229. *The Crystal Structures of the Acid Salts of Some Monobasic Acids. Part V.*[1] *Rubidium Hydrogen Di-*o*-nitrobenzoate and Potassium Hydrogen Di-*p*-nitrobenzoate.*

By H. N. SHRIVASTAVA and J. C. SPEAKMAN.

Acid salts, MHX_2, of monocarboxylic acids, HX, can be divided into two classes: in *A*, the two acidic radicals are equivalent and joined by a hydrogen bond that is crystallographically symmetrical; in *B*, the acidic radicals are non-equivalent, and X^- and HX can be distinguished in the crystal structure. The infrared spectra of type *B* compounds are essentially a superposition of those of the free acid and the neutral salt, whilst the spectra of type *A* are anomalous. On the basis of their dissimilar spectra, it had been suggested that the acid potassium salts of *o*- and *p*-nitrobenzoic acid belong to types *A* and *B* respectively. A structural study with *X*-rays has now confirmed that the *o*-nitro-salt, examined in the form of its rubidium isomorph, has a structure of type *A*, with a short hydrogen bond. Overcrowding in the acid radical is avoided by twisting of the carboxyl group well out of the plane of the benzenoid ring and nitro-group. The structure of potassium hydrogen di-*p*-nitrobenzoate has also been determined, and has been more fully refined by partial three-dimensional analysis. This structure is confirmed as being of type *B*. It embodies a very short hydrogen bond ($O \cdots O = 2{\cdot}49$ Å), of a non-symmetrical kind. Significant differences between these two representative structures are described.

THE crystalline acid salts of monocarboxylic acids (HX) studied in this laboratory fall into two structural types, *A* and *B*. (These types correspond in part to the classification of a wider range of hydrogen-bonded compounds described by Blinc, Hadži, and Novak.[2]) In type *B*, of which ammonium hydrogen disalicylate hydrate is an example,[1] the acidic radicals in the formula, M^+X^-,HX, are crystallographically distinct; one of them can be recognised as the anion and the other as in the neutral molecule. In type *A*, of which potassium hydrogen bisphenylacetate[3] is an example and to which most of the acid salts belong, X^- and HX are crystallographically equivalent; they are related to one another

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[1] Part IV, Downie and Speakman, *J.*, 1954, 787.

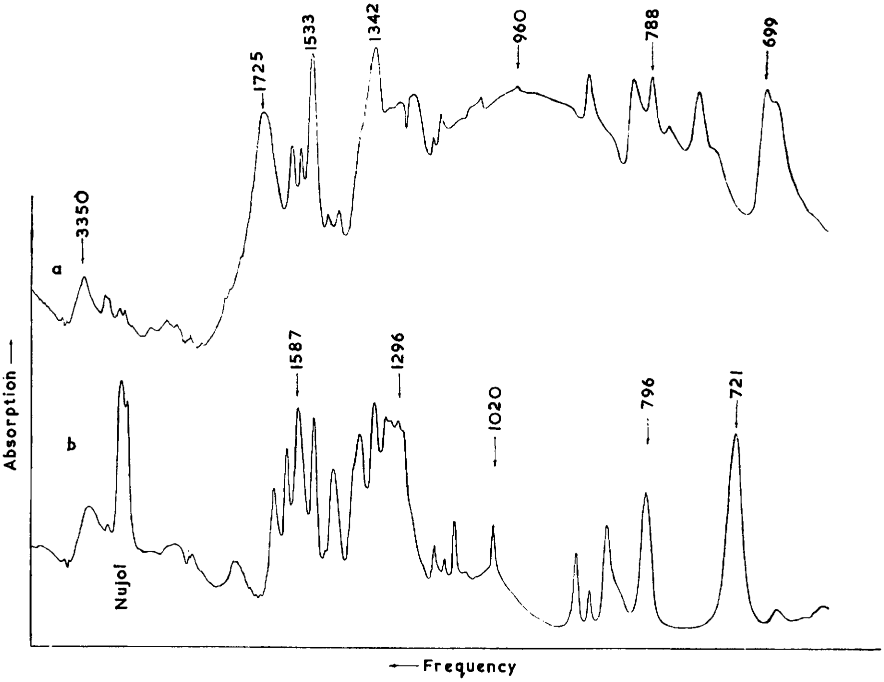
[2] Blinc, Hadži, and Novak, *Z. Elektrochem.*, 1960, **64**, 567.

[3] Part I, Speakman, *J.*, 1949, 3357.

by a symmetry element, across which they are linked by a hydrogen bond involving the acidic hydrogen atom. Such a bond, like those in the alkali bifluorides and a few other remarkable compounds, but unlike nearly all other hydrogen bonds, is therefore symmetrical—or, at least, formally so.

The infrared spectra of these acid salts have been studied particularly by Hadži and his co-workers,[4] who noticed that the two types give different types of spectrum. With type *B*, the spectrum approximates to a simple superposition of those of the free acid and neutral salt, each taken separately. With type *A* anomalous spectra are found: the OH stretching frequency, even if it be recognisable at all, is shifted to a much lower value than its normal one of ~3500 cm.$^{-1}$; and there is a wide plateau of high absorption spreading for several hundred wave-numbers on either side of its culmination somewhere in the region 700—1000 cm.$^{-1}$. These anomalies are presumed to be connected in some way with the symmetrical hydrogen bonding.[5]

FIG. 1. *Infrared spectra of* (a) *potassium hydrogen di-*o*-nitrobenzoate in* KCl *disc, and of* (b) *potassium hydrogen di-*p*-nitrobenzoate in Nujol mull. The frequencies marked are in cm.*$^{-1}$.



Acid potassium salts of *o*- and *p*-nitrobenzoic acid would have been expected to have similar infrared spectra. In fact they differ greatly, as can be seen in Fig. 1, and in the sense described above; and on this basis Hadži[6] predicted that their crystal structures would differ, the *ortho*-compound belonging to type *A*, the *para*-compound to type *B*. The *X*-ray analyses recorded in this paper confirm his prediction. The structure of the acid *o*-nitrobenzoate has for convenience been studied in the isomorphous rubidium salt. This analysis has been pursued only far enough to prove the structure to be of the symmetrical type (*A*). The structure of potassium hydrogen di-*p*-nitrobenzoate turned out to be a new variant of type *B*, and this analysis has been highly refined by two-, and partial three-, dimensional methods.

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[4] *E.g.*, Hadži and Novak, *Nuovo cim.*, 1955, **2**, Suppl. [x], 715; "Infrared Spectra of, and Hydrogen Bonding in, Some Acid Salts of Carboxylic Acids," University of Ljubljana, 1960.

[5] *E.g.*, Albert and Badger, *J. Chem. Phys.*, 1958, **29**, 1193.

[6] Hadži, personal communication, 1958.

EXPERIMENTAL

Acid salts of the nitrobenzoic acids were first described by Farmer.[7] In general they are easily prepared by dissolving 1 mole of the acid and ½ equivalent of alkali, or alkaline carbonate, in a little hot aqueous alcohol, and allowing the solution to cool, or evaporate. They may be recrystallised from the same medium; though, since these acid salts decompose into free acid and neutral salt in solution, care is needed lest the former crystallise out and be mistaken for the acid salt. There is no difficulty in preparing isomorphous potassium and rubidium acid *o*-nitrobenzoates. Both were studied with *X*-rays so far as to demonstrate their isomorphism; but structure analysis was mainly restricted to the rubidium compound, as the heavier atom led to a readier solution of the phase problem and as an accurate determination of atomic co-ordinates was not intended. From *p*-nitrobenzoic acid an acid potassium salt is easily made. But the failure of repeated attempts to prepare isomorphous ammonium, rubidium, or thallous salts suggested that the structure obtaining in the potassium compound depends critically upon the radius of the cation.

Crystal data were derived from single-crystal rotation, oscillation, and moving-film photographs; intensities were determined visually from multiple-film Weissenberg exposures; copper $K\alpha$-radiation was used throughout. For calculating structure factors, F_c, standard [8] atomic-scattering functions were used.

RUBIDIUM HYDROGEN DI-*o*-NITROBENZOATE

Crystal Data and Structure Analysis.—$RbH(C_7H_4NO_4)_2$, $M = 418{\cdot}7$, triclinic pinakoidal $a = 13{\cdot}8_0$, $b = 4{\cdot}74$, $c = 6{\cdot}08$ Å, $\alpha = 100{\cdot}5°$, $\beta = 99{\cdot}4°$, $\gamma = 95{\cdot}0°$, $U = 383{\cdot}0$ Å^3, $D_m = 1{\cdot}82$ (by flotation in $CHBr_3$-CCl_4), $Z = 1$, $D_c = 1{\cdot}815$, $F(000) = 208$, absorption coefficient for *X*-rays 53 cm.$^{-1}$.

An unsophisticated application of the Wilson-ratio and $N(z)$ tests to the $h0l$-intensity data suggested that the space group was $P1$. This erroneous conclusion was due to the effect of the heavy atom. When proper allowance was made for it, by Sim,[9] centrosymmetry was indicated, requiring the space group to be $P\bar{1}$. The stoicheiometric molecule, of the above formula, must therefore possess a centre of symmetry, and the rubidium and acidic hydrogen atoms must be in special positions of symmetry $\bar{1}$. This at once implies that the structure belongs to class *A*.

Confirmation followed from a structure analysis based on the $h0l$- and $hk0$-reflexions: an electron-density projection, computed first with all signs positive, revealed the approximate structure; the atomic positions were then used in calculations of F_c-values, which showed that a few terms should have negative signs. Inclusion of these negative terms led to adequate, final electron-density maps, one of which is reproduced in Fig. 2. Differentiation between carboxyl and nitro-groups was possible because of differences in the heights of the appropriate peaks for carbon and nitrogen atoms. Absorption corrections were applied to the $h0l$-data by a version of Albrecht's method adapted for ready calculation on the DEUCE computer. A uniform, isotropic value of 3·0 Å^2 was used for the Debye temperature factor, *B*. Calculated structure factors, and observed structure amplitudes ($|F_o|$) are listed in Table 1. For 130 observed reflexions in the $h0l$-zone, *R* is 18·8%; for 122 in $hk0$ it is 17·8%. Fractional co-ordinates are given in Table 2, where are also shown co-ordinates, in Å, with respect to orthogonal axes, X' being parallel to x, Y' perpendicular to x in the xy-plane, and Z' perpendicular to X' and Y'. In this Table—as elsewhere in this paper and in Part VI—co-ordinates are often given to more figures than are significant; this has been done to avoid the discrepancies in derived quantities that can otherwise arise from rounding-off. The numbering of atoms is given in Fig. 2.

