Laboratory, this false symmetry was reduced to that of $Pcm2_1$. The reduction was mainly due to the greater effectiveness of the small x parameter in relation to the long a axis in breaking down false symmetry compared with y and small b. This effect was enhanced by using the signs calculated for the $h0l$ terms from the refinement of the (010) projection in the evaluation of the three-dimensional series, together with phase angles for the iodine contribution alone for the remaining hkl terms. The distribution accordingly showed false mirror planes only at $y = \frac{1}{4}$ and at $\lambda = \frac{3}{4}$. Fig. 1a illustrates its character. The atoms each appeared accompanied by its mirror image at peak heights varying from 2·5 to 5 $e/\text{Å}^3$, together with a few spurious peaks of the same magnitude marked, probably significantly, by having no mirror image. Generally the two mirror-image peaks were almost identical in height; there was a slight bias in the direction chosen; 7 peaks of the selected configuration were definitely the stronger as against 3 of the alternative. Eight atoms lay very close either to $y = \frac{1}{4}$ or $y = \frac{3}{4}$, and were represented by single, often elongated, peaks. In two cases, where bonds crossed the mirror planes nearly at right angles, the object peak of one atom overlapped the mirror image of its neighbour. In this state of confusion, it was fortunate that approximate x and z parameters for most of the atoms were known from the projection work. This limited the interpretation of the three-dimensional series to the choice between two, or occasionally four, alternatives of a y parameter consistent with stereochemical considerations. In the majority of cases there was no ambiguity; even in the most difficult region where the atoms linking ring A to rings C and D lie close to the spurious mirror plane, there was definite bias in favour of one stereochemically consistent model. Only for the last four atoms were we unable to identify convincing atomic peaks near their expected positions (this was partly due to our wrong interpretation of the projection in this region which was included in the signs of the $h0l$ terms). These missing atoms were omitted from the next phasing calculations.



(a) (b)

FIG. 1. (a) Part of the section at $x = 0$ from $\rho 1$. (b) The corresponding portion of $\rho 2$.

Contour interval equals 1 electron/Å^3, except over the iodine atom where it is arbitrary. Negative contours broken.

At this stage (1954) it became possible, for the first time, to make use of the high-speed computing facilities offered by the SWAC computer in Los Angeles.[3] The second three-dimensional electron-density distribution, $\rho 2$, was phased on the assumed positions of all atoms in the molecule except the last four of the side-chain. It contained not only the 37 peaks corresponding to the atoms included in the structure factor calculation but also 4 additional peaks of only 1—2 $e/\text{Å}^3$ corresponding to the atoms that had been omitted. Fig. 1 illustrates how the spurious symmetry in $\rho 1$ had virtually disappeared in $\rho 2$. The new positions found for the 4 terminal atoms of the side-chain differed from those inferred from the two-dimensional work and corresponded to the opposite stereochemical configuration at C(24) to that suggested in the preliminary publication.[1] The occurrence of 4 peaks in reasonable positions for the 4

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[3] Sparks, Prosen, Kruse, and Trueblood, *Acta Cryst.*, 1956, **9**, 350.

missing atoms and the absence of mirror image peaks for the other atoms was taken as evidence that the molecular model that had been selected out of the various possibilities from the iodine-phased distributions was the correct one. Accordingly our subsequent work was limited to the refinement of this model alone.

The refinement followed a fairly normal course. A second set of structure factor calculations led us to change the scaling of the various layers of observed F values (October 1957). A revised three-dimensional electron-density distribution, $\rho3$, was then calculated with the re-scaled data (Fig. 2), together with one based on the calculated F values (May 1958). Although the peak shapes in both distributions were often distorted their centres were determined, as far as possible, by nineteen-point routine calculations and shifts applied from the relations between the two series. The atomic positions derived were then used as the starting point for a series of least-squares calculations which were carried out on an IBM 7090 computer at Los Angeles, but only after an interval of several years (to March 1962) during which the problem lay dormant.

Two separate series of least-squares refinements have been carried out, the first assigning anisotropic thermal parameters to the atoms and the second isotropic thermal parameters. Although R is rather lower for the first series, 11·9 as against 15·4 for the second, we prefer to record the atomic positions reached by the second procedure. With a structure as complex as the present, and imperfect data, the anisotropic refinement seems merely to add degrees of freedom which have no physical meaning.

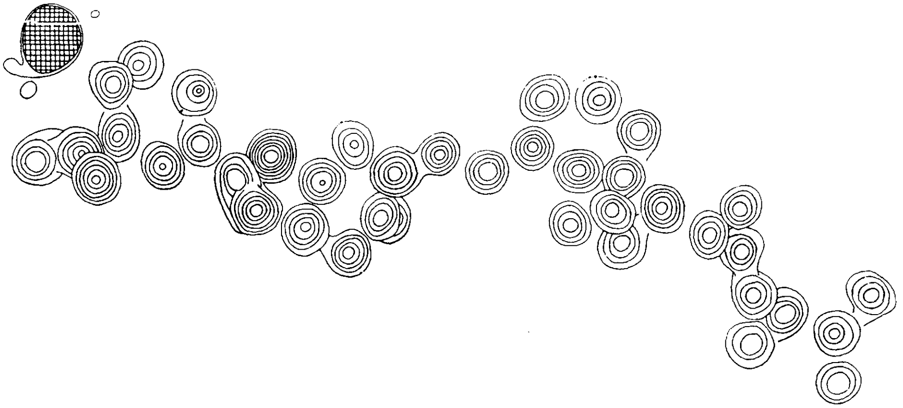

FIG. 2. Electron-density contours over the peak centres from $\rho3$. Iodine atom shaded. Contour interval $1e/\text{Å}^3$.

In the preferred analysis, the 1777 experimental F values were fitted to the 3 positional parameters and an individual isotropic temperature factor, B, for each atom, together with an overall scale factor. Three cycles were done with partial shifts (0·6 for positions, 0·4 for B's) and then two with full shifts. All the final shifts were smaller than one-third of the corresponding estimated standard deviations, except for B of C(21) which shifted by an amount equal to 1·4 times its estimated standard deviation.

Although further improvement in R could certainly now be obtained by re-introducing anisotropic thermal parameters it seems unlikely that these would lead to significant improvement in our knowledge of the structure, apart perhaps from a better description of the iodine atom. A difference map, calculated from the final parameters shows seventeen regions in which the electron density deviates from zero by more than $\pm 1{\cdot}0$ $e/\text{Å}^3$. Thirteen of these regions are in the neighbourhood of the iodine atom and the remaining four are small negative troughs 1 Å or more from any atom. None of them can indicate any significant changes in the atomic positions.

The observed and calculated F values are recorded in Table 1. In the latest structure-factor calculations, the f curve used for iodine was that of Thomas and Umeda,[4] and for oxygen, nitrogen, and carbon (trigonal and tetrahedral) those of McWeeny.[5]

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[4] Thomas and Umeda, *J. Phys. Chem.*, 1957, **26**, 293.
[5] McWeeny, *Acta Cryst.*, 1951, **4**, 513.

TABLE 1.

Observed and calculated structure factors for the *hkl* reflections. l, $F_{\text{obs.}}$, and $F_{\text{calc.}}$ are recorded in groups of constant h and k.

