648. lin-*Poly*-p-*xylylene. Part II.* The Crystal Structure of Di*-p-*xylylene.*

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One of the crystalline substances extracted from the polymer obtained by pyrolysis of *p*-xylene has been shown, solely by *X*-ray diffraction methods, to be a new compound, di-*p*-xylylene. A complete structure determination has been carried out, and it is found that the benzene rings are not flat; the two substituted carbon atoms in the *para*-positions are each displaced by 0·133 Å from the plane of the other four. The planes of these carbon atoms in a single molecule lie 3·09 Å apart. Bond lengths are all of normal values, the aromatic C–C distances being 1·39 and 1·40 Å, and the aliphatic 1·54 and 1·55 Å.

As described in Part I,* the products formed during the pyrolysis of *p*-xylene were largely polymeric, but extraction of some of these samples with chloroform (Soxhlet) yielded a mixture of crystalline compounds of comparatively low molecular weight. The major constituent was readily identified as 4 : 4′-dimethyldibenzyl, but one, insoluble in acetone, was unrecognised. A portion of the latter sample was recrystallised from pyridine, yielding tetragonal prisms which melted sharply at 285°.

The unit-cell dimensions of these crystals, which were obtained by measuring the layer-line spacings on *X*-ray rotation photographs, were $a = 7{\cdot}82$ and $c = 9{\cdot}33$ Å. The density of the crystals, as observed by flotation in sodium iodide solution, was 1·23, and hence the weight per unit cell was calculated to be *ca.* 420. Microanalysis gave a C : H ratio of 1 : 1, and since no other atoms were present, it seemed probable that the unit cell contained 32C + 32H, with weight of 416. A molecular-weight determination in the mass spectrometer gave the principal peak at 208, whence it appeared that the unit cell contained two molecules of $C_{16}H_{16}$.

All *X*-ray reflexions were present except those from planes $\{0kl\}$ with $(k + l)$ odd, indicating one glide plane in the tetragonal lattice. The space-group could therefore have been $P\bar{4}n2$ (D_{2d}^{8}), $P4_2nm$ (C_{4v}^{4}), or $P4_2/m.nm$ (D_{4h}^{14}). The first two of these are polar, and the third is centro-symmetrical; the choice could ideally have been made by a pyro- or piezo-electric test, but at the time there was scarcely sufficient specimen available. It was found in the course of the refinement of the structure that the space-group of highest symmetry $P4_2/m.nm$ (D_{4h}^{14}) was the correct one.

Apart from the information that the unit cell contained two molecules of a hydrocarbon derived from *p*-xylene of probable formula $C_{16}H_{16}$, nothing was known about the constitution of the substance at this stage. Since it was chemically reasonable that the substance should be 2 : 6- or 2 : 7-dimethylanthracene or 3 : 6-dimethylphenanthrene, samples of these compounds were examined by *X*-ray powder photography but their diffraction patterns were different from that of the new substance $C_{16}H_{16}$.

A complete set of *X*-ray intensity data was then obtained in the usual way, and attempts were made to fit a structure to them. The difficulty was to find a reasonable molecule $C_{16}H_{16}$ which would fit into the unit cell without overlapping its neighbours. Furthermore, the molecule must have the requisite symmetry. Fused-ring compounds were generally too bulky. It was evident that the molecule had to be fairly compact, and consideration was given to those of approximately spherical shape. When no further suitable trial structures could be suggested it was decided to compute a three-dimensional Patterson synthesis for a limited region around the origin, and as a preliminary to this, a two-dimensional Patterson synthesis was computed, using $F^2\{hk0\}$ terms only.

The result of this is shown in Fig. 1. There is a very pronounced peak *P* on the diagonal of this vector map at about 3 Å from the origin. This indicated that the majority of inter-atomic vectors superpose on this peak; the interpretation is that the peak would be accounted for by placing two benzene rings parallel to each other in planes 3 Å apart. A

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* Part I, preceding paper.

model was made up on this basis, and with the substituent methyl groups placed appropriately at 1·5 Å from each other; good agreement between calculated and experimental structure amplitudes was at once obtained. This led to the characterisation of the compound as di-*p*-xylylene as already reported briefly (Brown and Farthing, *Nature*, 1949, **164**, 915), and further Patterson syntheses were rendered unnecessary.