The hydrogen bond must lie acrosss the centre of inversion at 00½ between two carboxylic oxygen atoms, O(2) and O(2′). The co-ordinates lead to an O · · · O distance of 2·43 Å, the possible error of which may be informally assessed at not less than ±0·06 Å. That the structure is of type *A* is verified. A detailed consideration of the spectrum has suggested [2] that the hydrogen bond may be of the " single symmetric minimum " kind. The structure analysis is not inconsistent with this suggestion.

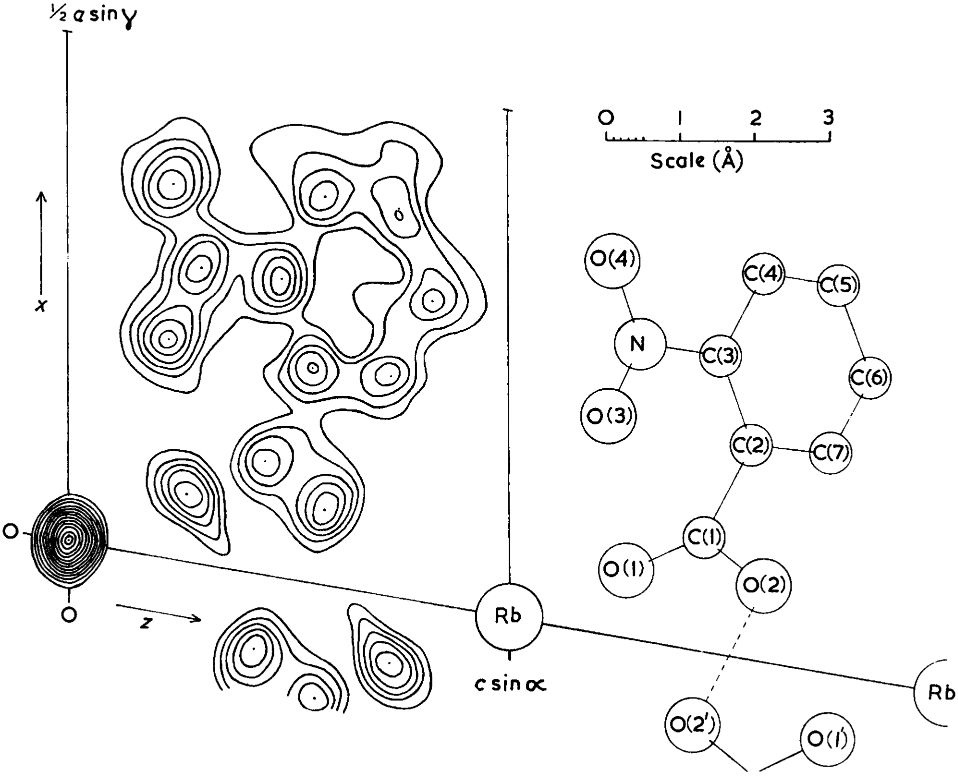
[7] Farmer, *J.*, 1903, **83**, 1440.

[8] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[9] Sim, *Acta Cryst.*, 1958, **11**, 123.

In the aromatic acid salts of type *A* examined hitherto, the metallic cations lie on two-fold symmetry axes; in this *o*-nitrobenzoate there is the minor difference that they lie at centres of symmetry. Were the nitrobenzoate residue planar, oxygen atoms 1 and 3 of the carboxyl and nitro-groups respectively would be separated by only about 1·5 Å. This severe overcrowding is relieved—and the distance increased to about 2·9 Å—by the carboxyl group's twisting through some 70° out of the plane of the benzene ring. The nitro-group is approximately in the plane. The Rb · · · O distances lie within the range 2·85—2·95 Å.

FIG. 2. *Rubidium hydrogen di-*o*-nitrobenzoate: electron-density projected along* b-*axis, with its interpretation and numbering of atoms.* (*Contour-line scale: for lighter atoms, intervals of* 2 *electrons* Å^{-2}, *starting from* 2; *for rubidium atom, intervals of* 5, *starting at* 5.)



POTASSIUM HYDROGEN DI-*p*-NITROBENZOATE

Crystal Data. KH(C$_7$H$_4$NO$_4$)$_2$, $M = 372·3$, triclinic pinakoidal, $a = 17·20$, $b = 4·05$, $c = 11·44$ Å, $\alpha = 93·8°$, $\beta = 104·1°$, $\gamma = 90·5°$, $U = 771·3$ Å^3, $D_m = 1·65$ (by flotation), $Z = 2$, $D_c = 1·606$, $F(000) = 380$, absorption coefficient for *X*-rays = 35·4 cm.$^{-1}$.

Statistical examination of the *h*0*l*-zone intensities suggested centro-symmetry and implied that the space group was $P\bar{1}$, and this was borne out by the subsequent analysis. No molecular symmetry is required. The crystals consist of thin laths, elongated in the *b*-direction and with the faces (100) most prominently developed.

Determination and Refinement of the Structure.—The structure was first determined as it appears projected along the short *b*-axis. Some 235 *h*0*l*-reflexions were originally recorded. At a late stage in the refinement an additional 90 weak reflexions were observed on films that had received a long exposure. The total of 325 is 70% of those accessible. The crystal used had a cross-section of 0·05 × 0·08 mm.^{2}, and absorption corrections were not applied.

The shortness of the *b*-axis implied that a well-resolved projection was obtainable, and that the nitrobenzoate residues were not tilted far out of the plane of projection. Nevertheless the solution of the phase problem proved difficult. The *p*-nitrobenzoate group has high pseudo-symmetry (*mmm*), so that its vector-set includes prominent peaks due to the coincidence—or near-coincidence—of several interatomic vectors. Against a background of two such independent sets, vector-peaks involving potassium atoms are less salient than normally. However,

TABLE 1. *Observed structure amplitudes and calculated structure factors for rubidium hydrogen di-*o*-nitrobenzoate.*