$h = 0, k = 0$		
2	13	2
4	123	136
6	30	21
8	70	74
10	26	14
12	63	67
14	30	26
16	30	31
$h = 1, k = 0$		
1	103	120
3	117	140
4	43	42
5	130	144
6	57	45
7	59	65
9	70	62
11	33	37
17	13	19
$h = 2, k = 0$		
0	220	275
1	26	35
3	23	14
4	150	173
5	59	54
6	37	25
7	30	30
8	90	101
12	59	65
16	23	26
$h = 3, k = 0$		
1	30	23
2	39	23
3	176	212
4	73	64
5	70	76
6	23	15
7	37	41
9	77	64
10	13	20
11	19	28
13	43	41
17	13	18
$h = 4, k = 0$		
0	127	150
1	90	96
2	46	38
3	37	27
4	107	126
5	30	26
6	17	6
7	37	30
8	83	93
12	33	35
16	17	16
$h = 5, k = 0$		
1	90	89
2	196	229
3	99	105
4	57	56
5	127	131
6	37	32
7	117	111
9	93	92
10	13	15
11	23	31
17	17	12
$h = 6, k = 0$		
0	240	275
1	43	42
2	73	68
3	37	12
4	37	99
5	63	57
7	50	49
8	93	114
10	13	5
12	43	47
13	26	20
$h = 7, k = 0$		
1	190	219
2	150	171
3	57	54
4	63	63
5	90	109
6	53	45
7	63	72
9	83	81
10	33	32
11	53	55
14	43	38
17	13	14
$h = 8, k = 0$		
0	214	242
1	37	29
2	59	53
3	79	78
4	140	151
5	46	45
6	63	59
7	26	23
8	79	83
10	13	14
12	77	84
$h = 9, k = 0$		
1	63	58
2	170	183
3	63	68
4	63	64
5	97	107
6	43	42
7	30	35
8	39	26
9	70	66
10	33	27
11	30	40
12	23	25
14	26	16
17	13	13
$h = 10, k = 0$		
0	170	173
1	66	61
2	23	21
3	30	21
4	59	65
5	46	45
6	46	46
7	39	33
8	57	61
9	50	44
10	37	23
11	30	31
12	53	54
16	13	22
$h = 11, k = 0$		
1	110	106
2	83	81
3	53	60
5	70	65
6	26	21
7	57	66
9	53	49
10	39	40
11	17	26
17	17	15
$h = 12, k = 0$		
0	57	53
1	13	12
3	39	43
4	66	66
5	70	56
7	63	68
8	63	60
9	43	42
11	19	24
$h = 13, k = 0$		
1	77	68
2	77	62
3	117	114
5	37	31
6	90	88
8	26	26
9	63	51
10	43	38
11	57	59
13	30	24
$h = 14, k = 0$		
0	93	96
1	63	47
3	50	57
4	43	35
5	59	57
7	57	68
8	46	44
10	33	22
11	17	21
$h = 15, k = 0$		
1	57	52
2	99	99
3	57	57
4	30	29
5	86	90
6	79	76
7	37	40
9	37	33
10	50	44
11	46	43
13	17	18
14	33	37
17	10	4
$h = 16, k = 0$		
0	90	97
1	77	72
2	37	36
3	70	72
4	33	22
5	63	63
7	37	36
8	53	53
9	43	39
10	50	35
12	30	32
13	23	17
17	10	14
$h = 17, k = 0$		
1	50	42
2	79	90
3	46	46
5	17	12
6	37	26
7	13	24
8	17	16
9	39	32
10	53	58
11	17	16
13	17	12
14	13	13
$h = 18, k = 0$		
0	30	25
1	77	75
3	30	39
4	26	24
5	17	12
7	43	44
8	46	48
11	26	25
12	17	16
13	23	21
$h = 19, k = 0$		
1	39	27
2	63	51
3	37	39
4	13	19
5	37	35
6	39	31
9	17	17
10	37	26
11	17	26
$h = 20, k = 0$		
0	46	42
1	59	49
3	57	48
4	37	32
5	43	35
6	17	12
7	50	52
9	23	17
11	17	14
13	13	18
$h = 21, k = 0$		
1	46	46
2	57	50
5	37	29
6	59	58
9	23	14
10	37	25
11	17	7
$h = 22, k = 0$		
0	19	17
1	50	39
3	43	41
4	37	30
5	59	52
7	30	28
9	37	38
11	17	18
13	13	13
15	10	17
$h = 23, k = 0$		
1	19	26
2	46	49
6	63	58
10	39	40
14	10	9
$h = 24, k = 0$		
1	46	45
2	19	19
3	43	32
5	30	31
7	37	41
9	30	31
10	17	6
11	17	19
13	17	12
$h = 25, k = 0$		
2	43	37
6	43	38
9	17	21
10	26	18
$h = 26, k = 0$		
0	30	25
1	30	29
3	30	19
5	17	14
7	37	32
9	17	9
11	13	19
$h = 27, k = 0$		
2	43	38
6	23	21
10	23	14
$h = 28, k = 0$		
1	43	42
3	43	40
5	17	20
9	13	9
$h = 29, k = 0$		
2	43	38
6	39	31
10	17	13
$h = 30, k = 0$		
0	17	19
1	23	24
3	23	22
5	17	12
7	13	20
9	13	13
$h = 31, k = 0$		
2	30	28
6	13	26
10	17	12
$h = 32, k = 0$		
1	17	20
5	19	23
7	13	13
9	10	14
$h = 33, k = 0$		
2	19	15
6	13	17
$h = 34, k = 0$		
1	13	17
3	13	9
5	13	16
$h = 35, k = 0$		
2	23	21
$h = 0, k = 1$		
1	134	144
2	153	133
3	43	43
4	22	11
5	86	86
6	13	7
7	109	107
8	19	6
9	49	49
10	20	24
11	47	45
13	55	50
16	15	11
$h = 1, k = 1$		
0	79	70
1	88	80
2	153	147
3	19	16
4	38	41
5	34	37
6	115	119
7	38	25
8	15	12
9	19	17
10	72	92
11	19	15
12	15	13
14	41	42
$h = 2, k = 1$		
0	130	129
1	30	22
2	130	124
3	111	110
4	26	27
5	88	91
6	49	44
7	107	109
8	26	19
9	57	61
11	41	49
12	19	18
13	41	42
14	15	13
15	15	14
16	15	9
$h = 3, k = 1$		
0	118	88
1	88	77
2	160	170
3	30	32
4	26	21
5	60	68
6	96	114
7	57	42
8	30	25
10	76	83
11	22	24
12	19	22
14	45	42
15	15	17
$h = 4, k = 1$		
0	88	73
1	126	84
2	53	42
3	149	136
4	68	45
5	122	126
6	45	36
7	92	97
8	38	47
9	57	57
11	45	50
12	19	16
13	19	16
14	15	13
15	15	18
16	15	10
$h = 5, k = 1$		
0	183	164
1	141	116
2	214	224
3	49	55
4	41	43
6	134	132
7	30	20
9	26	23
10	49	54
11	15	11
14	45	48
$h = 6, k = 1$		
0	115	93
1	164	152
2	88	84
3	64	64
4	60	46
5	79	88
6	30	25
7	68	66
8	45	42
9	41	49
10	34	22
11	41	43
12	15	13
13	22	31
15	15	22
16	15	14
$h = 7, k = 1$		
0	79	74
1	26	23
2	191	204
3	45	49
4	49	55
5	38	36
6	68	82
7	41	36
9	30	35
10	60	61
11	15	9
12	15	14
13	15	14
14	41	41
15	15	14
$h = 8, k = 1$		
0	84	84
1	103	105
2	49	43
3	99	89
4	49	56
5	76	84
6	30	22
7	26	27
8	41	36
9	53	59
11	38	37
12	22	25
13	15	25
15	15	10
16	15	12
$h = 9, k = 1$		
0	26	14
1	88	92
2	134	133
3	41	38
4	11	20
5	68	67
6	64	71
7	45	43
9	22	30
10	45	46
11	15	13
12	15	10
14	26	20
15	15	11
$h = 10, k = 1$		
0	92	95
1	103	98
2	53	49
3	84	83
4	72	86
5	76	92
6	11	16
7	64	58
8	26	26
9	30	27
10	19	21
11	41	44
12	45	47
14	15	8
16	15	9
$h = 11, k = 1$		
0	19	17
1	34	39
2	111	104
3	64	65
4	30	32
5	68	50
6	84	87
7	30	31
8	22	13
9	45	50
10	34	30
11	22	15
12	30	20
13	15	17
14	22	18
$h = 12, k = 1$		
0	41	46
1	60	60
2	22	23
3	134	131
4	76	88
5	76	72
6	11	12
7	72	69
8	45	45
9	41	47
10	22	19
11	15	19
12	41	33
13	15	19
15	19	21
16	15	15
$h = 13, k = 1$		
0	22	27
1	41	38
2	118	106
3	38	35
4	38	42
5	26	18
6	64	63
7	38	37
9	22	23
10	49	51
13	15	11
14	19	24
$h = 14, k = 1$		
0	72	70
1	53	58
2	26	32
3	88	93
4	79	86
5	38	47
7	41	37
8	41	45
9	30	40
10	22	13
11	15	16
12	26	23
13	15	21
15	15	13
16	11	15
$h = 15, k = 1$		
0	11	6
1	49	54
2	88	89
3	38	44
4	15	15
5	38	39
6	53	57
7	45	48
9	19	16
10	41	43
13	15	16
14	19	12
15	15	14
$h = 16, k = 1$		
0	79	80
1	49	52
2	26	19
3	53	49
4	76	90
5	26	27
7	34	24
8	45	36
9	22	25
10	22	18