No previous mention of di-*p*-xylylene could be found. Since this work was completed, its preparation has been achieved by other workers (Cram and Steinberg, *J. Amer. Chem. Soc.*, 1951, **73**, 5691). Attention was drawn to the analogous di-*o*-xylylene (Baker, Banks, Lyon, and Mann, *J.*, 1945, 27), on which some *X*-ray work was proposed, but apparently never commenced, and to di-*m*-xylylene, originally prepared by Pellegrin (*Rec. Trav. chim.*, 1899, **18**, 458) and more recently confirmed by Baker, McOmie, and Norman (*Chem. and Ind.*, 1950, **77**; *J.*, 1951, 1114). The complete structure determination of di-*m*-xylylene by *X*-ray diffraction, using crystals kindly supplied by Baker, has now been completed (Brown, *J.*, 1953, 3278).

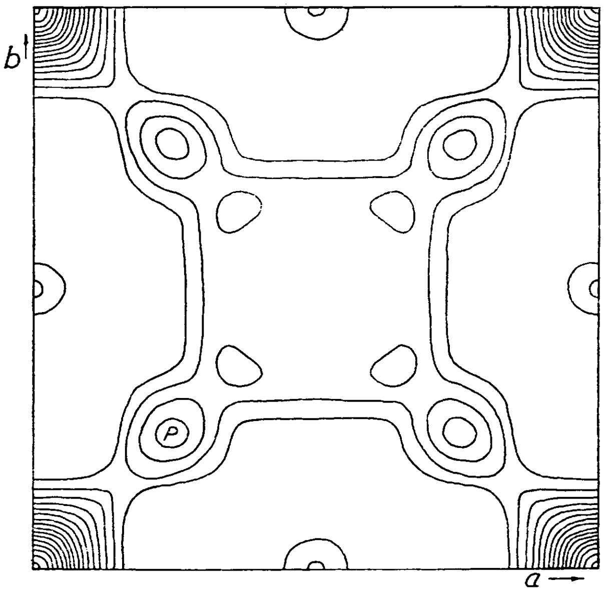


FIG. 1. *Patterson vector map obtained by projection along* c *axis.*

As di-*p*-xylylene would generally be regarded as a stereochemically impossible compound owing to the distortions necessary, a complete quantitative *X*-ray study was made, so as to determine the bond lengths and inter-bond angles. After the two-dimensional Patterson synthesis, refinement was carried out first by means of two-dimensional Fourier syntheses, projecting along *c* and then along *a*. The *c* projections were not very fruitful as they gave only *x* co-ordinates, and the resolution of the atoms was poor because only 40 {*hk*0} reflexions were observed. The *a* projections gave both *x* and *z* co-ordinates, but the resolution was still poor as only 45 {0*kl*} reflexions were observed. It thus became necessary to employ three-dimensional syntheses.

At this stage, no choice had been made between the three permissible space-groups. That of the lowest symmetry, $P\bar{4}n2$, was chosen for structure amplitude calculations, and the whole set of F{*hkl*} computed. The sum of the *B* components ($F^2 = A^2 + B^2$) of the terms used in the synthesis was almost zero, with the result that the non-equivalent atoms moved from their original positions to positions which they would occupy in the space-group $P4_2/m.nm$. This led to adoption of this centrosymmetrical space-group, and as nothing emerged in the subsequent refinement to throw doubt on the choice, this space-group may be regarded as established. In this space-group, which has a 16-fold general position, out of the 32 carbon atoms in the unit cell, 16 lie in a general position, all related by symmetry elements, and the remaining 16 in two groups of 8 in 8-fold special positions, thus (the nomenclature being that of the International Tables for *X*-Ray Crystallography) :

16 *k* : $x, y, z;\ \bar{x}, \bar{y}, z;\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}+z;\ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}+z;\ x, y, \bar{z};\ \bar{x}, \bar{y}, \bar{z};$
$\tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}-z;\ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}-z;\ y, x, z;\ \bar{y}, \bar{x}, z;\ \tfrac{1}{2}+y, \tfrac{1}{2}-x, \tfrac{1}{2}+z;$
$\tfrac{1}{2}-y, \tfrac{1}{2}+x, \tfrac{1}{2}+z;\ y, x, \bar{z};\ \bar{y}, \bar{x}, \bar{z};\ \tfrac{1}{2}+y, \tfrac{1}{2}-x, \tfrac{1}{2}-z;\ \tfrac{1}{2}-y, \tfrac{1}{2}+x, \tfrac{1}{2}-z.$