h	$\|F_o\|$	F_c
	*h*00	
2	2·1	−5·5
3	48·6	57·5
4	15·8	17·5
5	22·1	24·6
6	3·2	−3·7
7	2·5	−3·9
8	10·1	15·3
9	16·3	11·5
10	31·7	32·0
11	5·5	10·7
13	19·9	23·7
14	9·6	15·8
16	6·5	6·2
	*h*01	
$\bar{12}$	14·3	20·3
$\bar{11}$	14·1	11·8
$\bar{9}$	22·1	24·2
$\bar{8}$	19·9	19·9
$\bar{7}$	26·3	33·1
$\bar{6}$	48·5	45·6
$\bar{5}$	39·1	44·0
$\bar{4}$	51·9	54·7
$\bar{3}$	32·1	31·7
$\bar{2}$	48·1	49·8
$\bar{1}$	29·9	29·8
0	24·4	−20·1
1	11·6	9·3
2	28·4	28·4
3	29·8	25·5
4	19·4	22·1
5	25·5	26·7
6	29·2	30·5
7	22·0	23·4
8	19·6	19·3
9	16·2	13·2
10	4·4	9·9
11	10·1	11·0
12	10·8	10·4
13	9·5	10·6
15	6·6	4·7
	*h*02	
$\bar{16}$	7·1	12·9
$\bar{15}$	8·4	13·0
$\bar{13}$	4·4	3·9
$\bar{12}$	11·3	17·3
$\bar{11}$	17·6	17·5
$\bar{10}$	17·2	15·0
$\bar{9}$	25·8	28·3
$\bar{8}$	6·6	9·3
$\bar{7}$	23·6	30·5
$\bar{6}$	56·5	60·8
$\bar{5}$	14·1	13·2
$\bar{4}$	7·1	7·7
$\bar{3}$	30·3	25·2
$\bar{2}$	50·2	46·9
$\bar{1}$	46·6	42·7
1	42·1	32·7
2	34·0	31·0
3	7·4	6·7
4	36·5	28·8
6	3·7	4·9
7	36·6	28·8
8	26·3	18·6
9	25·9	13·8
10	22·6	11·8
11	17·1	12·0
12	9·4	12·1
	*h*03	
$\bar{13}$	17·1	21·5
$\bar{12}$	19·0	25·5
$\bar{11}$	12·1	22·3
$\bar{10}$	20·0	26·0
$\bar{9}$	13·5	18·4
$\bar{8}$	25·7	31·4
$\bar{7}$	24·4	22·8
$\bar{5}$	14·3	14·6
$\bar{4}$	16·0	15·2
$\bar{3}$	13·0	12·3
$\bar{2}$	30·2	28·6
$\bar{1}$	9·5	6·2
0	14·5	14·3
1	42·0	38·4
2	33·5	27·2
3	31·1	23·7
4	28·1	22·0
5	25·0	21·6
6	23·3	22·0
7	13·8	9·2
	*h*04	
$\bar{14}$	13·0	20·6
$\bar{13}$	11·1	16·2
$\bar{10}$	5·6	9·5
$\bar{8}$	18·7	24·2
$\bar{7}$	14·9	12·1
$\bar{6}$	14·5	12·3
$\bar{5}$	29·4	34·6
$\bar{4}$	28·8	33·7
$\bar{3}$	26·7	27·4
$\bar{2}$	7·5	7·0
$\bar{1}$	24·9	22·2
0	41·6	37·6
1	8·6	8·7
2	14·0	9·2
3	14·5	13·0
4	8·4	5·1
5	13·4	11·5
	*h*05	
$\bar{12}$	13·8	16·5
$\bar{11}$	11·5	15·1
$\bar{10}$	7·0	13·5
$\bar{9}$	16·1	18·2
$\bar{8}$	16·1	17·5
$\bar{7}$	5·7	10 2
$\bar{6}$	7·3	9·7
$\bar{5}$	17·5	17·9
$\bar{4}$	15·9	15·9
$\bar{3}$	15·4	14·0
$\bar{2}$	19·4	17·5
$\bar{1}$	18·2	16·5
0	15·4	12·8
1	17·0	7·9
2	18·5	12·0
3	10·8	8·6
5	18·0	10·5
6	16·7	9·3
8	9·6	6·5
9	5·7	8·7
	*h*06	
$\bar{10}$	8·8	15·3
$\bar{9}$	10·6	17·3
$\bar{7}$	17·8	23·9
$\bar{6}$	30·8	32·8
$\bar{5}$	6·9	2·9
$\bar{4}$	7·0	7·5
$\bar{3}$	10·9	8·2
$\bar{2}$	10·4	7·1
$\bar{1}$	9·4	8·1
1	10·5	6·7
2	8·4	5·6
3	16·0	9·3
4	17·0	15·1
6	7·1	3·2
7	10·4	14·1
	*h*07	
$\bar{8}$	8·7	11·1
$\bar{5}$	7·5	6·1
$\bar{4}$	7·7	7·1
$\bar{3}$	8·5	9·5
$\bar{2}$	9·4	7·9
$\bar{1}$	10·7	8·4
0	13·6	11·1
1	9·7	8·0
2	7·7	5·8
	*h*10	
$\bar{14}$	9·0	10·2
$\bar{13}$	15·6	13·2
$\bar{12}$	13·0	12·7
$\bar{11}$	12·4	13·3
$\bar{10}$	18·9	20·5
$\bar{9}$	32·0	22·9
$\bar{8}$	23·9	24·8
$\bar{7}$	24·3	28·6
$\bar{6}$	22·4	18·8
$\bar{5}$	12·4	17·6
$\bar{4}$	18·7	12·6
$\bar{3}$	19·3	16·4
$\bar{2}$	19·6	21·8
$\bar{1}$	4·3	−11·6
0	25·2	39·7
1	76·9	68·0
2	26·4	25·6
3	46·7	49·2
4	31·1	36·0
5	24·5	24·9
6	21·8	24·3
7	8·7	8·2
8	21·8	21·1
10	22·7	9·1
11	34·8	25·0
13	9·6	5·4
14	11·5	12·5
	*h*20	
$\bar{14}$	8·1	11·2
$\bar{13}$	15·6	15·4
$\bar{12}$	8·1	5·1
$\bar{11}$	8·7	10·9
$\bar{10}$	12·4	16·9
$\bar{9}$	12·7	15·6
$\bar{8}$	8·4	6·2
$\bar{7}$	7·1	−0·8
$\bar{6}$	25·8	30·6
$\bar{5}$	29·8	29·0
$\bar{4}$	9·0	13·4
$\bar{3}$	28·9	36·0
$\bar{2}$	21·8	19·0
$\bar{1}$	23·3	27·2
0	61·5	51·8
1	23·0	21·0
2	11·2	9·1
3	27·0	25·7
4	39·5	37·0
5	23·9	19·8
7	7·5	8·2
8	15·8	13·9
9	8·4	8·7
10	8·0	8·7
11	10·5	8·5
12	12·4	10·4
13	14·9	13·6
14	14·0	12·5
	*h*30	
$\bar{14}$	7·1	8·3
$\bar{13}$	8·1	8·9
$\bar{12}$	7·8	8·1
$\bar{11}$	17·1	18·0
$\bar{10}$	18·3	19·3
$\bar{9}$	16·7	15·7
$\bar{8}$	16·5	18·2
$\bar{7}$	8·0	5·0
$\bar{6}$	5·6	5·9
$\bar{5}$	13·4	17·2
$\bar{4}$	11·5	3·6
$\bar{3}$	9·6	5·3
$\bar{2}$	9·9	12·1
$\bar{1}$	19·6	16·1
0	31·8	27·8
1	16·5	16·9
2	18·0	18·5
3	21·1	24·0
4	19·9	18·7
5	22·7	27·3
6	18·0	14·5
7	8·0	4·6
8	14·0	14·6
	*h*40	
$\bar{10}$	8·7	13·2
$\bar{9}$	11·5	12·8
$\bar{8}$	11·7	14·1
$\bar{7}$	9·6	9·1
$\bar{6}$	13·9	14·7
$\bar{5}$	15·2	15·1
$\bar{4}$	8·1	6·7
$\bar{3}$	11·8	13·2
$\bar{2}$	9·3	4·8
$\bar{1}$	8·0	5·8
0	21·7	22·3
1	16·7	9·8
2	8·1	3·6
3	10·9	12·2
4	12·1	11·8
5	9·6	10·1
7	9·3	7·9
8	8·7	10·2
9	6·2	7·2
10	8·1	7·9
11	6·5	5·2
	*h*50	
$\bar{7}$	9·3	10·1
$\bar{6}$	10·8	7·3
$\bar{2}$	8·7	9·4
$\bar{1}$	8·4	2·9
1	10·2	8·8
2	10·2	7·5
3	12·4	14·2
4	10·5	7·9
5	6·2	6·2

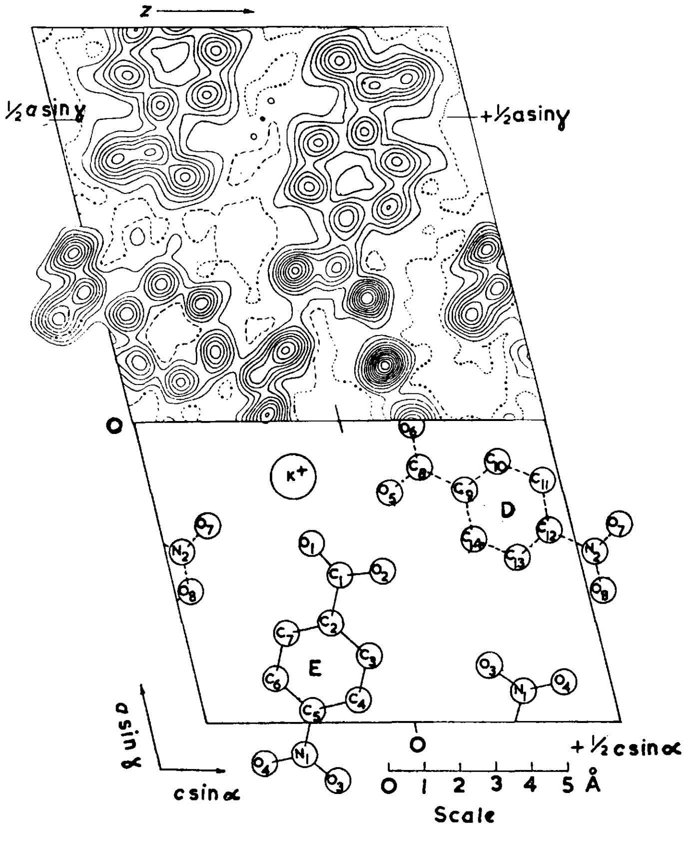
TABLE 2. *Rubidium hydrogen di-*o*-nitrobenzoate, fractional co-ordinates* (x, y, *and* z), *and orthogonal co-ordinates in* Å (X′ *parallel to* x, Y′ *perpendicular to* x *in the* xy*-plane, and* Z′ *perpendicular to* X′ *and* Y′). *Origin at centre of inversion.*

Atom	*x*	*y*	*z*	*X′*	*Y′*	*Z′*
Rb	0·0000	0·0000	0·0000	0·000	0·000	0·000
O(1)	0·0680	0·5870	0·2730	0·425	2·444	1·604
O(2)	0·0780	0·9250	0·5800	0·118	3·672	3·409
O(3)	0·2190	1·0270	0·2320	2·368	4·571	1·364
O(4)	0·3730	0·9870	0·2410	4·500	4·372	1·416
N	0·2916	0·9450	0·3000	3·336	4·103	1·763
C(1)	0·1127	0·7400	0·4470	0·806	2·958	2·627
C(2)	0·2150	0·6790	0·5530	2·137	2·543	3·250
C(3)	0·2950	0·7870	0·4800	3·269	3·141	2·821
C(4)	0·3850	0·7320	0·5810	4·434	2·760	3·415
C(5)	0·3900	0·5800	0·7420	4·406	1·849	4·361
C(6)	0·3050	0·4670	0·8200	3·202	1·222	4·819
C(7)	0·2200	0·5200	0·7200	2·106	1·592	4·232

the failure to prepare crystals in which the potassium was isomorphously replaced made it necessary to solve the structure by an intensive study of the Patterson projection along [*b*].

For this purpose the projection was moderately sharpened by the function, $\{\hat{f} \exp(\sin^2\theta/\lambda^2)\}^{-2}$, in which $\hat{f}$ is an averaged unitary atomic-scattering function and the other symbols have their usual meanings. Previous experience had suggested that such a structure might be elucidated *via* the Buerger minimum function [10] when the Patterson map was superposed upon itself with its origin on the peak corresponding to the K · · · K vector. This procedure was followed for several prominent peaks that might so correspond; but what was in fact the correct structure was not recognised in this way until it had also been indicated by another approach, which is described in the next paragraph.

FIG. 3. *Potassium hydrogen di-*p*-nitrobenzoate: electron-density projected along* b*-axis, with its interpretation and numbering of atoms. (Contour-line scale: intervals of one electron* Å^{-2} *with zero-line broken, except for potassium atom, around which only the even contours are shown beyond* 2.)