TABLE 1. (*Continued.*)

11	19	16
12	26	22
13	15	19
$h = 17, k = 1$		
0	22	26
1	45	42
2	49	42
3	68	79
5	60	59
6	34	32
7	41	43
8	19	14
9	22	24
10	22	24
11	34	34
12	15	13
15	15	4
$h = 18, k = 1$		
0	76	79
1	30	25
3	45	42
4	38	44
5	34	34
6	15	13
7	41	33
8	53	52
9	22	23
11	22	9
12	26	19
13	15	8
15	15	12
$h = 19, k = 1$		
1	41	47
2	49	48
3	41	47
5	49	57
6	19	13
7	41	45
8	19	17
9	22	28
10	15	16
11	22	16
12	15	6
$h = 20, k = 1$		
0	68	69
1	41	37
3	41	43
4	49	53
5	34	35
6	19	17
7	34	27
8	45	47
9	22	27
10	15	17
11	19	13
12	22	18
13	15	8
$h = 21, k = 1$		
1	38	44
2	41	34
3	45	50
5	38	37
6	22	19
7	34	34
11	15	13
13	15	17
$h = 22, k = 1$		
0	49	39
1	15	15
3	30	29
4	57	67
5	19	26
6	15	13
7	15	13
8	38	38
9	15	21
11	15	11
12	19	18
$h = 23, k = 1$		
1	49	48
2	19	18
3	38	41
5	45	45
6	15	12
7	26	20
8	15	7
10	15	12
11	15	17
$h = 24, k = 1$		
0	57	56
4	53	48
8	30	31
12	22	16
$h = 25, k = 1$		
1	49	51
3	34	25
5	30	26
7	38	35
9	22	23
$h = 26, k = 1$		
0	41	31
4	38	25
8	22	21
12	22	17
$h = 27, k = 1$		
1	30	29
3	30	27
5	30	27
7	26	27
9	19	21
$h = 28, k = 1$		
0	30	21
4	41	42
7	3	7
8	15	13
12	19	14
$h = 29, k = 1$		
1	26	25
3	22	22
5	26	28
7	19	18
9	15	15
$h = 30, k = 1$		
0	30	25
4	34	32
8	19	19
$h = 31, k = 1$		
1	19	14
3	15	11
5	15	12
7	15	17
9	11	11
$h = 32, k = 1$		
0	19	15
4	22	15
8	19	18
$h = 33, k = 1$		
3	15	9
5	15	16
7	11	7
$h = 34, k = 1$		
0	15	10
4	15	17
$h = 35, k = 1$		
3	11	12
5	15	19
$h = 36, k = 1$		
0	15	20
4	11	13
$h = 0, k = 2$		
0	145	186
1	45	48
2	26	16
3	15	20
4	166	154
5	51	46
7	34	42
8	94	93
9	34	24
10	38	28
11	15	10
12	51	50
13	17	8
16	26	31
$h = 1, k = 2$		
0	22	8
1	99	121
2	45	48
3	149	154
4	26	16
5	103	92
6	26	19
7	68	77
8	38	20
9	34	42
10	38	18
11	41	38
13	38	38
14	15	11
$h = 2, k = 2$		
0	240	250
1	49	74
2	45	30
3	15	20
4	149	156
5	22	21
6	53	40
7	34	41
8	76	78
9	34	21
10	26	23
11	26	16
12	34	34
13	22	19
14	15	13
16	22	25
$h = 3, k = 2$		
0	22	30
1	88	122
2	60	63
3	84	88
4	26	15
5	111	98
6	76	39
7	88	83
8	22	10
9	45	45
10	11	9
11	41	33
12	19	20
13	22	20
14	15	5
$h = 4, k = 2$		
0	134	149
1	92	100
2	38	21
3	22	9
4	118	135
5	22	25
6	34	21
7	41	23
8	76	62
9	22	13
11	15	15
12	30	33
13	22	10
14	15	12
16	11	20
$h = 5, k = 2$		
0	57	47
1	111	125
2	57	32
3	64	63
4	19	6
5	122	118
6	30	39
7	76	73
8	11	11
9	34	37
10	22	20
11	22	29
12	30	28
13	26	24
$h = 6, k = 2$		
0	153	139
1	38	28
2	41	24
3	72	64
4	118	132
5	84	67
6	64	54
7	11	24
8	57	58
9	38	35
10	19	15
11	15	6
12	53	53
13	15	16
$h = 7, k = 2$		
0	7	17
1	141	154
2	118	114
3	41	42
4	64	46
5	92	89
6	45	43
7	72	63
9	53	56
10	26	19
11	30	33
13	15	18
14	19	12
15	19	22
$h = 8, k = 2$		
0	103	88
1	72	63
2	68	43
3	38	38
4	149	145
5	76	54
6	19	11
7	26	18
8	88	85
9	38	32
10	11	8
11	30	18
12	45	43
13	19	10
16	19	18
$h = 9, k = 2$		