8 *j* : $x, x, z;\ \bar{x}, \bar{x}, z;\ \tfrac{1}{2}+x, \tfrac{1}{2}-x, \tfrac{1}{2}+z;\ \tfrac{1}{2}-x, \tfrac{1}{2}+x, \tfrac{1}{2}+z;\ x, x, \bar{z};\ \bar{x}, \bar{x}, \bar{z};$
$\tfrac{1}{2}+x, \tfrac{1}{2}-x, \tfrac{1}{2}-z;\ \tfrac{1}{2}-x, \tfrac{1}{2}+x, \tfrac{1}{2}-z.$

There are therefore seven parameters to be determined, x, y, and z for the carbon atoms in the general position, and x and z for each of the two carbon atoms in special positions. As shown in Fig. 2, in any given molecule of di-*p*-xylylene, only three of the sixteen carbon atoms are crystallographically different. This is due to the three mirror reflexion planes at right angles in the molecule meeting in a centre of symmetry, which coincides with a centre of symmetry in the unit cell.

Two sets of three-dimensional Fourier syntheses were computed successively in order to determine the seven parameters. After the first, it was observed that carbon atom 2 was displaced from the position it should occupy if the benzene ring were rigidly planar. It was restored to this position in the plane before the structure amplitudes were re-calculated, but the second synthesis confirmed the displacement. The final atomic co-ordinates are :

	x	y	z
Carbon 1	0·070	0·070	0·030
Carbon 2	0·128	0·128	0·150
Carbon 3	0·248	0·032	0·075

The corresponding composite electron-density map is shown in Fig. 3. If the benzene ring were rigidly planar, the x and y co-ordinates of carbon atom 2 would be each 0·140 instead of 0·128, so the displacement of carbon 2 from the plane of the other four atoms in the ring is given by $0{\cdot}012a\sqrt{2} = 0{\cdot}133$ Å. That the displacement is genuine is shown by the results of the two successive three-dimensional syntheses, and there is therefore evidence of a slightly bent, boat-shaped benzene ring. The bending is presumably occasioned by the necessity of reducing the strain in the system; this can be done without altering the bond-lengths or angles very greatly from their standard values, as shown in Table 1. Two views of the molecule at right angles to each other are shown in Fig. 4.

TABLE 1.

(a) *Bond lengths* (Å) :
C_1–C_1' (aliphatic) = **1·55**, C_1–C_2 (aliphatic) = **1·54**, C_2–C_3 (aromatic) = **1·39**, C_3–C_3' (aromatic) = **1·40**.

(b) *Inter-bond angles* :
$C_2\widehat{C_1}C_1'$ = **114° 37′**, $C_3\widehat{C_2}C_3'$ = **118° 36′**, $C_1\widehat{C_2}C_3$ = **119° 55′**, $C_2\widehat{C_3}C_3'$ = **120° 14′**.

(c) *Intra-molecular distances* (Å) *between non-bonded atoms* :
C_2–C_2' = **2·83**, C_3–C_3' = **3·09**.

(d) *Inter-molecular distances* (Å) :
C_1–C_1' (along c axis) = **3·73**, C_1–C_3 (along **111**] approx.) = **4·06**.

After the positions of the carbon atoms had been determined, an attempt was made to locate the hydrogen atoms by computing three-dimensional difference syntheses, using F(exp.) —F(calc.) as coefficients. The result of this was that, although there were regions of positive electron density in places where hydrogen atoms would be expected to occur, there were no very clearly defined maxima in these regions. Theoretical positions were therefore chosen for the hydrogen atoms at distances of 1·08 Å from the carbon atoms to which they are attached, as follows :

	x	y	z
Hydrogen 1 (attached to Carbon 1)	0·210	0·020	0·362
Hydrogen 2 (attached to Carbon 3)	0·332	0·948	0·133

The co-ordinates of the other hydrogen atom attached to carbon 1 may, of course, be derived from those of hydrogen 1 by the usual symmetry operation of the space-group,

