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The Crystal and Molecular Structure of 1:4-Dimethoxybenzene

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1:4-Dimethoxybenzene crystallizes in the space group *Pbca* with four centro-symmetrical molecules per unit cell. A quantitative X-ray investigation, based on visual intensity measurements of about 170 reflexions from crystallographically different planes in the axial zones, has led to a complete determination of the structure, and the results have been refined by double Fourier projections on the planes (100) and (010). The co-ordinates of all the atoms are given. The methyl groups lie in the plane of the ring, and the following bond lengths have been found:

$$C(1)\text{–}C(2) = 1{\cdot}36\ \text{A.},\ C(2)\text{–}C(3) = 1{\cdot}37\ \text{A.},\ C(3)\text{–}C(1') = 1{\cdot}44\ \text{A. (all in the benzene ring);}$$
$$C(1)\text{–}O = 1{\cdot}36\ \text{A.};\ O\text{–}C(CH_3) = 1{\cdot}35\ \text{A., all}\ \pm 0{\cdot}02\ \text{A.}$$

The valency angle of oxygen is 121 ± 2°. Some of these results are rather unexpected, and though some brief comments are made, detailed consideration is withheld pending their confirmation by the study of other similar compounds.

1. Introduction

Very little accurate structural information is available at present regarding the ethers. Sutton & Brockway (1935) have studied dimethylether in the vapour phase by the electron-diffraction method and find $C\text{–}O = 1{\cdot}44 \pm 0{\cdot}03$ A., and $\angle\, C\text{–}O\text{–}C = 111 \pm 4°$. Their results are inconclusive as to whether rotation of the methyl groups about the C–O bonds occurs since the addition of terms allowing for rotation made only very slight changes in the positions calculated for the maxima and minima. In the aromatic ethers dipole-moment investigations have provided the main evidence as to the valency angle of oxygen, figures up to 140° having been suggested. Following the criticisms by Bennett (1934*a*, *b*) of earlier work, Sutton & Hampson (1935) came to the conclusion that the angle will vary in different ethers and in many cases will be greater than 110°; in particular, they expected a value of 125° in anisole. 1:4-Dimethoxybenzene has a dipole moment of 1·67 D. in benzene solution and so cannot be centro-symmetrical under these conditions although our X-ray results show it to be so in the crystalline state. Recently Pleith (1947) has described briefly the crystal structure of *p*:*p*′-di-iodophenoxybenzene (di-iododiphenylether). Only the positions of the iodine atoms appear to have been determined, but, on the assumption of normal bond lengths in the remainder of the molecule, the C–O–C angle is calculated to be 123 ± 3°.

The cell dimensions and space group of 1:4-dimethoxybenzene indicate that a reasonably accurate X-ray determination of the structure should be feasible by ordinary two-dimensional projection methods. The results of such an investigation are described below, and the positions of all the atoms are obtained with some precision. In the crystal the molecule assumes a *trans* planar configuration, and the value obtained for the oxygen valency angle is 121° with a maximum error of 3½° and a probable error not greater than 2°. There is no evidence for rotation of the methoxy groups or even of the methyl groups in the crystal. Our detailed measurements of bond lengths are shown in Fig. 3. The variations found in the benzene ring are difficult to explain, and while they may be subject to some error, the departure from regularity appears to be significant. We think, however, that this result should be confirmed or refuted by the study of other similar structures before any detailed conclusions are based on the present findings.

2. Crystallographic measurements

1:4-Dimethoxybenzene, $C_8H_{10}O_2$, mol. wt. = 138·08; m.p. = 56° C.; $d_{\text{calc.}} = 1{\cdot}199$, $d_{\text{obs.}} = 1{\cdot}190$ g.cm.$^{-3}$. Orthorhombic bipyramidal:

$$a = 7{\cdot}29 \pm 0{\cdot}02;\quad b = 6{\cdot}30 \pm 0{\cdot}02;\quad c = 16{\cdot}55 \pm 0{\cdot}03\ \text{A.}$$

Volume of unit cell = 760 A.^{3} Absent spectra: $\{hkl\}$ no general halvings; $\{0kl\}$, $\{h0l\}$, $\{hk0\}$ absent when k, l, h odd respectively. Space group *Pbca*. Molecules per unit cell = 4; electrons per unit cell = $F(000) = 296$. Absorption coefficient for Cu $K\alpha$ radiation

$$(\lambda = 1{\cdot}54\ \text{A.}) = 8{\cdot}14\ \text{cm.}^{-1}$$

Refractive indices:

$$\alpha = 1{\cdot}506 \text{ parallel to } a;\quad \beta = 1{\cdot}610 \text{ parallel to } b;$$
$$\gamma = 1{\cdot}632 \text{ parallel to } c.$$