0	38	8
1	88	91
2	57	59
3	79	50
4	26	23
5	92	93
6	76	80
7	72	68
9	53	56
10	30	23
11	34	39
12	15	7
13	19	17
$h = 10, k = 2$		
0	84	81
1	64	64
2	64	60
3	41	38
4	134	124
5	30	18
6	19	3
7	26	29
8	79	69
9	15	19
11	19	32
12	41	37
13	19	11
16	11	10
$h = 11, k = 2$		
0	34	20
1	41	39
2	72	70
3	30	32
4	26	27
5	64	56
6	38	44
7	38	44
8	15	20
9	45	42
10	26	21
11	19	19
13	38	35
14	19	16
$h = 12, k = 2$		
0	68	62
1	53	45
2	22	20
3	45	49
4	79	79
5	41	50
7	30	36
8	57	62
9	41	26
10	22	18
11	26	24
12	34	28
13	15	7
16	15	15
$h = 13, k = 2$		
0	68	64
1	64	72
2	88	76
3	34	30
4	38	44
5	64	58
6	45	54
7	30	35
9	19	20
10	34	28
11	22	19
13	19	14
14	19	15
15	15	16
$h = 14, k = 2$		
0	103	116
1	64	56
2	30	22
3	88	90
4	53	58
5	34	25
6	22	24
7	34	32
8	38	29
9	30	35
11	19	14
12	26	20
13	19	12
16	15	13
$h = 15, k = 2$		
1	38	37
2	92	87
3	72	75
4	26	23
5	60	64
6	19	59
7	26	20
9	26	20
10	38	32
11	26	28
13	19	13
14	15	21
$h = 16, k = 2$		
0	76	69
1	41	39
2	19	17
3	41	48
4	41	42
5	22	13
7	41	36
8	30	27
9	26	23
11	22	32
12	30	23
13	15	16
15	15	14
16	11	8
$h = 17, k = 2$		
1	38	33
2	57	59
3	26	28
4	30	24
5	45	55
6	53	65
7	15	15
9	26	24
10	38	41
11	22	19
13	15	11
14	19	15
$h = 18, k = 2$		
0	30	30
1	53	59
3	30	28
4	30	23
5	30	30
6	22	31
7	22	22
8	41	40
10	22	20
11	22	21
12	19	13
13	15	13
14	11	8
16	11	9
$h = 19, k = 2$		
1	22	26
2	45	41
4	15	13
5	30	24
6	19	69
7	30	26
8	15	16
9	22	18
10	38	36
13	15	9
14	11	4
$h = 20, k = 2$		
0	19	14
1	41	46
2	11	7
3	26	25
4	34	32
5	34	27
7	26	30
8	19	22
11	19	23
12	19	14
13	15	13
14	11	6
$h = 21, k = 2$		
1	30	20
2	57	61
3	26	24
4	30	32
5	30	23
6	34	23
7	22	26
8	15	13
10	30	25
14	15	15
$h = 22, k = 2$		
1	30	26
2	15	20
3	53	67
4	26	22
5	26	16
7	41	36
9	34	32
11	15	12
13	11	14
$h = 23, k = 2$		
0	19	12
2	49	49
4	15	14
5	19	14
6	41	33
7	15	20
9	30	22
10	26	25
14	11	14
$h = 24, k = 2$		
0	22	27
1	41	44
3	34	41
5	30	25
6	15	8
7	15	20
9	22	20
11	15	14
13	11	15
$h = 25, k = 2$		
2	30	31
6	45	45
9	19	10
10	19	17
$h = 26, k = 2$		
1	30	37
3	19	15
5	26	25
6	15	17
7	15	15
9	15	13
11	11	13
$h = 27, k = 2$		
2	26	19
4	15	14
6	38	33
10	15	20
$h = 28, k = 2$		
0	15	15
1	22	21
3	19	21
5	19	11
7	15	13
9	15	13
11	15	13
$h = 29, k = 2$		
2	30	31
6	19	14
10	15	15
$h = 30, k = 2$		
1	26	28
3	19	25
5	22	25
7	15	13
9	11	18
$h = 31, k = 2$		
2	26	30
6	15	16
10	11	8
$h = 32, k = 2$		
1	15	21
5	15	20
7	15	13
$h = 33, k = 2$		
2	19	18
$h = 35, k = 2$		
2	11	16
$h = 37, k = 2$		
2	11	16
$h = 0, k = 3$		
1	49	55
2	38	56
3	88	92
4	22	23
5	49	50
6	34	31
7	64	71
8	7	24
9	53	50
11	38	40
13	41	34
$h = 1, k = 3$		
1	41	48
2	64	99
3	38	20
5	7	16
6	79	82
7	41	26
9	26	15
10	49	45
11	11	3
14	30	28
$h = 2, k = 3$		
0	64	55
1	53	66
2	11	23
3	76	101
4	49	11
5	72	67
6	26	19
7	68	71
8	45	30
9	64	59

TABLE 1. (*Continued.*)