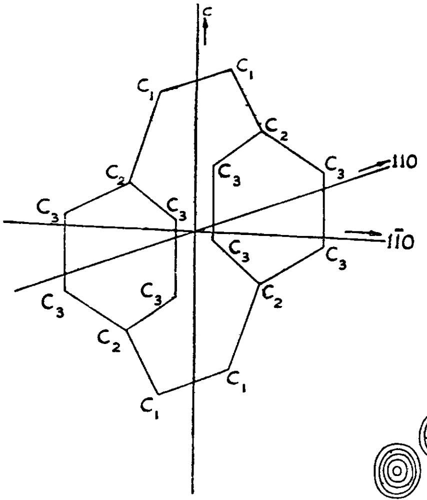


FIG. 2. *Molecule of di*-p-*xylylene showing location with respect to three axes and three mirror reflexion planes at right angles.*

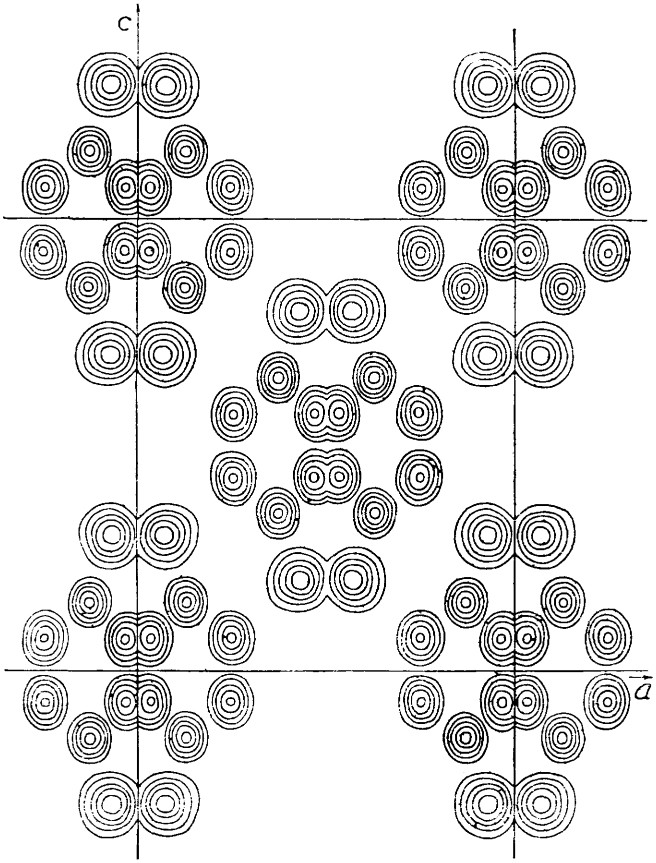
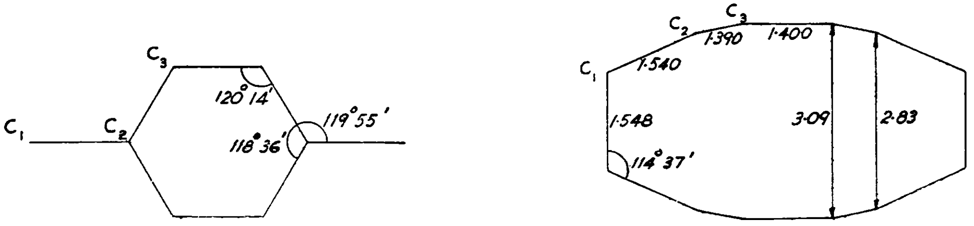


FIG. 3. *Composite electron-density map resulting from sections of a three-dimensional Fourier synthesis at appropriate values of y. Contours are at intervals of* 1 eÅ^{-3}.

FIG. 4. *Two views of the molecule of di*-p-*xylylene at right angles, showing dimensions and distortion from planarity.*



i.e., reflexion across (110). These hydrogen atomic co-ordinates were used in calculating the structure amplitudes listed in Table 2.