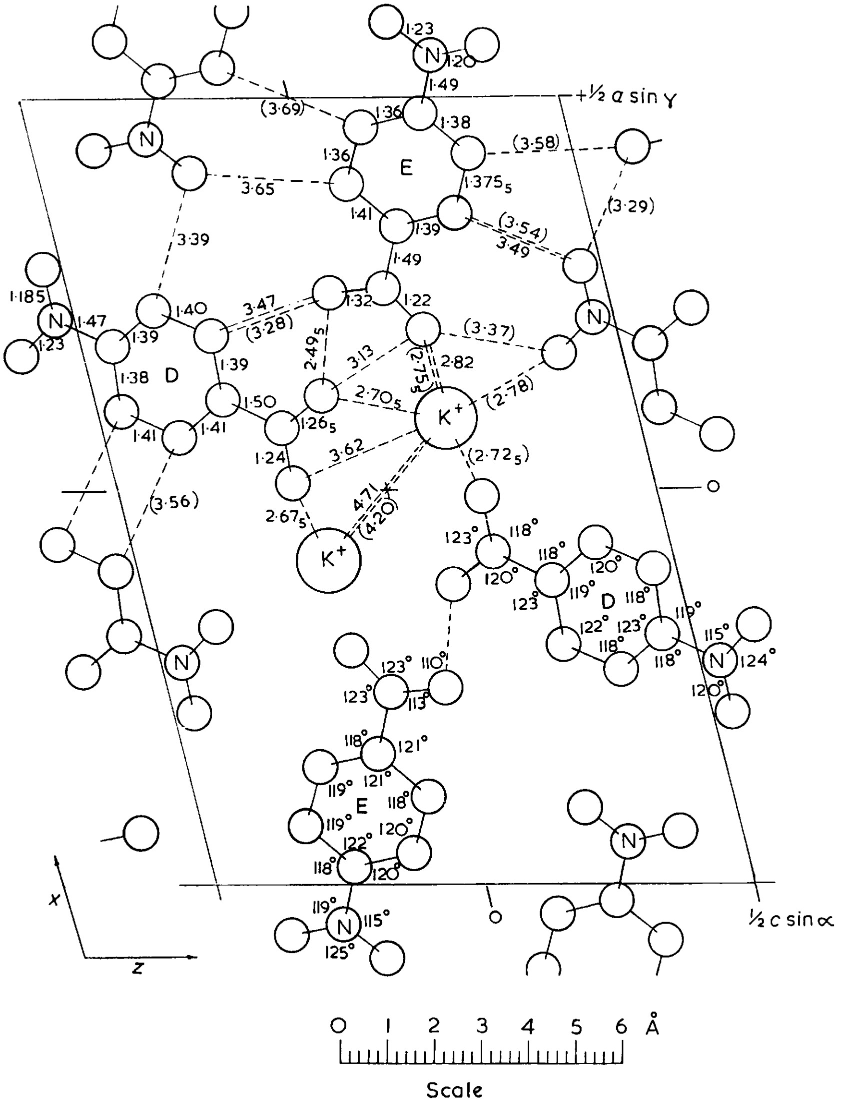


The weighted vector-diagram for a single *p*-nitrobenzoate residue was drawn, to scale, on tracing paper. It includes a high-weight vector, about 6·7 Å from its origin, due to the pair of long O · · · O separations. It was placed with its origin on that of the sharpened Patterson map, and rotated into all the positions in turn where this O · · · O vector coincided with a Patterson peak. Each of the 12 positions was given a figure-of-merit based on the number and weights of any other coincidences. Three orientations were indicated as most probable. Next the Patterson map was searched for centre-to-centre vector-peaks between pairs of acid radicals related by the centre of symmetry. On each of the possible peaks the vector-diagram was placed, in each of its three most probable orientations; and it thus became possible to reject all

[10] Buerger, " Vector Space," Wiley, New York, 1959.

but two peaks and two orientations. These corresponded to the two independent nitrobenzoate residues. Thus the structure was revealed, so far as the acidic radicals were concerned, and the minimum function could be interpreted. The preliminary structure showed an agreement (R) of 33% between $|F_o|$ and $|F_c|$ computed with a Debye factor (B) of 3·0 Å^2, and it served as the starting point for refinement.

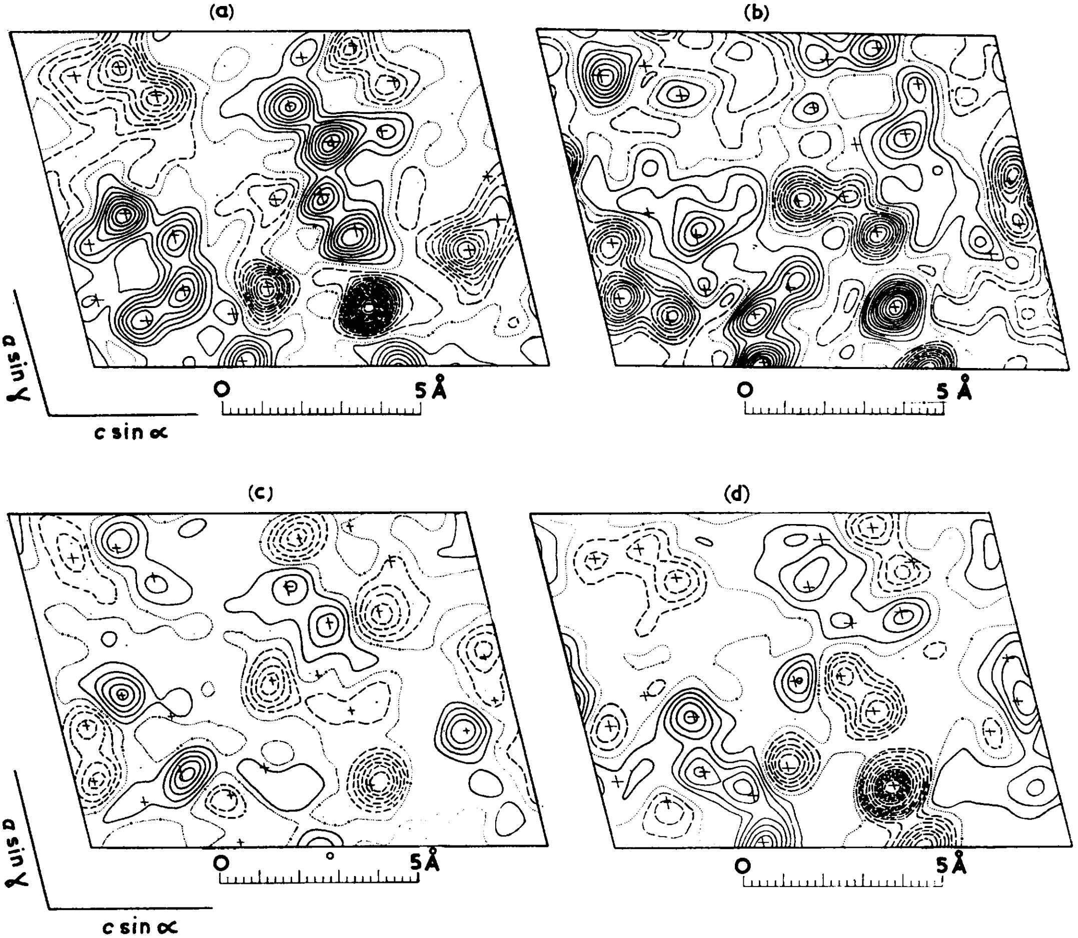
FIG. 4. *Potassium hydrogen di-*p*-nitrobenzoate: projection of the structure along the* b*-axis, showing intramolecular dimensions and the more important intermolecular contacts (in* Å).



Two further cycles of electron-density syntheses reduced R to 19·0%; thereafter three cycles of " difference syntheses," with B now allowed to vary, reduced it to 13·0%. During the latter phase, the additional 90 reflexions were introduced; allowance for unobserved reflexions was made by giving them a structure amplitude equal to half the minimum locally observable; and the hydrogen atoms attached to carbon were included in F_c-calculations. A final cycle brought R to 11·5% for the original 235 terms, and to 14·0% for the 325. The map in Fig. 3 shows the last electron-density synthesis, in which only the 235 terms were used. It is interpreted in the lower part of the diagram, where the numbering of atoms is also shown. Fig. 4 covers a more extensive region of the same projection. In the initial stages of refinement, no distinction was made between carbon and nitrogen atoms, so as not to prejudge the question of the identities of carboxyl and nitro-groups. The question could soon be answered, in the sense of Fig. 3, because the electron-density peaks for nitrogen were higher.

With well-established—though not final—values for x- and z-, y-co-ordinates were sought by

FIG. 5. *Potassium hydrogen di*-p-*nitrobenzoate*: *generalised projections along* b-*axis*. (a) cosine *part, and* (b) sine *part, with* hll-*data*; *and* (c) cosine *part, and* (d) sine *part with* $h2l$-*data*. (*Zero-contour line dotted, negative contours broken*: *lines at intervals of one electron* Å^{-2}.)



way of some 240 hll- and 180 $h2l$-reflexions. (These are respectively 52 and 55% of the totals accessible in these reciprocal-lattice nets.) By trial a set of y-co-ordinates was found, and they were refined by six cycles of generalised projections, first for the hll-terms, then for the $h2l$-terms, both sine and cosine components being evaluated in each case. Maps representing these generalised projections, in their final forms, are shown in Fig. 5.