11	26	23
12	30	8
13	22	18
14	15	12
$h = 3, k = 3$		
1	30	33
2	72	108
3	30	13
4	22	8
5	45	29
6	103	99
7	22	14
8	7	12
9	38	9
10	64	63
11	26	15
12	11	11
13	20	15
14	30	26
$h = 4, k = 3$		
1	38	40
2	15	6
3	57	64
4	26	21
5	60	56
6	22	12
7	57	57
8	68	38
9	64	54
11	30	36
12	22	13
13	15	3
14	11	3
$h = 5, k = 3$		
1	7	13
2	99	126
3	22	13
4	57	36
5	41	45
6	96	89
7	22	14
8	26	24
10	57	51
11	15	9
13	19	19
14	34	32
$h = 6, k = 3$		
0	49	41
1	64	67
2	38	39
3	96	91
4	11	33
5	72	67
6	22	16
7	41	41
8	34	25
9	49	48
11	26	25
12	15	8
13	19	14
$h = 7, k = 3$		
0	26	21
1	49	53
2	96	103
3	30	17
4	15	16
5	30	37
6	96	79
7	41	32
8	11	15
10	30	26
11	34	22
14	26	22
$h = 8, k = 3$		
0	30	29
1	96	96
2	26	28
3	84	74
4	72	40
5	45	46
6	26	24
7	53	46
8	26	19
9	34	28
10	19	12
11	34	30
12	34	21
13	26	19
$h = 9, k = 3$		
0	45	51
1	53	47
2	84	86
3	22	21
4	41	30
5	30	11
6	57	59
7	26	13
8	7	9
9	34	17
10	38	28
11	38	26
13	15	12
14	26	16
$h = 10, k = 3$		
0	72	77
1	68	74
2	57	44
3	60	57
4	68	56
5	57	53
7	34	33
8	49	30
9	53	52
10	15	19
11	22	19
12	38	27
13	19	13
$h = 11, k = 3$		
0	41	30
1	41	45
2	72	70
3	57	46
4	15	11
5	30	18
6	60	62
7	38	34
9	34	27
10	38	38
11	11	23
13	11	5
14	26	20
$h = 12, k = 3$		
0	53	47
1	41	34
2	22	21
3	76	74
4	60	65
5	34	32
7	34	28
8	49	39
9	38	32
11	19	14
12	19	14
13	19	14
$h = 13, k = 3$		
0	15	6
1	57	55
2	96	89
3	34	24
4	38	25
5	22	16
6	60	60
7	38	34
9	30	34
10	38	29
11	11	8
13	11	13
14	15	18
$h = 14, k = 3$		
0	38	44
1	41	37
2	30	33
3	60	58
4	41	48
5	45	33
6	15	19
7	38	37
8	34	30
9	34	33
10	11	21
11	11	13
12	22	17
13	11	12
$h = 15, k = 3$		
1	49	47
2	49	41
3	49	44
5	30	33
6	49	47
7	26	27
10	19	21
11	26	29
14	7	9
$h = 16, k = 3$		
0	49	48
1	41	44
3	34	29
4	38	36
5	30	29
7	30	37
8	38	36
9	11	15
11	19	13
12	19	12
$h = 17, k = 3$		
1	45	46
2	34	33
3	30	31
4	7	23
5	26	29
6	38	41
7	34	21
9	19	22
10	22	19
11	26	17
$h = 18, k = 3$		
0	53	59
1	26	28
2	26	29
3	30	29
4	49	52
5	26	26
6	11	10
7	15	18
8	41	40
9	19	14
11	11	9
12	15	18
$h = 19, k = 3$		
1	30	33
2	30	29
3	38	43
4	15	15
5	30	30
6	22	20
7	19	15
9	19	19
10	15	17
11	26	23
14	11	13
$h = 20, k = 3$		
0	45	55
1	11	16
2	19	19
3	41	39
4	34	36
5	11	13
7	11	7
8	38	38
9	19	18
12	11	14
$h = 21, k = 3$		
0	19	22
1	41	47
2	41	40
3	38	34
5	26	27
6	19	13
7	11	11
8	11	24
9	15	18
11	15	18
14	7	12
$h = 22, k = 3$		
0	41	54
1	19	22
2	19	17
3	26	29
4	30	36
5	11	13
8	30	29
$h = 23, k = 3$		
1	30	44
2	19	22
3	26	27
5	11	12
6	15	10
7	11	17
9	11	15
11	11	12
$h = 24, k = 3$		
0	26	21
2	11	10
4	30	31
6	15	14
7	11	14
8	22	26
12	7	11
$h = 25, k = 3$		
1	19	17
3	22	28
5	11	19
7	11	13
9	15	17
11	7	11
$h = 26, k = 3$		
0	26	39
1	11	7
2	15	19
4	30	36
7	11	9
8	22	24
$h = 27, k = 3$		
1	26	33
3	19	19
7	11	10
9	7	23
$h = 28, k = 3$		
0	26	31
2	11	9
3	11	13
4	15	18
8	22	21
$h = 29, k = 3$		
1	22	25
3	11	13
7	7	8
$h = 30, k = 3$		
0	19	21
4	22	16
8	7	11
$h = 32, k = 3$		
0	7	13
4	11	16
8	11	13
$h = 34, k = 3$		
0	11	22
$h = 36, k = 3$		
0	7	14
$h = 0, k = 4$		
0	99	125
1	38	44
2	11	11
3	30	21
4	66	78
6	26	25
7	15	36
8	26	17
9	22	10
12	34	34
$h = 1, k = 4$		
1	38	60
2	26	18
3	64	72
4	38	23
5	60	65
6	34	10
7	45	38
8	22	18
9	30	29
10	26	8
11	26	22
$h = 2, k = 4$		
0	84	114
1	22	30
4	72	82
5	26	19
6	34	30
7	15	15
8	49	54
9	30	11
12	26	25
$h = 3, k = 4$		
0	26	20
1	49	59
2	22	32
3	60	66
4	26	34
5	60	66
6	41	19
7	38	34
8	15	6
9	30	35
10	26	8
$h = 4, k = 4$		
0	57	65
1	26	7
2	19	15
4	88	94
5	45	39
8	60	58
9	26	16
11	26	6
12	26	26
$h = 5, k = 4$		
0	26	20
1	53	60
2	30	31
3	41	42
4	34	21
5	30	40
6	22	25
7	72	62
8	34	34
9	38	33
10	34	14
$h = 6, k = 4$		
0	57	58
1	38	35
2	34	19
3	22	11
4	88	90
5	38	35
6	34	19
7	19	22
8	34	38
9	26	15
12	26	26
$h = 7, k = 4$		
1	53	51
2	26	31
3	34	31
4	26	31
5	64	67
6	34	28
7	57	45
8	22	20
9	26	23
10	26	7
11	26	27
$h = 8, k = 4$		
0	68	66
1	30	28
3	30	28
4	53	56
5	34	25
6	19	20
8	22	22
12	38	34
$h = 9, k = 4$		
1	60	58
2	60	44
3	34	34
4	15	14
5	38	42
6	26	16
7	53	44
9	41	45
10	26	17
11	26	19
$h = 10, k = 4$		
0	57	58
1	41	37
3	34	29
4	57	62
5	38	27
7	26	17
8	38	39
9	19	13
12	26	25
$h = 11, k = 4$		
1	53	44
2	45	38
3	41	40
4	15	15
5	49	48
6	45	49
7	38	33
9	19	19
10	19	16
$h = 12, k = 4$		
0	53	56
1	34	29
2	19	9
3	30	35
4	68	63
5	30	27
7	22	25
8	34	30
9	19	19
$h = 13, k = 4$		
1	34	31
2	15	19
3	34	29
4	30	27
5	45	45
6	38	34
7	26	22
8	19	13
10	19	19
11	26	10
$h = 14, k = 4$		
0	38	30
1	34	29
2	15	3
3	26	28
4	38	39
5	38	33
7	22	25
8	26	24
9	26	27
$h = 15, k = 4$		
0	19	19
1	34	24
2	41	44
3	15	14
4	38	31
5	22	20
6	22	30
7	22	20
$h = 16, k = 4$		
0	38	44
1	45	42
2	15	13
3	41	38
4	22	24
5	34	30
6	19	13
7	19	21
8	30	29
$h = 17, k = 4$		
1	34	38
2	49	53
3	34	40
5	34	29
6	34	28
7	22	21
$h = 18, k = 4$		
0	34	43
1	22	20
3	30	28
4	41	42
5	34	29
7	19	17
$h = 19, k = 4$		
1	26	23
2	41	38
5	22	23
6	19	22
$h = 20, k = 4$		
0	19	19
1	26	21
3	26	25
4	26	28
5	22	25
7	19	16
$h = 21, k = 4$		
2	34	28
4	19	10
6	30	32
$h = 22, k = 4$		
0	19	18
1	30	32
3	30	32
5	22	25
$h = 23, k = 4$		
2	30	26
6	19	28
$h = 24, k = 4$		
3	26	32
$h = 25, k = 4$		
2	26	27
$h = 27, k = 4$		
2	26	34
$h = 0, k = 5$		
1	24	34
2	6	21
3	33	49
4	13	7
5	31	33
6	26	36
7	33	42
8	26	8
9	33	34
11	17	16
12	13	4
13	13	6
$h = 1, k = 5$		
2	50	67
3	17	17
4	10	13
5	17	30
6	26	30
7	13	10
10	26	35
$h = 2, k = 5$		
1	39	51
3	17	27
4	23	12
5	39	42
7	46	53
9	26	24
$h = 3, k = 5$		
0	19	6
1	10	12
2	46	57
3	17	20
4	19	9
6	43	49
7	23	5
8	26	28