TABLE 2.

hkl	F (exp.)	F (calc.)	*hkl*	F (exp.)	F (calc.)	*hkl*	F (exp.)	F (calc.)	*hkl*	F (exp.)	F (calc.)
000	—	224	341	9·8	+ 8·2	363	1·3	− 0·6	146	1·4	+ 2·1
020	16	+16	351	3·4	+ 4·0	383	1·5	+ 0·6	156	1·4	− 1·5
040	8·2	+ 7·8	361	2·6	− 2·2	443	4·1	− 3·3	166	3·0	+ 2·5
060	7·0	− 5·9	371	5·5	+ 2·8	453	2·4	− 1·3	176	0·7	+ 0·3
080	4·1	+ 1·6	441	2·6	+ 2·2	463	1·3	− 0·7	186	0·8	+ 0·4
110	38	+46	451	4·0	+ 3·5	473	2·2	+ 1·3	226	4·8	+ 8·8
120	34	−36	551	7·1	− 5·0	573	1·5	+ 0·5	236	4·2	− 5·1
130	7·0	− 4·7	561	2·3	− 1·2	583	1·4	+ 0·6	246	1·0	− 0·7
140	12	−11	661	1·7	− 0·8	663	2·5	+ 0·7	256	2·2	+ 2·1
150	6·8	− 6·3	002	1·5	− 1·1	004	16	−17	266	2·0	+ 1·6
160	2·1	− 1·8	022	10	−12	024	1·8	+ 1·2	286	1·2	− 0·6
180	2·4	− 1·5	042	16	+15	044	1·8	+ 1·5	336	1·3	+ 1·9
190	0·4	− 0·2	082	1·7	+ 1·5	084	2·0	− 1·7	346	2·3	− 2·4
220	38	−38	112	18	−22	114	1·8	− 1·9	017	2·1	+ 2·0
230	18	−17	122	4·0	+ 5·0	124	6·0	+ 6·9	037	3·4	− 4·5
250	2·2	− 2·3	132	0·6	− 0·6	134	3·8	+ 4·2	057	3·2	− 3·3
260	7·6	− 7·0	142	1·2	− 1·0	164	1·0	− 1·1	117	1·0	− 1·1
270	3·1	+ 2·4	152	3·3	+ 4·1	174	1·0	− 1·3	127	4·0	+ 5·6
280	2·0	+ 0·5	162	3·0	− 2·4	184	0·5	+ 0·4	137	1·4	− 1·5
290	1·6	− 0·5	172	1·0	+ 1·3	194	0·5	− 0·3	147	4·1	− 4·4
330	4·0	+ 5·4	182	1·5	− 1·0	224	6·2	+ 7·1	157	2·6	+ 2·5
340	1·8	− 1·1	222	20	−23	234	2·2	+ 1·4	167	0·9	+ 0·5
350	2·0	+ 1·9	232	11	+12	254	2·0	− 2·8	177	1·3	+ 0·6
360	5·4	+ 3·7	242	3·0	+ 1·8	274	1·3	− 1·0	227	2·8	− 4·9
370	1·8	− 1·9	262	2·4	− 1·0	334	2·3	− 2·5	237	2·2	+ 3·0
380	2·0	+ 1·6	282	2·0	+ 1·4	344	3·0	− 2·6	267	1·2	+ 0·9
440	14	+13	342	6·8	+ 7·8	354	2·0	− 1·6	337	5·2	− 5·7
450	4·5	− 6·1	362	2·2	+ 2·1	364	2·2	− 1·9	008	4·5	− 6·6
460	2·0	− 0·7	382	1·6	+ 0·4	444	3·9	− 4·1	028	1·4	− 1·4
470	2·2	+ 1·0	442	3·2	+ 2·4	564	2·4	+ 1·1	048	2·5	− 2·7
550	2·0	+ 2·2	462	2·0	− 0·7	015	12	−16	068	1·4	+ 1·2
560	5·2	− 3·9	552	1·4	− 1·0	035	4·2	− 5·5	118	1·3	− 1·7
580	1·3	− 0·3	013	7·0	+ 7·0	075	1·2	+ 0·8	128	0·9	+ 0·9
660	1·7	+ 0·1	033	9·3	+10·0	115	2·7	+ 4·0	138	1·0	− 0·8
670	1·4	+ 0·2	053	2·7	+ 2·3	125	1·0	+ 0·8	148	1·6	+ 1·7
011	37	+35	073	3·0	− 2·9	135	2·6	+ 4·4	158	0·7	+ 0·3
031	7·3	+ 5·9	093	1·2	− 0·7	145	2·3	− 2·6	168	1·2	+ 1·0
051	1·0	+ 1·3	113	3·1	+ 3·0	155	3·4	+ 3·8	178	0·5	+ 0·5
071	2·2	+ 3·3	123	4·4	+ 5·6	165	3·1	+ 3·7	228	1·9	+ 2·9
091	0·6	+ 0·4	133	0·8	+ 0·7	175	1·2	+ 0·6	258	1·5	+ 1·3
111	14	−17	143	5·8	+ 5·4	225	3·8	+ 4·3	268	2·0	+ 1·2
121	25	−24	153	5·1	− 5·3	235	2·4	+ 2·4	019	2·4	− 2·3
131	6·1	− 6·5	163	2·6	− 3·1	245	2·3	+ 3·4	059	0·8	+ 0·3
141	5·8	+ 5·8	173	2·3	− 1·0	255	1·7	− 2·8	119	1·0	+ 1·1
151	4·2	− 3·6	183	1·8	− 1·5	345	1·0	− 1·7	139	0·9	+ 0·9
161	3·7	− 4·6	193	0·5	+ 0·4	355	1·3	+ 1·5	169	0·5	+ 0·3
171	1·2	− 0·5	223	6·8	+ 5·9	365	1·8	+ 1·3	229	1·3	+ 1·3
181	3·8	+ 2·3	233	1·7	− 2·1	006	2·2	− 4·5	269	0·6	− 0·2
191	2·0	− 1·2	243	3·7	− 4·7	126	1·4	+ 1·5	0.2.10	0·9	+ 0·8
221	8·1	− 8·2	253	2·4	− 2·0	046	8·2	− 8·7	0.4.10	0·9	+ 0·6
231	8·2	− 8·3	263	4·4	− 3·8	066	1·1	+ 0·8	1.1.10	0·8	+ 0·5
241	1·8	+ 2·4	273	1·4	− 1·2	116	3·6	+ 4·0	1.2.10	0·7	+ 0·5
251	2·3	− 3·2	343	4·2	− 3·5	126	1·4	− 1·6	1.3.10	1·0	+ 0·8
261	3·0	+ 2·2	353	3·8	− 4·3	136	1·2	− 1·6	2.5.10	1·4	− 0·6
331	10·7	+10·7									