In a last phase, a partial three-dimensional least-squares refinement was effected with the available reflexions (nearly 750) of types $h0l$, hll, and $h2l$, provision being made for anisotropic thermal parameters. The weighting system was that described in Part VI. In the last two of three cycles of refinement, unobserved reflexions were included, at half the minimum value of $|F_o|$ locally observable, for all those reflexions (some 250) for which $|F_c|$ exceeded this minimum. The value of R was thus reduced to 10·4% for all observed reflexions. Final positional parameters are listed in Table 3, which also includes co-ordinates, in Å, with respect to orthogonal axes chosen with Y' parallel to y, Z' perpendicular to y in the yz-plane, and X' perpendicular to both Y' and Z', and anisotropic B-factors parallel to each of the principal axes. (Individual values of $B//y$ are of qualitative, rather than quantitative, significance.) During the final least-squares cycle, hydrogen atoms were included in the calculation of F_c, though their parameters were not refined. Their y-co-ordinates, shown in Table 3, were derived geometrically from the already assigned x- and z-co-ordinates, with the assumption that the hydrogen atoms must lie in the (mean) planes of their respective benzenoid rings. For one

TABLE 3. *Potassium hydrogen di-*p*-nitrobenzoate, fractional co-ordinates* (x, y, *and* z), *orthogonal co-ordinates* (*in* Å, *with* Y′ *parallel to* y, Z′ *perpendicular to* y *in the* yz*-plane, and* X′ *perpendicular to* Y′ *and* Z′), *and thermal parameters* (B) *parallel to each principal axis. Origin at a centre of inversion.*

Atom	x	y	z	X'	Y'	Z'	$B//x$	$B//y$	$B//z$
K	0·09075	0·34914	0·14252	1·5140	1·2932	1·2475	4·5	2·8	5·1
O(1)	0·20249	−0·13449	0·14498	3·3782	−0·6851	0·8086	4·2	1·9	6·4
O(2)	0·24954	−0·29750	−0·01429	4·1632	−1·2339	−1·2062	4·7	5·3	3·6
O(3)	0·59816	0·57259	0·21544	9·9794	2·0630	−0·0411	6·6	10·0	8·4
O(4)	0·56426	0·69715	0·38155	9·4138	2·4489	1·9968	7·1	9·3	7·9
O(5)	0·11834	0·39474	−0·07826	1·9745	1·6382	−1·3880	4·9	4·8	4·8
O(6)	0·00551	0·14065	−0·17499	0·0919	0·6993	−2·0206	4·9	2·4	7·3
O(7)	0·17253	−0·52368	−0·61787	2·8784	−1·6872	−7·7746	7·4	6·4	5·5
O(8)	0·28551	−0·28577	−0·53461	4·7633	−0·8039	−7·2964	6·5	6·9	7·3
N(1)	0·55283	0·55892	0·28326	9·2231	1·9643	0·9226	5·5	9·1	5·8
N(2)	0·21729	−0·35078	−0·53672	3·6356	−1·0548	−7·0379	6·0	4·7	5·2
C(1)	0·25553	−0·13531	0·09116	4·2631	−0·6567	−0·0275	5·3	1·6	5·5
C(2)	0·33435	0·04238	0·13938	5·5781	0·0144	0·1934	4·2	1·5	5·4
C(3)	0·38818	0·08298	0·06542	6·4762	0·2255	−0·8759	4·2	1·8	5·6
C(4)	0·46070	0·23061	0·11710	7·6860	0·7733	−0·5891	4·2	3·5	6·7
C(5)	0·47530	0·37792	0·23075	7·9296	1·2827	0·6472	4·4	4·5	6·1
C(6)	0·42284	0·34705	0·30373	7·0544	1·1116	1·6996	4·9	4·8	5·0
C(7)	0·34986	0·18937	0·25634	5·8368	0·5200	1·4637	5·0	3·0	5·1
C(8)	0·07646	0·22000	−0·16724	1·2756	1·0036	−2·2287	3·6	4·1	5·8
C(9)	0·11485	0·07500	−0·26249	1·9161	0·4814	−3·4765	5·0	1·1	4·0
C(10)	0·06697	−0·11652	−0·36086	1·1172	−0·2133	−4·3994	4·0	4·1	5·0
C(11)	0·10039	−0·25701	−0·45330	1·6748	−0·7186	−5·5943	5·1	1·3	5·1
C(12)	0·18103	−0·19924	−0·44415	3·0202	−0·5043	−5·8270	5·9	2·4	4·0
C(13)	0·23040	−0·01721	−0·34710	3·8438	0·1526	−4·9255	4·3	2·9	5·0
C(14)	0·19601	0·11568	−0·25640	3·2701	0·6286	−3·7463	3·3	3·5	4·2

	x	y	z		x	y	z
H of C(3) ...	0·375	−0·021	−0·026	H of C(10) ...	0·007	−0·151	−0·362
H of C(4) ...	0·504	0·250	0·068	H of C(11) ...	0·063	−0·123	−0·537
H of C(6) ...	0·441	0·442	0·402	H of C(13) ...	0·292	0·015	−0·345
H of C(7) ...	0·310	0·179	0·308	H of C(14) ...	0·223	0·251	−0·176

TABLE 4. *Standard deviations* (Å) *in atomic positions* (r) *and bond-lengths.*

Atom	$\sigma(r)$	Bond	σ
K^+	0·0053	K^+ · · · O (carboxyl)	0·015
O (carboxyl)	0·0144	K^+ · · · O (nitro)	0·019
O (nitro)	0·018	O · · · O (hydrogen bond)	0·020
N	0·020	N–O	0·027
C	0·022	C–O	0·026
		C–C	0·031

TABLE 5. *Observed structure amplitudes and calculated structure factors for potassium hydrogen di-*p*-nitrobenzoate. (Terms marked with an asterisk were not observed because of their low values of* sin θ.)