TABLE 1. (*Continued.*)

10	26	27
$h = 4, k = 5$		
1	26	41
2	17	24
3	26	34
4	19	2
5	50	45
6	23	14
7	43	42
8	26	24
9	33	31
$h = 5, k = 5$		
0	10	6
2	50	51
3	37	32
4	19	15
5	26	30
6	39	37
7	30	23
9	13	7
10	26	31
$h = 6, k = 5$		
0	10	17
1	43	46
3	39	42
4	43	25
5	26	22
7	30	24
8	33	18
9	26	17
$h = 7, k = 5$		
2	63	61
3	33	29
4	10	13
5	43	38
6	23	21
7	13	14
9	13	7
10	26	30
$h = 8, k = 5$		
0	23	23
1	57	52
2	19	28
3	33	37
4	30	15
5	26	17
6	39	30
7	43	40
8	57	11
9	26	16
$h = 9, k = 5$		
1	26	22
2	63	56
3	30	21
6	39	30
7	17	16
9	26	17
10	26	26
$h = 10, k = 5$		
0	39	36
1	26	28
3	19	18
5	43	33
6	30	21
7	37	33
8	19	13
9	26	21
$h = 11, k = 5$		
1	30	28
2	43	45
4	39	25
5	17	12
6	37	33
7	26	22
8	13	9
9	19	14
10	26	23
$h = 12, k = 5$		
0	37	36
1	19	25
3	13	17
4	33	32
5	37	25
7	19	22
8	19	11
9	19	14
$h = 13, k = 5$		
0	23	27
1	23	21
2	43	34
3	39	31
4	17	21
5	37	23
6	33	31
7	33	24
$h = 14, k = 5$		
0	23	16
1	23	19
3	13	18
4	46	30
6	13	11
7	26	18
8	19	19
$h = 15, k = 5$		
1	23	21
2	46	39
3	39	26
4	17	20
5	26	23
6	13	9
7	13	9
$h = 16, k = 5$		
0	37	40
1	26	19
3	17	13
4	33	15
8	13	17
$h = 17, k = 5$		
1	26	23
2	26	30
3	17	17
5	26	22
$h = 18, k = 5$		
0	23	25
3	13	14
4	19	22
8	23	25
$h = 19, k = 5$		
3	26	29
$h = 20, k = 5$		
0	26	35
4	19	27
8	19	23
$h = 22, k = 5$		
0	23	26
$h = 0, k = 6$		
0	19	20
4	28	21
8	39	26
9	28	17
$h = 1, k = 6$		
1	23	35
3	28	32
5	19	20
9	28	16
$h = 2, k = 6$		
0	39	48
1	23	10
4	19	23
8	34	22
9	28	14
$h = 3, k = 6$		
1	19	32
2	23	21
3	28	29
5	39	38
6	28	12
7	53	43
9	28	19
$h = 4, k = 6$		
0	39	51
4	39	39
5	19	17
7	39	12
8	39	23
9	28	12
$h = 5, k = 6$		
1	28	22
2	19	5
3	28	32
5	34	31
6	34	20
7	28	16
$h = 6, k = 6$		
0	14	26
1	19	13
4	28	28
5	28	17
6	28	24
$h = 7, k = 6$		
1	19	18
3	19	18
7	14	12
9	23	16
$h = 8, k = 6$		
0	39	50
1	19	12
3	19	25
4	28	26
8	28	18
$h = 9, k = 6$		
1	19	29
7	23	22
$h = 10, k = 6$		
0	23	27
1	14	17
3	19	24
4	28	32
5	23	10
6	19	8
7	19	18
8	28	24
$h = 11, k = 6$		
3	14	21
5	23	22
6	28	13
7	23	17
$h = 12, k = 6$		
0	23	31
1	23	25
4	23	26
5	28	21
7	19	15
$h = 13, k = 6$		
0	23	21
1	14	11
2	23	29
5	28	24
6	19	23
$h = 14, k = 6$		
0	23	36
4	19	12
5	23	14
$h = 16, k = 6$		
0	23	29
2	19	4
$h = 17, k = 6$		
1	23	14
$h = 18, k = 6$		
2	19	11

RESULTS

The set of atomic parameters obtained from the last least-squares cycle is given in Table 2. The estimated standard deviations in the positions of the carbon, nitrogen, and oxygen atoms lie mostly in the range 0·03—0·05 Å. Apart from C–I, 1·96 Å (e.s.d. 0·03 Å), the estimated standard deviation (e.s.d.) of an average bond is thus about 0·06 Å with a corresponding limit of error (95% significance level) of about 0·12 Å. In these circumstances, the numerical values that have been derived for the individual bond distances from the parameters of Table 2 are of little interest and we do not reproduce or discuss

TABLE 2.

Calciferyl 4-iodo-5-nitrobenzoate : atomic parameters.

	x	*y*	*z*	*B* (Å²)
C(1)	0·1234	−0·102	−0·126	3·1
C(2)	0·1050	−0·008	−0·205	3·9
C(3)	0·0778	0·167	−0·175	2·9
C(4)	0·1021	0·301	−0·125	4·9
C(5)	0·1255	0·189	−0·047	2·7
C(6)	0·1233	0·252	0·033	3·7
C(7)	0·1427	0·168	0·111	2·4
C(8)	0·1458	0·268	0·192	2·9
C(9)	0·1271	0·444	0·218	2·9
C(10)	0·1491	0·018	−0·072	4·7
C(11)	0·0963	0·432	0·305	3·4
C(12)	0·1197	0·309	0·369	2·8
C(13)	0·1398	0·130	0·342	3·9
C(14)	0·1672	0·164	0·263	1·9
C(15)	0·1903	−0·041	0·246	3·7
C(16)	0·1958	−0·117	0·341	4·1
C(17)	0·1710	0·005	0·404	2·1
C(18)	0·1013	−0·018	0·321	2·6
C(19)	0·1927	0·010	−0·058	7·5
C(20)	0·1543	−0·112	0·484	3·3
C(21)	0·1253	0·017	0·541	7·2
C(22)	0·1898	−0·176	0·533	3·5
C(23)	0·2037	−0·340	0·554	4·6
C(24)	0·2401	−0·411	0·598	3·3
C(25)	0·2340	−0·493	0·680	9·8
C(26)	0·2115	−0·375	0·752	4·4
C(27)	0·2056	−0·694	0·687	6·0
C(28)	0·2670	−0·548	0·548	5·4
C(1′)	0·0290	0·335	−0·380	3·8
C(2′)	0·0448	0·510	−0·395	5·3
C(3′)	0·0301	0·622	−0·465	6·6
C(4′)	0·0062	0·575	−0·528	3·7
C(5′)	−0·0083	0·374	−0·513	3·3
C(6′)	−0·0014	0·227	−0·446	4·5
C(7′)	0·0341	0·200	−0·308	3·6
O(8′)	0·0650	0·269	−0·258	5·5
C(9′)	0·0160	0·052	−0·287	6·4
N(10′)	−0·0405	0·300	−0·582	3·1
O(11′)	−0·0221	0·281	−0·659	14·7
O(12′)	−0·0708	0·239	−0·565	6·9
I	−0·0086	0·742	−0·626	5·8

them here. It would hardly be possible on the basis of these bond distances alone even to distinguish double from single bonds with confidence. Nevertheless, the average distances for different types of bonds, based on formula (I) are reasonable, although associated with large average deviations in keeping with the above accuracy estimates. These average values are given in Table 3.