EXPERIMENTAL

Crystals of di-*p*-xylylene grown from pyridine were tetragonal prisms {110} exhibiting rather imperfect {111} pyramids. The cross-section of some specimens resembled a cross, but the suggested presence of multiple twins of lower symmetry was never confirmed. A section cut parallel to (001) gave an excellent uniaxial interference figure in convergent polarized light. The tetragonal system was further confirmed by the perfect identity of oscillation photographs about *c* taken 90° apart.

X-Ray intensity data were obtained from Weissenberg moving-film photographs of the zero and three layers about *a*, and the zero and four layers about *c*. Owing to a relatively high temperature factor which caused the reflexions to fall off to zero before $\theta = 90°$ with

Cu-$K\alpha$ radiation, all the diffraction data obtainable at room temperature were recorded on these photographs, totalling in all about 270 reflexions. The multiple-film technique was employed, and the intensities estimated visually with the aid of a time-exposure calibrated film strip. The usual corrections were applied for polarization and angular velocity.

Structure Amplitude Calculations.—In order to obtain agreement with the experimental F's, it was necessary to apply a rather large value of B ($8{\cdot}0 \times 10^{-16}$ Å^2) to the atomic scattering factors used in calculating the structure amplitudes. This is an unusually large temperature factor for a crystal which melts as high as 285°. As about 94% of the F's had values less than 10, one place of decimals was used for these small terms in both the experimental and calculated structure amplitudes, which are listed in Table 2. There are about 50 planes with small unobserved intensities within the range observable with Cu-$K\alpha$ X-rays, and these have been omitted from the Table. The usual residual $R = \frac{\Sigma|\mathrm{F(exp.)}| - |\mathrm{F(calc.)}|}{\Sigma \mathrm{F(exp.)}}$ amounts to 0·18 when the hydrogen atoms are neglected, and 0·14 when they are included, summed over all values of (hkl).

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