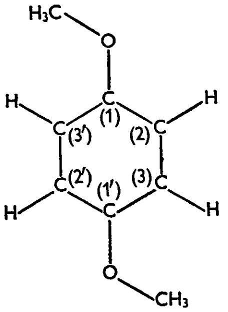
Negative birefringence $\gamma - \alpha = 0{\cdot}126$.

The crystals were rather soft, colourless plates tabular on {001}.

3. Analysis of the structure

The molecule being centro-symmetrical, the asymmetric unit consists of four carbon, one oxygen and five hydrogen atoms. In the analysis of the structure by trial and error it was assumed that the benzene ring was a regular plane hexagon of edge 1·39 A. with the oxygens lying at 1·36 A. from the ring carbon atoms

(Robertson, 1936; Palin & Powell, 1947) and the methyl carbon atoms at 1·43 A. from the oxygen atoms. The C–O–C angle was assumed to be 110°.



Since the birefringence of a single molecule of this substance would be high and negative, and since this coincides with the optical description of the crystals, it was clear that the molecules must lie roughly perpendicular to the a axis to which α is parallel. Since also γ is for vibrations parallel to the long c axis, it seemed likely that the long direction of the molecule would be more or less parallel to c though this was less certain since $\gamma-\beta$ is only 0·022.

Bearing these optical properties in mind, considerations of packing and of certain outstanding intensities suggested a probable orientation of the molecules which led to a measure of agreement between the observed and calculated intensities. Refinement of the structure by four successive double Fourier syntheses led to a projection on (100) in which all the carbon and oxygen atoms were well resolved and their y and z co-ordinates accurately determinable (see Fig. 1). In the last of these the benzene ring conformed to the regular planar hexagonal shape assumed at the outset. This assumption was therefore continued, with those regarding bond lengths, and the x co-ordinates of all carbon and oxygen atoms were calculated using the y and z co-ordinates given by the last projection on (100); hence the $\{h0l\}$ structure factors were deduced and used to carry out a Fourier projection on (010). In this only C(3′) was completely resolved. Refinement of the x co-ordinates of the other carbon and oxygen atoms was, therefore, much more difficult, but it also appeared that the bonds C(1)–C(2) and C(1)–C(3′) were considerably longer than C(2)–C(3), and thus the idea that the benzene ring is a regular hexagon had to be abandoned. As we had no reason to suppose that C(1)–C(2) and C(1)–C(3′) were unequal, atomic co-ordinates conforming to this criterion were tried, but it was not until the inequality of these bonds too was admitted that substantial agreement between $F_{\text{obs.}}$ and $F_{\text{calc.}}$ resulted. The subsequent Fourier projection showed more clearly the positions of C(1) and O as well as C(2), but also showed that the bond O–C(CH$_3$) is only 1·35 A. (see Fig. 2).

4. Hydrogen atoms

At this stage it was decided to include the hydrogen atoms in the calculations, assuming C(CH$_3$)–H = 1·09A., C(benzene ring)–H = 1·08 A., ∠ H–C(CH$_3$)–H = 109½°, and ∠ H–C(benzene ring)–C(benzene ring) = 120°. The methyl hydrogens lie on a circle which projects on to (100) and (010) as ellipses, and the minor axes of these were calculated by supposing C(CH$_3$)–O = 1·35 A. The positions of the hydrogen atoms were allocated in conformity with the above criteria and with the two-electron contour of the fourth Fourier projection on (100). The resulting improvement in the agreement between $F_{\text{obs.}}$ and $F_{\text{calc.}}$ is indicated by the fact that the discrepancy $D=100\Sigma\,|(F_{\text{obs.}}-F_{\text{calc.}})|\div\Sigma\,|F_{\text{obs.}}|$ fell from 18·2 to 15·0 for the 26 planes most affected. When the positions of the hydrogen atoms were inverted through their centre of gravity, D became 20, i.e. worse than when they were omitted entirely. An attempt to estimate the effect of rotation of the methyl group about the axis O–C(CH$_3$) by taking the mean values of $F_{\text{calc.}}$ with the hydrogen atoms in the two sets of positions already described gave $D=17$. We therefore consider that the hydrogen atoms have been located. The final discrepancies for all structure factors of the $\{h0l\}$ and $\{0kl\}$ zones were 11·5 and 12·2 respectively. Fig. 1 shows the final projection on (100) and Fig. 2 that on (010), the former including one weak plane whose sign had changed on including the hydrogen atoms.