h	$\frac{1}{2}F_o$	$\frac{1}{2}F_c$
	*h*00	
2	1·9	−1·6
3	21·9	−22·8
4	4·9	−4·9
5	1·8	1·3
6	25·1	−27·1
7	8·2	−8·1
8	4·5	−4·6
9	15·6	14·7
10	11·9	10·8
11	14·2	13·0
12	5·9	5·7
	*h*01	
$\overline{19}$	3·3	−2·8
$\overline{18}$	5·7	−5·7
$\overline{17}$	4·3	−4·7
$\overline{15}$	8·1	8·5
$\overline{14}$	4·4	−4·4
$\overline{13}$	7·1	7·1
$\overline{12}$	6·2	6·1
$\overline{11}$	1·5	1·8
$\overline{10}$	5·5	−5·6
$\overline{9}$	3·9	4·8
$\overline{8}$	7·1	7·3
$\overline{7}$	1·4	−2·1
$\overline{6}$	8·8	−9·6
$\overline{5}$	17·0	−18·8
$\overline{4}$	2·4	2·1
$\overline{3}$	1·9	2·0
$\overline{2}$	1·3	−0·1
$\overline{1}$	8·7	7·8
0	9·3	8·4
1	1·4	−2·1
2	16·2	17·7
3	14·6	16·4
4	10·4	−12·2
6	6·4	−6·6
7	11·7	−12·2
8	22·8	23·7
9	4·2	4·8
10	8·1	8·5
11	3·7	3·1
12	3·5	1·8
13	2·9	−2·9
14	3·4	−4·5
19	3·2	2·0
20	2·8	2·1
	*h*02	
$\overline{20}$	2·8	−2·5
$\overline{19}$	3·0	−2·8
$\overline{17}$	2·8	−2·4
$\overline{16}$	4·6	4·6
$\overline{15}$	2·1	−2·6
$\overline{13}$	3·4	3·3
$\overline{11}$	2·7	−3·4
$\overline{10}$	8·6	−8·0
$\overline{9}$	15·5	−15·3
$\overline{8}$	14·7	−14·4
$\overline{7}$	1·6	1·5
$\overline{6}$	5·7	−6·8
$\overline{5}$	8·9	9·7
$\overline{4}$	11·3	11·9
$\overline{3}$	12·6	13·5
$\overline{2}$	26·0	−27·1
$\overline{1}$	28·2	29·6
0	11·4	−12·5
1	8·5	−10·0
2	26·3	−29·5
3	14·2	−14·1
4	4·9	6·3
5	18·9	−20·3
6	3·8	−4·1
7	3·9	3·5
8	23·5	23·4
12	3·3	−3·4
13	2·3	−1·9
14	5·4	−5·0
15	2·6	−2·2
16	1·5	−1·6
18	2·1	2·6
19	1·5	1·6
	*h*03	
$\overline{21}$	1·3	−1·1
$\overline{20}$	2·8	−1·9
$\overline{19}$	2·8	−2·0
$\overline{18}$	1·4	0·4
$\overline{16}$	12·2	11·8
$\overline{15}$	3·7	−3·7
$\overline{13}$	1·7	−1·4
$\overline{12}$	2·5	−2·0
$\overline{11}$	5·8	−5·8
$\overline{10}$	24·3	−24·5
$\overline{9}$	12·4	−13·1
$\overline{8}$	4·1	3·9
$\overline{7}$	8·0	9·4
$\overline{6}$	2·7	3·4
$\overline{5}$	15·7	17·0
$\overline{4}$	3·3	−3·3
$\overline{3}$	10·4	−10·7
$\overline{2}$	6·2	−5·7
$\overline{1}$	4·5	−4·3
0	19·3	−20·4
1	32·4	−36·1
2	5·6	−5·6
4	9·6	9·4
5	5·9	5·6
6	6·5	−6·1
7	10·0	9·6
10	8·9	−8·6
11	9·8	−9·4
12	1·5	−1·5
13	2·8	−2·6
18	1·3	1·2
	*h*04	
$\overline{20}$	1·1	1·3
$\overline{17}$	5·8	5·4
$\overline{16}$	2·1	3·0
$\overline{13}$	1·4	−1·1
$\overline{12}$	8·4	−8·4
$\overline{11}$	10·4	−10·2
$\overline{10}$	5·4	−5·6
$\overline{9}$	5·8	−6·4
$\overline{8}$	22·2	23·0
$\overline{7}$	5·4	5·9
$\overline{6}$	12·1	14·1
$\overline{5}$	2·0	1·9
$\overline{4}$	1·8	1·9
$\overline{3}$	13·4	14·0
$\overline{2}$	23·4	−23·7
$\overline{1}$	23·9	−26·2
0	13·1	−13·1
1	7·2	−8·2
2	3·1	2·8
3	3·8	−3·8
4	8·0	8·4
5	5·8	7·1
7	4·4	4·4
9	1·9	−1·3
12	3·7	−3·4
13	5·0	−4·9
	*h*05	
$\overline{20}$	1·1	1·1
$\overline{19}$	5·2	4·4
$\overline{18}$	3·9	3·0
$\overline{17}$	2·5	2·7
$\overline{15}$	4·1	4·2
$\overline{13}$	4·8	−4·8
$\overline{12}$	3·7	−4·2
$\overline{11}$	4·0	−4·4
$\overline{10}$	1·8	−0·9
$\overline{9}$	5·3	4·4
$\overline{8}$	10·8	10·9
$\overline{7}$	3·5	4·1
$\overline{6}$	11·2	11·5
$\overline{5}$	21·1	21·3
$\overline{4}$	10·4	10·2
$\overline{3}$	10·8	−10·1
$\overline{2}$	19·4	−19·3
$\overline{1}$	7·2	−7·7
0	4·1	−3·3
1	11·6	11·9
2	19·8	19·6
3	10·8	11·3
4	1·9	1·5
6	1·8	−1·6
7	1·3	−2·1
8	5·4	−5·3
9	10·1	−9·8
	*h*05	
11	2·4	2·0
12	9·2	8·1
13	4·6	5·0
	*h*06	
$\overline{21}$	2·6	2·0
$\overline{19}$	2·1	1·5
$\overline{17}$	1·4	−1·8
$\overline{16}$	4·9	−4·5
$\overline{15}$	7·2	−6·8
$\overline{14}$	4·1	4·4
$\overline{13}$	7·3	7·4
$\overline{12}$	8·8	8·6
$\overline{11}$	3·2	3·7
$\overline{9}$	9·6	8·9
$\overline{8}$	3·0	3·2
$\overline{7}$	2·6	3·1
$\overline{6}$	9·1	−8·8
$\overline{5}$	14·1	−14·0
$\overline{4}$	2·7	1·9
$\overline{3}$	6·5	5·7
$\overline{2}$	3·2	3·1
$\overline{1}$	3·2	−3·1
0	1·1	2·2
1	19·7	20·7
2	2·3	−3·0
3	8·5	8·5
4	10·1	10·8
5	7·2	7·4
6	4·3	−4·3
7	7·5	−7·4
8	5·3	−4·8
9	2·6	−1·9
10	1·5	2·4
11	1·5	−1·4
12	3·5	3·2
13	3·6	2·5
14	2·8	2·1
15	1·2	1·2
	*h*07	
$\overline{20}$	1·6	1·5
$\overline{18}$	4·6	−4·4
$\overline{17}$	6·4	−5·4
$\overline{16}$	3·6	−3·3
$\overline{15}$	1·8	−1·5
$\overline{14}$	1·9	−2·2
$\overline{13}$	7·0	−7·8
$\overline{12}$	5·3	5·4
$\overline{11}$	15·4	14·9
$\overline{10}$	9·1	8·6
$\overline{9}$	1·4	2·1
$\overline{8}$	3·9	−3·8
$\overline{7}$	8·6	−8·1
$\overline{6}$	4·4	−5·2
$\overline{5}$	5·0	−5·1
$\overline{4}$	3·1	−3·2
$\overline{3}$	1·7	−1·6
$\overline{2}$	1·9	−2·6
$\overline{1}$	3·9	4·3
0	8·5	7·9
1	6·6	6·1
3	1·6	−2·0
5	3·3	−3·6
6	1·5	−1·7
7	2·3	−2·0
8	4·3	−4·3
9	6·1	6·4
	*h*08	
$\overline{19}$	1·3	−1·2
$\overline{18}$	4·2	−3·4
$\overline{17}$	3·5	−3·1
$\overline{16}$	3·0	−3·0
$\overline{15}$	2·3	2·0
$\overline{13}$	2·6	2·5
$\overline{12}$	3·4	2·7
$\overline{11}$	3·9	3·9
$\overline{9}$	4·2	−4·5
$\overline{8}$	8·9	−8·1
$\overline{7}$	8·5	−9·5
$\overline{5}$	9·7	−10·5
$\overline{4}$	2·3	2·8
$\overline{3}$	4·2	4·5
$\overline{2}$	4·4	3·8
$\overline{1}$	2·3	2·2
	*h*08	
0	6·7	6·7
2	5·5	−6·3
3	6·7	−7·7
4	2·3	−2·0
9	4·3	4·2
	*h*09	
$\overline{18}$	1·9	−1·7
$\overline{17}$	1·5	−1·5
$\overline{15}$	4·6	5·3
$\overline{12}$	2·1	2·4
$\overline{10}$	3·5	−3·5
$\overline{9}$	5·4	−5·7
$\overline{8}$	5·0	−4·1
$\overline{6}$	4·0	−3·6
$\overline{5}$	3·5	−3·9
$\overline{4}$	7·9	8·3
$\overline{3}$	2·9	3·3
1	3·6	−3·9
2	5·6	−5·5
3	3·4	−3·3
5	2·1	1·7
8	4·2	3·8
	*h*0,10	
$\overline{17}$	2·6	1·8
$\overline{16}$	4·5	4·1
$\overline{15}$	1·8	1·1
$\overline{12}$	1·5	1·6
$\overline{11}$	3·3	−2·3
$\overline{10}$	4·5	−4·8
$\overline{9}$	5·1	−4·3
$\overline{8}$	2·1	−3·4
$\overline{7}$	8·5	8·7
$\overline{6}$	2·6	−3·5
$\overline{5}$	3·8	4·2
$\overline{4}$	5·5	5·6
$\overline{3}$	8·2	8·5
$\overline{2}$	4·0	4·1
$\overline{1}$	5·6	−5·8
0	7·5	−6·4
1	4·4	−4·4
2	1·8	−1·6
3	3·7	−4·4
6	3·0	2·6
7	3·7	3·2
8	3·8	2·9
10	2·6	−2·1
11	1·5	−1·5
	*h*0,11	
$\overline{17}$	4·4	3·4
$\overline{16}$	2·6	2·3
$\overline{13}$	2·9	−2·3
$\overline{12}$	1·9	−1·3
$\overline{10}$	1·4	−1·7
$\overline{8}$	3·6	2·6
$\overline{7}$	4·7	4·2
$\overline{1}$	2·6	2·5
0	2·1	2·2
1	1·5	0·4
2	4·8	−4·2
4	2·7	2·4
5	1·8	1·2
7	1·1	−0·4
	*h*0,12	
$\overline{16}$	1·7	1·4
$\overline{14}$	1·6	−1·5
$\overline{13}$	3·8	−3·2
$\overline{12}$	1·2	−1·1
$\overline{9}$	4·7	3·8
$\overline{8}$	6·7	6·2
$\overline{7}$	1·4	0·8
$\overline{5}$	1·4	−1·8
$\overline{2}$	3·9	−3·6
$\overline{1}$	4·8	−3·4
1	4·4	4·6
2	2·4	1·3
3	2·3	1·6
	*h*0,13	
$\overline{13}$	1·8	−1·6
$\overline{10}$	2·3	1·5
$\overline{9}$	1·8	0·9
	*h*0,13	
$\overline{8}$	1·2	1·5
$\overline{6}$	1·2	−1·5
$\overline{4}$	1·9	−1·8
$\overline{3}$	2·3	−1·4
0	2·7	2·3
1	1·8	1·4
	*h*0,14	
$\overline{10}$	2·2	1·3
$\overline{7}$	1·3	−0·9
$\overline{6}$	2·1	−2·1
$\overline{4}$	2·6	−1·7
	*h*10	
$\overline{8}$	6·4	−6·6
$\overline{7}$	7·5	−7·7
$\overline{5}$	8·3	7·9
$\overline{4}$	7·7	7·8
$\overline{3}$	55·5	67·3
$\overline{2}$	*	22·9
$\overline{1}$	*	7·0
0	3·9	−3·6
1	*	12·6
2	7·9	−5·7
3	34·0	−31·5
4	11·6	11·3
5	10·3	10·4
6	24·7	22·6
7	9·4	−9·3
8	13·3	12·5
	$h1\overline{1}$	
$\overline{11}$	8·0	9·2
$\overline{10}$	9·9	−11·4
$\overline{9}$	13·9	−12·9
$\overline{8}$	14·7	−13·6
$\overline{7}$	7·2	−6·7
$\overline{4}$	10·4	11·3
$\overline{3}$	23·6	22·4
$\overline{2}$	47·1	42·9
$\overline{1}$	3·9	−1·9
0	6·9	6·0
1	*	−35·3
2	50·6	−42·7
3	16·8	−14·6
4	25·2	−23·3
5	4·1	−2·2
6	11·3	11·5
8	8·5	8·1
9	7·9	7·8
10	6·4	6·0
14	6·9	−7·2
15	6·3	−6·7
	*h*11	
$\overline{9}$	4·4	−4·8
$\overline{8}$	4·1	−4·0
$\overline{7}$	11·3	10·9
$\overline{6}$	6·9	6·9
$\overline{5}$	20·2	21·9
$\overline{4}$	26·0	25·0
$\overline{3}$	18·4	18·1
$\overline{2}$	24·6	22·7
$\overline{1}$	*	1·0
0	3·5	5·9
1	17·6	−14·7
2	4·4	−5·1
3	16·0	−15·1
4	4·2	5·4
5	35·8	34·0
6	11·8	13·2
7	12·6	12·2
11	7·1	−7·0
	$h1\overline{2}$	
$\overline{6}$	14·5	−16·3
$\overline{5}$	12·1	−12·3
$\overline{3}$	9·7	9·1
$\overline{2}$	17·5	19·1
$\overline{1}$	76·2	−83·8
0	6·0	−4·2
1	17·7	17·3
2	24·5	23·9
3	13·9	−13·1
4	17·3	−18·3
5	5·9	−6·0
	$h1\overline{2}$	
6	6·1	−6·0
8	6·3	−7·1
9	4·5	−3·9
13	8·3	6·8
14	10·0	−8·7
15	5·7	−5·1
16	6·5	−6·8
	*h*12	
$\overline{10}$	4·4	5·1
$\overline{9}$	5·8	−5·9
$\overline{8}$	7·3	6·8
$\overline{7}$	9·9	8·4
$\overline{6}$	13·0	12·8
$\overline{4}$	11·3	−12·0
$\overline{3}$	5·9	−6·4
$\overline{2}$	7·0	5·6
$\overline{1}$	10·2	−10·4
0	5·2	−4·1
2	7·7	7·7
3	11·0	11·5
4	8·3	9·3
5	25·4	25·2
6	5·8	−5·4
8	6·6	−6·8
9	10·8	−10·7
	$h1\overline{3}$	
$\overline{10}$	7·0	8·1
$\overline{9}$	5·1	−7·4
$\overline{8}$	5·6	7·4
$\overline{6}$	7·2	−7·8
$\overline{5}$	11·6	−11·6
$\overline{4}$	21·3	−23·4
$\overline{3}$	12·6	−13·1
$\overline{1}$	12·9	13·8
0	5·2	4·3
1	15·4	14·3
2	17·8	18·4
3	5·4	5·9
4	6·1	6·1
5	5·0	−4·6
6	20·9	−20·8
7	24·0	−25·3
8	9·2	−8·5
10	7·6	7·2
13	15·5	14·1
	*h*13	
$\overline{15}$	7·4	−7·0
$\overline{10}$	8·4	8·5
$\overline{8}$	12·6	12·7
$\overline{6}$	16·9	−16·5
$\overline{5}$	21·0	−19·8
$\overline{4}$	15·2	−14·1
$\overline{3}$	5·5	−5·9
$\overline{2}$	15·4	−15·3
$\overline{1}$	2·8	−1·4
0	2·8	−2·1
1	9·5	−9·2
2	3·3	1·9
3	14·7	14·4
4	15·1	13·8
6	5·8	−5·8
7	6·6	−6·3
10	8·4	−7·5
11	11·1	−10·6
	$h1\overline{4}$	
$\overline{10}$	5·6	5·8
$\overline{9}$	3·6	−1·5
$\overline{8}$	3·3	2·8
$\overline{7}$	7·8	8·7
$\overline{6}$	8·3	10·2
$\overline{5}$	2·8	−3·7
$\overline{4}$	9·4	−9·4
$\overline{3}$	7·0	−6·2
$\overline{2}$	7·4	−8·1
$\overline{1}$	5·1	−5·6
1	15·1	16·6
2	14·8	13·8
3	14·5	13·4
4	2·9	3·0
5	15·0	16·2
6	13·9	−15·0
7	4·9	−5·3