TABLE 3.

Average interatomic distances (Å) for different types of bond.

Type	Number	Range	Mean	Average devn.	Type	Number	Average Distance
					—C—N—	1	1·55
≥C—C′≤	18	1·40—1·66	1·54	0·06	—C═O	1	1·22
≥C—C═	7	1·41—1·60	1·45	0·04	$-\underset{\|}{\mathrm{C}}-\mathrm{O}-$	1	1·33
═C—C═	2	1·45—1·46	1·46	0·01	≥C—O—	1	1·51
					≥C—I	1	1·96
·—C⋯C—	6	1·26—1·58	1·42	0·09			
·—C═C—	4	1·27—1·44	1·35	0·06			
·—N⋯O	2	1·07—1·31	1·19	0·12			

The *B* values listed in Table 2 are associated with estimated standard deviations of up to 1 Å^2 and hence most of the variations in the thermal parameters among the different atoms have little physical meaning; the very high value of *B* for O(11′) probably only reflects the greater uncertainty attached to the placing of this atom which is confused by diffraction effects around the iodine atom.

In spite of the unreliability of individual bond distances and angles, the overall stereochemical relation of the atoms in the molecule are clear. In Fig. 3 the molecule is shown in projection down the *b*- and *c*-axes in the correct absolute configuration as defined by recent experiments;[6,7] the stereochemical configurations about the two asymmetric atoms, C(20) and C(24), can be described as *R* and *S*, respectively, where the secondary carbon atom substituents are given priority over the double bond.[8] This stereochemical arrangement about C(24) is the opposite to that proposed in our preliminary work but it was already described correctly in our second note and is in agreement with other recent stereochemical studies.[9] The conformation adopted by the side-chain in the crystal is interesting in that the main chain is not in the planar zigzag form, as can be seen from Fig. 3. This conformation appears, from consideration of models at least, to be rather favourable as far as non-bonded repulsive interactions are concerned. C(26) and C(27) are, respectively, antiperiplanar and synclinal with respect to C(28).

Rings C and D, as expected, are *trans*-fused. Ring D adopts the conformation with the two atoms at the ring junctions on opposite sides of the plane of the other three [C(13), + 0·47 Å; C(14), − 0·24 Å]; ring C is in the chair form and so is ring A. The *trans*-conjugated diene system, including the atoms C(10), C(4), C(5), C(6), C(7), C(8), C(9), and C(14), is planar to within 0·13 Å; however, if one takes the two halves of this system separately, the angle between the two planes, about the central C(6)–C(7) bond, is 9°. The *cis*-diene system is definitely non-planar; it seems best described in terms of two planes, one defined by atoms C(1), C(10), C(5), and C(19), the other by C(5), C(4), C(6), and C(10), which are at 54° to one another. The angle between the first of these planes and the *trans*-diene system is 52°. With this type of arrangement, too close contact between hydrogen atoms attached to C(7) and C(19) is avoided. In spite of the irregular interatomic distances present, all the atoms of the benzene ring lie within 0·02 Å of a single

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[6] Viscontini and Miglioretto, *Helv. Chim. Acta*, 1955, **38**, 930.

[7] Brenneisen, Tamm, and Reichstein, *Helv. Chim. Acta*, 1956, **39**, 1233.

[8] Cahn, Ingold, and Prelog, *Experientia*, 1956, **12**, 81.

[9] Maio and Romeo, *Gazzetta*, 1959, **89**, 1626.

plane; to this plane, the mean plane of the nitro-group is inclined at 60°, and the mean plane of the ester group at 12°.

The molecular packing is of an exceptionally intricate nature, as is evident from Fig. 4, and is one to which the unit-cell dimensions give no clue. The shortest intermolecular distances involve the esterified carboxyl group and the iodine atom and nitro-group and probably arise as a result of dipole interactions; they vary between 3·26 and 3·45 Å and are listed in Table 4. All other contacts involve distances greater than 3·5 Å. The iodine atom environment is particularly noteworthy. The atom lies almost midway

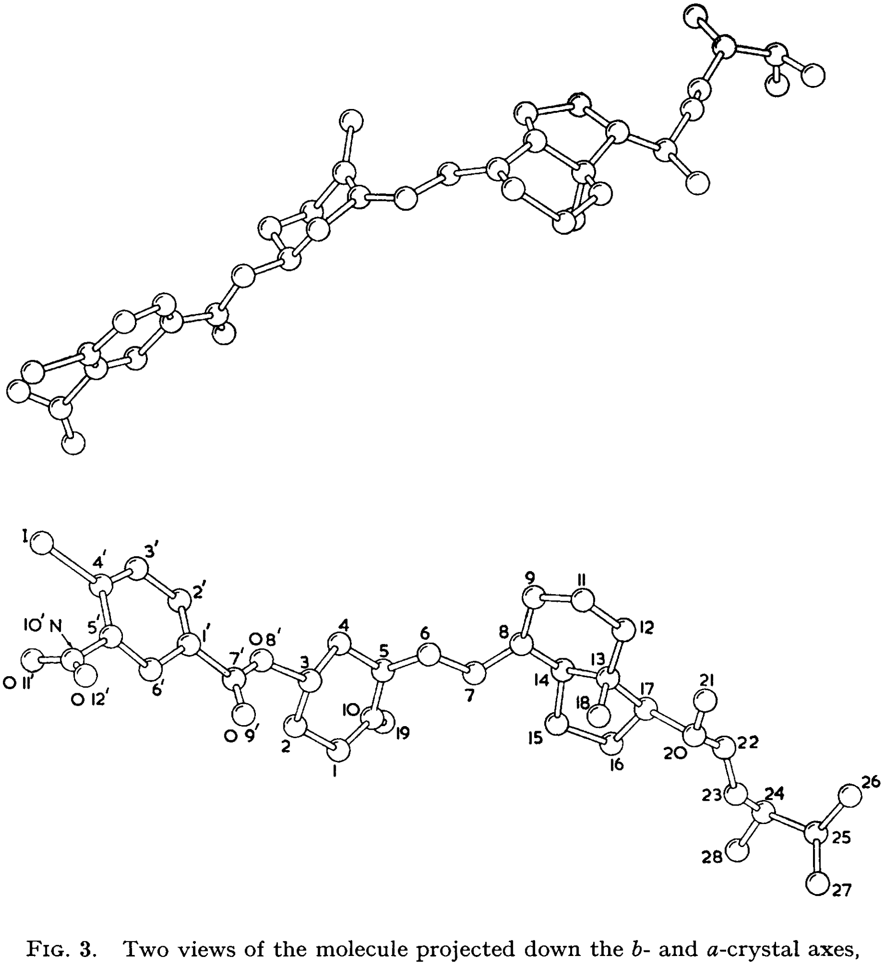

FIG. 3. Two views of the molecule projected down the *b*- and *a*-crystal axes, respectively, to show its stereochemical form.