5. Co-ordinates, orientation and dimensions

Table 1 gives the co-ordinates of all the carbon and oxygen atoms in the asymmetric unit both in Ångström units (X, Y, Z) and as fractions of the cell edges (x, y, z). Table 2 similarly gives the co-ordinates of the hydrogen

Table 1. *Co-ordinates of carbon and oxygen atoms*

Atom	X (A.)	Y (A.)	Z (A.)	x	y	z
C(1)	0·040	0·502	1·286	0·0055	0·0797	0·0777
C(2)	0·676	−0·672	1·013	0·0927	−0·1066	0·0612
C(3)	0·712	−1·176	−0·258	0·0977	−0·1866	−0·0156
O	0·076	0·996	2·551	0·0104	0·1581	0·1541
C(CH$_3$)	−0·556	2·152	2·863	−0·0763	0·3415	0·1730

Table 2. *Co-ordinates of hydrogen atoms*

Atom	X (A.)	Y (A.)	Z (A.)	x	y	z
H(2)	1·20	−1·19	1·80	0·165	−0·189	0·108
H(3)	1·26	−2·09	0·46	0·173	−0·332	0·028
H(1) of CH$_3$	−0·12	2·98	2·27	−0·016	0·473	0·137
H(2) of CH$_3$	−0·42	2·36	3·92	−0·058	0·375	0·237
H(3) of CH$_3$	−1·62	2·06	2·64	−0·222	0·327	0·159

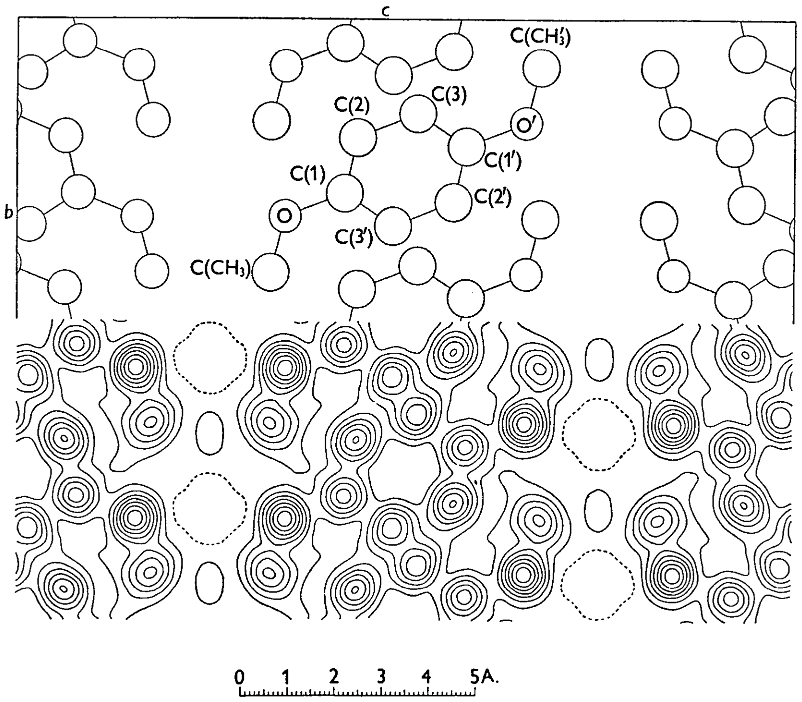


Fig 1 Projection of 1:4-dimethoxybenzene on (100). Contours at intervals of approximately 1 e.A.$^{-2}$. First contour dotted.