TABLE 5. (*Continued.*)

h	$\frac{1}{2}F_o$	$\frac{1}{2}F$
	$h1\bar{4}$	
8	7·3	−8·7
9	3·7	−3·5
12	5·1	5·4
13	5·3	5·6
14	13·5	13·6
	$h14$	
$\bar{15}$	8·4	−8·9
$\bar{14}$	10·9	−11·7
$\bar{13}$	8·7	−8·5
$\bar{11}$	12·9	13·2
$\bar{9}$	7·2	8·1
$\bar{7}$	4·2	3·7
$\bar{6}$	6·9	6·9
$\bar{5}$	25·9	−26·5
$\bar{4}$	32·6	−31·5
$\bar{3}$	20·7	−20·9
$\bar{2}$	3·4	2·7
$\bar{1}$	13·8	14·8
0	7·2	−8·0
$\bar{1}$	18·2	19·2
2	3·9	4·0
3	11·6	−10·8
4	16·3	−15·7
5	7·2	−7·1
	$h1\bar{5}$	
$\bar{7}$	8·2	8·7
$\bar{6}$	5·6	6·1
$\bar{3}$	9·0	−9·3
$\bar{1}$	3·8	−4·9
2	13·0	11·8
3	15·1	17·9
4	9·7	9·7
5	11·1	10·5
6	4·0	4·4
7	9·7	−9·9
14	10·2	9·8
	$h15$	
$\bar{14}$	8·3	9·6
$\bar{7}$	5·0	−4·9
$\bar{6}$	9·3	−9·1
$\bar{5}$	10·5	−11·0
$\bar{3}$	7·5	8·4
$\bar{2}$	7·9	7·2
$\bar{1}$	10·6	11·1
1	9·1	8·8
2	3·2	3·9
3	4·3	−5·6
4	7·1	−6·8
5	14·8	−13·6
6	8·8	−7·7
	$h1\bar{6}$	
$\bar{4}$	12·3	12·8
2	10·5	−11·5
4	9·2	9·5
5	5·4	5·0
6	8·9	8·7
7	6·8	−8·2
12	5·3	−6·4

h	$\frac{1}{2}F_o$	$\frac{1}{2}F_c$
	$h16$	
$\bar{14}$	6·8	6·1
$\bar{13}$	8·2	7·5
$\bar{12}$	5·6	6·4
$\bar{7}$	9·0	−9·4
$\bar{3}$	8·4	8·4
$\bar{2}$	16·3	17·7
0	4·3	4·4
1	5·6	5·2
2	6·9	6·8
3	8·9	−8·7
4	11·0	−11·0
7	9·2	8·6
9	9·0	8·3
	$h1\bar{7}$	
3	12·3	−12·3
4	15·4	−15·4
6	6·0	6·9
7	5·3	7·6
8	6·1	6·0
13	9·7	−9·4
14	10·2	−9·7
	$h17$	
$\bar{15}$	6·6	6·9
$\bar{14}$	6·8	6·5
$\bar{8}$	5·4	−5·4
$\bar{6}$	11·4	11·4
$\bar{4}$	7·1	8·0
$\bar{3}$	10·0	11·3
$\bar{2}$	5·1	5·8
2	5·6	−6·0
3	5·1	−4·5
4	3·6	−4·1
6	10·4	9·5
	$h1\bar{8}$	
$\bar{3}$	6·7	7·6
2	11·0	−11·2
9	6·6	7·3
12	6·8	−6·9
13	8·1	−9·6
	$h18$	
$\bar{15}$	6·7	5·6
$\bar{8}$	10·6	−10·4
$\bar{7}$	6·5	6·6
$\bar{6}$	5·8	6·1
$\bar{5}$	3·5	3·9
$\bar{4}$	3·5	−3·6
$\bar{3}$	3·5	−4·3
	$h19$	
$\bar{13}$	4·5	−4·6
$\bar{12}$	6·7	−7·5
$\bar{7}$	11·1	10·8
$\bar{3}$	7·4	−7·7
$\bar{2}$	13·3	−12·0
$\bar{1}$	13·1	−12·3

h	$\frac{1}{2}F_o$	$\frac{1}{2}F$
	$h20$	
$\bar{9}$	6·1	6·6
$\bar{8}$	6·4	6·7
$\bar{7}$	5·5	4·3
$\bar{6}$	11·4	12·2
$\bar{3}$	10·1	−15·1
	$h2\bar{1}$	
$\bar{7}$	6·5	6·5
$\bar{6}$	7·1	6·2
$\bar{5}$	3·0	4·0
$\bar{4}$	14·7	−15·3
$\bar{3}$	14·4	14·4
$\bar{2}$	17·0	−15·7
$\bar{1}$	*	−19·6
0	*	−9·6
1	*	−16·7
	$h21$	
$\bar{10}$	10·4	10·1
$\bar{8}$	9·8	9·0
$\bar{7}$	10·4	10·4
$\bar{6}$	6·0	6·7
$\bar{5}$	7·2	−6·7
$\bar{4}$	7·1	−5·3
$\bar{3}$	6·1	−3·5
$\bar{2}$	9·9	−7·7
	$h2\bar{2}$	
$\bar{10}$	5·8	−7·5
$\bar{9}$	4·3	−5·3
$\bar{6}$	6·1	5·5
$\bar{5}$	13·6	11·7
$\bar{4}$	20·4	−20·3
$\bar{3}$	14·3	13·8
$\bar{1}$	12·0	−11·6
0	30·6	−26·0
1	24·1	−16·4
	$h22$	
$\bar{11}$	6·3	5·8
$\bar{10}$	4·3	5·2
$\bar{7}$	15·3	−14·8
$\bar{5}$	10·7	10·0
$\bar{4}$	6·1	6·2
$\bar{2}$	6·6	−6·6
	$h2\bar{3}$	
$\bar{8}$	4·3	−5·7
$\bar{7}$	6·5	−5·5
$\bar{3}$	11·9	−12·8
$\bar{2}$	12·6	11·6
$\bar{1}$	6·4	5·6
0	16·1	15·8
1	*	10·6
	$h23$	
$\bar{13}$	10·4	10·1
$\bar{12}$	7·9	7·9
$\bar{11}$	8·9	8·7
$\bar{8}$	8·9	−8·8
$\bar{7}$	10·8	−10·8
$\bar{6}$	5·2	−3·4
$\bar{5}$	12·3	−11·3

h	$\frac{1}{2}F_o$	$\frac{1}{2}F_c$
	$h23$	
$\bar{3}$	6·3	7·5
$\bar{2}$	19·9	17·6
$\bar{1}$	5·9	4·2
0	2·8	4·5
	$h2\bar{4}$	
$\bar{8}$	5·8	−7·0
$\bar{2}$	31·9	33·4
$\bar{1}$	20·7	22·3
0	*	1·9
1	*	−8·7
2	*	3·3
	$h24$	
$\bar{9}$	7·1	−7·2
$\bar{8}$	8·1	−8·8
$\bar{7}$	7·0	−7·2
$\bar{5}$	4·9	4·5
$\bar{4}$	6·8	6·4
$\bar{3}$	5·4	−6·0
$\bar{2}$	13·0	11·9
$\bar{1}$	4·5	4·8
0	7·2	−8·2
	$h2\bar{5}$	
$\bar{1}$	7·5	5·9
	$h25$	
$\bar{11}$	5·7	−6·2
$\bar{10}$	5·8	−6·6
$\bar{9}$	5·0	−4·5
$\bar{8}$	4·1	−5·1
$\bar{7}$	4·1	−4·6
$\bar{6}$	5·7	5·5
$\bar{5}$	8·1	5·5
$\bar{4}$	4·2	3·6
$\bar{2}$	7·0	7·4
$\bar{1}$	6·5	−6·1
0	12·4	−11·1
1	7·7	−7·6
2	7·0	−7·2
	$h26$	
$\bar{10}$	7·0	−8·2
$\bar{9}$	6·2	7·4
$\bar{8}$	4·1	4·9
$\bar{7}$	3·6	3·5
$\bar{6}$	5·0	5·9
$\bar{5}$	10·5	11·0
$\bar{2}$	7·7	−8·3
$\bar{1}$	4·3	−6·1
0	7·1	−8·5
1	8·3	−8·5
4	8·1	8·8
6	10·9	12·4
	$h27$	
$\bar{9}$	10·7	12·6
$\bar{3}$	5·8	6·1
$\bar{2}$	4·8	5·9
0	6·6	−6·8
2	4·3	6·1
3	5·3	5·5