Atoms not marked with an element symbol are carbon.

TABLE 4.

Short intermolecular contact distances (Å).

O(9') . . . C(7')	3·26	O(9') . . . C(1')	3·28	O(11') . . . I	3·45
O(9') . . . O(8')	3·28	O(9') . . . C(2')	3·38	Cf. O(11') . . . I	3·29 intramol.

between two nitro-groups, one in the same molecule and one in the succeeding molecule along the *b* axis so that the distance O(11′)–I, intra, 3·29 Å is very little shorter than O(11′)–I, inter, 3·45 Å. This seems significant in view of the usefulness of the iodonitrobenzoate group in promoting the crystallisation of a molecule as irregular in shape as calciferol.

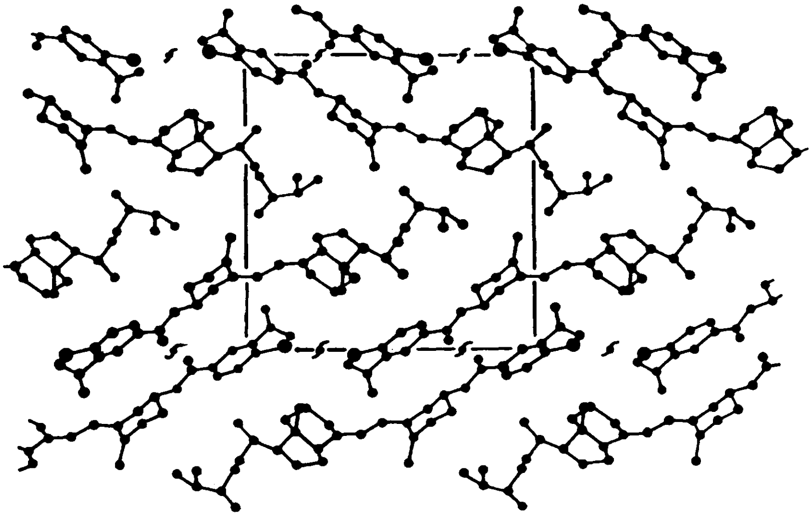

FIG. 4. The packing of molecules in the crystal, viewed down *b*. The *a*-axis points upwards, the *c*-axis to the right; the outlined portion is *a*/2 by *c*.

We are grateful to Mrs. M. Webster for her help during some of the intermediate stages of this investigation. Further, we gratefully acknowledge the gift of the calciferol used in this investigation by Dr. E. H. Carr (British Drug Houses Ltd.) and the co-operation, in carrying out the necessary computations, of the Mathematical Division of the National Physical Laboratory, England, the Numerical Analysis Research Department and later Computing Faculty of the University of California, Los Angeles, and of the Oxford University Computing Laboratory. We received technical assistance from Miss Ruth Cox and Mrs. U. Ledwith.

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[*Received, March* 19*th*, 1963.]

APPENDIX

Calciferyl 4-*iodo*-5-*nitrobenzoate*

By R. H. CORNFORTH and J. W. CORNFORTH.

Since the 4-iodo-5-nitrobenzoyl group has now been used as a heavy-atom marker in several investigations the preparative chemistry employed is reported here. Light petroleum used was the fraction of b. p. 60—80°.

4-*Iodo*-5-*nitrobenzoyl chloride*. *p*-Iodobenzoic acid (3·6 g.) was added to a mixture of concentrated sulphuric acid (13 ml.), fuming sulphuric acid (4 ml.; 20% SO_3), and fuming nitric acid (6 ml.; *d* 1·5). The mixture was warmed on a steam-bath until the solid dissolved and for ¼ hr. thereafter. To the cooled solution water was added dropwise without further cooling. The crystalline 4-iodo-5-nitrobenzoic acid was collected and recrystallised from aqueous methanol, forming yellow prisms (3·6 g.), m. p. 210°. This acid (3·6 g.) was warmed with phosphorus pentachloride (2·8 g.) and benzene (10 ml.) for ½ hr. on a steam-bath. The residue after evaporation at low pressure was recrystallised from dried light petroleum, to give 4-*iodo*-5-*nitrobenzoyl chloride* (3·4 g.) as pale yellow prisms, m. p. 40—41·5° (Found: C, 27·3; H, 1·2; N, 4·75. $C_7H_3ClINO_3$ requires C, 27·0; H, 1·0; N, 4·5%). When first prepared, this substance formed long yellow prismatic needles, m. p. 49—51°, from cyclohexane; this form was not again encountered.

Calciferyl 4-*iodo*-5-*nitrobenzoate*. Calciferol (326 mg.) and 4-iodo-5-nitrobenzoyl chloride (406 mg.) in pyridine (3·2 ml.) were heated at 95° for ½ hr. A few drops of water were added and, after a few minutes, ether and more water. The ether was washed with aqueous sodium carbonate before and after being washed with dilute sulphuric acid. The residue after evaporation was freed from ether and water by two evaporations at low pressure of its solution in benzene; it was redissolved in benzene–light petroleum (1 : 2) and put on a column of alumina (15 g.; previously washed with methyl formate). Elution with the same solvent mixture gave a yellow resin (467 mg.) which crystallised on dissolution in a little acetone and seeding with the original specimen (obtained by the same procedure except that chromatography was omitted, the product being precipitated from acetone by methanol and recrystallised from acetone). The yellow crystals (265 mg.; m. p. 115—117°) were recrystallised from acetone with slow cooling, to give deep yellow prisms (185 mg.) of *calciferyl* 4-*iodo*-5-*nitrobenzoate*, m. p. 117·5—118·5°, $[\alpha]_D^{20}$ +79° (*c* 0·73 in benzene) (Found: C, 62·7; H, 6·8; N, 2·2; I, 18·5. $C_{35}H_{46}INO_4$ requires C, 62·6; H, 6·9; N, 2·1; I, 18·9%). The crystallographic identity of this material with the original specimen was verified at Oxford.

The above iodonitrobenzoate (100 mg.) in benzene (2 ml.) was left at 0° for 19 hr. with a 3% solution of potassium hydroxide in methanol (8 ml.). Water and ether were added; the ether was washed with water, dried ($MgSO_4$), and evaporated at low pressure. The residue on recrystallisation from acetone gave calciferol (15 mg.), m. p. 113—115° alone or mixed with authentic material. The infrared spectra (in compressed KCl) of the product and of authentic calciferol were superimposable. Additional material (24 mg.) of the same m. p. and mixed m. p. was obtained from the mother-liquor by crystallisation from 90% methanol. Since the conditions of hydrolysis were too mild to effect appreciable thermal isomerisation of precalciferol[10] it follows that the iodonitrobenzoate was indeed a derivative of calciferol. A specimen of precalciferol was kindly supplied by Glaxo Laboratories Ltd. When treated with iodonitrobenzoyl chloride according to the original procedure it gave only traces of the ester, m. p. 117—118°.

National Institute for Medical Research, London N.W.7.

[10] Velluz and Amiard, *Compt. rend.*, 1949, **228**, 692, 853.