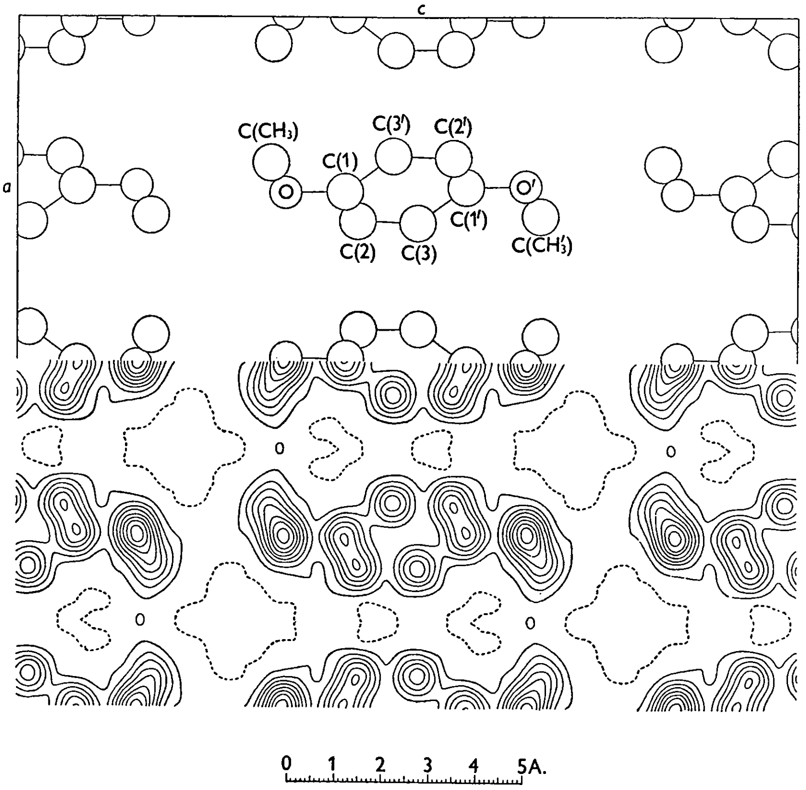


Fig. 2. Projection of 1:4-dimethoxybenzene on (010). Contours at intervals of approximately 1 e.A.$^{-2}$. First contour dotted.

atoms. If the co-ordinates of any atoms in the asymmetric unit are x, y, z, then those of the atoms derived from it by the operation of the symmetry elements are

$$\pm[x,y,z;\ \tfrac{1}{2}+x,\ \tfrac{1}{2}-y,\ -z;\ -x,\ \tfrac{1}{2}+y,\ \tfrac{1}{2}-z;\ \tfrac{1}{2}-x,\ -y,\ \tfrac{1}{2}+z].$$

The atoms C(1) and C(2) and the origin lie on the plane

$$x+0{\cdot}604y-0{\cdot}267z=0,$$

and all other atoms of the molecule lie on or near this plane (C(3), the most distant, is only 0·06 A. away) except H(1) of CH_3 and H(3) of CH_3, which straddle it. The atoms OC(1)C(1′)O′ are collinear with the centre of the ring, and this direction was therefore chosen as the molecular axis L. The second axis, M, lay in the above plane and perpendicular to L, the third, N, being at right angles to L and M. The complete orientation of the molecule is then given by the angles χ, ψ, ω which L, M and N make with the crystallographic axes a, b and c. These are shown in Table 3, while Table 4 gives the co-ordinates of the carbon and oxygen atoms with respect to the molecular axes. The bond lengths and valency angles are shown in Fig. 3; the former are, we believe, accurate to ±0·02 A. and the latter to ±2°. The molecules are inclined to the plane (100) at 33·4°.

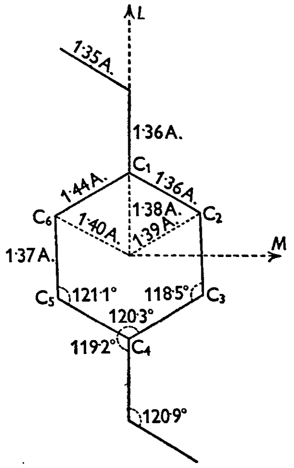


Fig. 3. Bond lengths and valency angles in 1:4-dimethoxybenzene.