h	$\frac{1}{2}F_o$	$\frac{1}{2}F_c$
	$h28$	
$\bar{10}$	10·2	11·6
$\bar{9}$	6·2	6·3
$\bar{4}$	4·9	−5·8
$\bar{3}$	10·6	−10·3
$\bar{1}$	9·7	11·4
0	8·8	8·3
1	5·8	N.C.
	$h29$	
$\bar{11}$	6·8	−2·5
$\bar{4}$	4·8	−4·9
$h2l$ (Lower half of film)		
	$h20$	
2	6·6	9·0
3	11·5	15·8
4	4·5	−7·3
5	11·4	15·4
8	3·2	−2·9
9	8·4	−9·1
11	5·9	−7·3
	$h2\bar{1}$	
2	12·1	10·3
3	10·5	7·3
4	6·2	−5·6
6	3·5	2·8
7	3·2	4·0
8	4·6	−5·2
9	7·3	−7·9
10	5·4	−6·4
11	4·5	−5·1
	$h21$	
0	17·0	12·9
1	29·0	20·4
2	13·9	10·9
6	4·3	−4·1
7	10·8	−10·1
8	9·7	−10·3
10	11·9	12·6
11	10·9	11·2
	$h2\bar{2}$	
2	2·6	4·3
3	3·9	−3·2
5	4·9	−4·4
6	16·9	16·0
7	5·1	5·9
8	3·1	3·2
11	8·8	−8·8
13	4·7	−5·1
	$h22$	
$\bar{1}$	18·1	15·2
0	11·1	8·3
1	13·4	11·6
2	22·6	19·4
3	9·4	8·7

h	$\frac{1}{2}F_o$	$\frac{1}{2}F_c$
	$h22$	
5	10·8	−9·1
6	6·9	−7·3
7	5·1	−5·1
8	4·3	−3·6
11	6·7	6·7
12	10·0	9·8
	$h2\bar{3}$	
2	6·5	−5·8
3	6·9	−6·9
4	8·9	−7 6
5	5·4	−4·9
7	5·5	6·1
8	4·6	4·8
9	4·8	5·2
10	10·5	11·3
	$h23$	
2	6·9	−7·7
3	7·3	−7·0
6	5·4	−5·9
	$h2\bar{4}$	
3	6·5	−7·2
4	7·8	−7·6
5	11·3	−9·3
6	4·7	−5·0
8	12·3	12·0
9	12·8	12·3
10	5·9	6·7
11	7·6	8·1
12	6·4	−8·3
	$h24$	
1	21·2	−19·3
2	6·3	−6·5
6	4·8	−6·3
7	8·0	8·6
	$h2\bar{5}$	
0	*	11·1
1	*	5·6
2	*	0·6
3	*	−0·7
4	10·7	−10·0
10	4·8	6·5
11	7·6	9·3
	$h25$	
6	4·8	5·2
7	6·4	7·6
	$h2\bar{6}$	
8	4·8	−5·8
9	3·5	−5·3
	$h2\bar{7}$	
8	5·9	−7·9
9	3·0	−6·1
10	3·2	−4·4

carbon atom, C(7), a plausible emendation of the y-co-ordinate was made on chemical grounds: the value resulting from the least-squares refinement would have put this atom 0·06 Å out of the plane of its benzene ring and given less probable lengths for the two C–O bonds; since the co-ordinate is near to $\frac{1}{4}$, its value is insensitive to the $h1l$-data, and hence it seemed valid to make the small modification embodied in Table 3 to bring the atom into the plane. This change has no appreciable effect on R.

The accuracy of the analysis was assessed from the least-squares residuals. The programme used involves 9 parameters for each atom, so that, including a scaling factor, altogether 226 parameters were determined. Against these were some 750 observed reflexions; but for the y-co-ordinates the $h0l$-reflexions provide no useful information, and the excess of observations over parameters is then less adequate. The standard deviations (σ) were derived by the usual formula. They will be a little inflated because unobserved reflexions were included only for the most unfavourable terms. To take account of the σ-values for all 75 individual positional parameters was not deemed justifiable in view of the modest excess of observations; and the values shown in Table 4 are averages for atoms of each chemical type. Also shown are derived values of σ for bond-lengths. For bond-angles σ is about 2°. The more important of these dimensions are embodied in Fig. 4. Later it will be convenient to discuss this structure in terms of a "representative molecule;" it is comprised by the atoms with the co-ordinates listed in Table 3 for nitrobenzoate residue D, and for E by the atoms with co-ordinates listed for x and z but with y increased to $y + 1$. When two contacts between a given pair of atoms are noted in Fig. 4, one of them refers to a second representative molecule, one primitive translation removed along y; the distance corresponding to this latter molecule is shown in parentheses. Values of $|F_o|$ and F_c are listed in Table 5.

DISCUSSION

The first object of this work was to discover whether the structures of these acid nitrobenzoates differ in the manner suggested by their spectra. The suggestion has been verified and the structure of the *o*-nitrobenzoate has already been described. Attention can now be shifted to potassium hydrogen di-*p*-nitrobenzoate, the details of whose structure are of some interest in themselves.

The two nitrobenzoate residues are crystallographically distinct. That marked D in Figs. 3 and 4 is the anion, X^-; that marked E the neutral molecule, HX. The evidence for this assignment is as follows: D makes contacts with potassium ions through three of its oxygen atoms—O(5) and O(6) belonging to its carboxyl group, and O(8) of its nitro-group—whilst E makes contact only through one carboxylic atom, O(1); the dimensions of the two carboxyl groups differ in the sense required: *e.g.*, D has the C–O lengths nearly equal, E has them unequal; in the final difference synthesis, a peak of height 1·0 electron per Å^2 appeared nearly on the line O(2) $\cdots$ O(5) and nearly in the position appropriate to a hydrogen atom covalently linked to O(2).

Both benzenoid rings are substantially planar. For ring E the mean plane is given by the equation,

$$-0{\cdot}374X' + 0{\cdot}809Y' - 0{\cdot}213Z' = -2{\cdot}092$$

and for D by

$$-0{\cdot}187X' + 0{\cdot}795Y' - 0{\cdot}420Z' = 1{\cdot}473$$

The average deviations of the carbon atoms from these planes are 0·01 Å for D and 0·03 Å for E. In each residue the nitro- and carboxyl groups are slightly, but significantly, twisted out of the plane of the benzene ring; the twists are in the same direction about the longest axis of each residue, and they amount to 5° for both groups in D, and to 5° for NO_2 and 10° for CO_2^- in E. The two potassium ions related by the centre of inversion chosen as origin are separated by 4·71 Å, and those related by the centre at $0\tfrac{1}{2}0$ by 4·20 Å. These close approaches are mitigated by an environment of oxygen atoms. Each potassium is surrounded by six oxygen atoms of six different nitrobenzoate groups, the oxygen atoms lying at the corners of a distorted octahedron. That one K $\cdots$ O contact is with oxygen of a nitro-group is noteworthy.

The hydrogen bond, with O $\cdots$ O = 2·492 ± 0·020 Å, joins residues D and E together to give a well-defined anionic complex. This complex corresponds to the representative molecule. In contrast to the symmetrical anionic complex in the *o*-nitrobenzoate and in other acid salts of type A, which may be formulated as $\overset{-}{\overbrace{X{-}H{-}X}}$, this complex is unsymmetrical and may be formulated as $\bar{X}\cdots H{-}X$. Such units are linked together into infinite columns in the y-direction by electrovalent forces between their carboxylic oxygen atoms and the ascending zig-zag of potassium ions; and the parallel columns are tied together in the z-direction because residue D makes contact at either end with potassium ions. Thus are constituted strongly bound, infinite layers parallel to (100), which is the prominent morphological plane. In keeping with the ready cleavage, only van der Waals forces operate between the layers, though the fit between neighbouring layers is a good one: the protuberant *E*-residue of one layer occupies the indentation between two *E*-residues of the next, as can be seen in Figs. 3 and 4. Intermolecular contacts less than 3·8 Å have been noted in Fig. 4. Only one calls for comment—that of 3·28 Å between O(2) and C(14). The aromatic hydrogen atom should be about 2·95 Å from the oxygen. Similarly short contact distances have been reported previously.[11]

The hydrogen bond is " very short," and indeed shorter than the average (~2·5 Å) for all the salts of type *A* so far studied. This proves that mere shortness of hydrogen bonding is not the cause of the spectral anomaly shown by the latter. Some other cause must be sought; and two facts, implicit in the previous paragraph, may now be emphasised:

(1) The hydrogen-bonded unit ($-\mathrm{Y\overset{-}{H}Y}-$, where Y is a carboxyl groups, or part of one) in the *p*-nitrobenzoate is unsymmetrical, whereas the unit in type *A* acid salts is effectively symmetrical; and (2) these units in the *p*-nitrobenzoate form part of a hydrogen bond–electrovalency sequence ($\cdots \mathrm{Y\overset{-}{H}Y}\ \overset{+}{\mathrm{M}}\ \mathrm{Y\overset{-}{H}Y}\ \overset{+}{\mathrm{M}}\ \mathrm{Y\overset{-}{H}Y} \cdots$) that runs in only *one* dimension, as spiral chains, whereas the units in type *A* acid salts belong to sequences that extend infinitely in *two* or *three* dimensions (as nets or lattices). An explanation of the spectral anomaly must take account of these special features. A discussion of them is essayed in Part VI.

In the later stages of this work most of the calculations were done on the Glasgow University DEUCE computer, and we are indebted to the Director of the Computing Laboratory for this facility. The large-scale crystallographic programmes, developed by Dr. J. S. Rollett, were made available by courtesy of the Superintendent of the Mathematics Division of the National Physical Laboratory. We are also indebted to the University of Sauger (India) for granting study-leave and financial assistance to H. N. S. We appreciate the interest shown in this work by Professor J. M. Robertson, F.R.S.

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[11] Abrahams and Sime, *Acta Cryst.*, 1960, **13**, 1.