Table 3. *Orientation of molecule*

$\chi_L=88{\cdot}3°$	$\chi_M=56{\cdot}6°$	$\chi_N=33{\cdot}4°$
$\psi_L=68{\cdot}7°$	$\psi_M=141{\cdot}6°$	$\psi_N=59{\cdot}8°$
$\omega_L=21{\cdot}4°$	$\omega_M=73{\cdot}2°$	$\omega_N=102{\cdot}9°$
$\cos\chi_L=0{\cdot}0290$	$\cos\chi_M=0{\cdot}5499$	$\cos\chi_N=0{\cdot}8348$
$\cos\psi_L=0{\cdot}3635$	$\cos\psi_M=-0{\cdot}7836$	$\cos\psi_N=0{\cdot}5038$
$\cos\omega_L=0{\cdot}9313$	$\cos\omega_M=0{\cdot}2887$	$\cos\omega_N=-0{\cdot}2228$

Table 4. *Co-ordinates of carbon and oxygen atoms with respect to molecular axes*

Atom	L (A.)	M (A.)	N (A.)
C(1)	1·382	0	0
C(2)	0·719	1·191	0
C(3)	−0·647	1·239	0·059
O	2·739	−0·002	−0·003
C(CH_3)	3·433	−1·165	−0·018

6. Arrangement of molecules and intermolecular distances

Inspection of Fig. 1 shows that the molecules, each roughly perpendicular to the a axis, form distinct layers perpendicular to c, while Fig. 2 indicates further pronounced separation, parallel to a, of the molecules within the layers.

The intermolecular distances call for little comment. If the molecules having their centres at (0, 0, 0), ($\tfrac{1}{2}$, $\tfrac{1}{2}$, 0) and ($\tfrac{1}{2}$, 0, $\tfrac{1}{2}$) are designated a, b, c, then the closest distances of approach of atoms in different molecules are $O(1)^b$–$C(CH_3)^c$ = 3·52 A. and $C(1)^a$–$C(2)^b$ = 3·54 A. The distance $O(1')^a$–$C(CH_3)^b$ = 3·75 A. is the only other intermolecular distance of less than 3·86 A., so that it is clear that the prevailing intermolecular forces are all of the normal van der Waals type. Both the general arrangement and the intermolecular distances are in agreement with the observed volatility of the compound.

7. Interatomic distances and valency angle of oxygen

Until more information is available about the bond lengths in other similar structures it is probably unwise to base any detailed conclusions on the findings of the present investigation. Nevertheless, the following comments may be made:

(*a*) The shortness of the C(1)–O bond (1·36 A.) agrees with the similar length in resorcinol (Robertson, 1936) and indicates that even with formally saturated side chains the bonds attaching them to the ring have considerable double-bond character; therefore, in the particular case of 1:4-dimethoxybenzene the methyl carbons are likely to lie in the plane of the ring, as found.

(*b*) Baker & Nathan (1935), Mulliken, Rieke & Brown (1941) and others have recognized that a methyl group attached directly to an unsaturated group (as in toluene) or to another methyl group (as in ethane) is able to induce double-bond character into the intervening single bond by undergoing delocalization of its electrons (hyperconjugation). Here the H_3C group is separated by the C–O bond from the partially unsaturated O–C(1) bond, and hence the intermediate bond should be shortened, as found.

(*c*) We have calculated the resonance energy of 1:4-dimethoxybenzene. From the heat of combustion of the solid ($\Delta H=-1015{\cdot}1$ kg.cal. determined by Stohmann, Rodatz & Herzberg (1887) corrected to the gas phase by a correction of −15·3 kg.cal.) the heat of formation from atoms of carbon, oxygen and hydrogen is $\Delta H_f=-1696$ kg.cal. The sum of the bond energies gives $\Delta H_f=-1631$ kg.cal., whence the resonance energy is 65 kg.cal., compared with 40 kg.cal. in benzene and 44 kg.cal. in p-xylene. This value may not be quite correct, but unless there is a gross error in the heat of combustion it is quite evident that the resonance energy of 1:4-dimethoxybenzene is much greater than that of benzene, and hence other resonance besides that of the benzene ring must be quite important.

(*d*) When two double bonds are separated by a single bond, the compound with the *trans* configuration is more stable than that with the *cis*. This is exemplified by the *cis* and *trans* azobenzenes (Hartley, 1938) by the parallel arrangement of the double bonds in diethyl muconate (Knaggs & Lonsdale, 1942) and in sorbic acid (Lonsdale, Robertson & Woodward, 1941), etc. In the present case this would suggest that if C(CH_3) is nearer to C(3′) than to C(2) then C(1)–C(2) should be shorter than C(1)–C(3′), as is found.

(*e*) The observed valency angle of oxygen (121 ± 2°) is, as expected, considerably greater than the value of 90° predicted by the simplest possible application of wave mechanics to this atom.

8. Experimental

(1) *Preparation*

Quinol dimethylether was prepared from hydroquinone by methylation with dimethyl sulphate and caustic soda as described by Vermeulen (1906). The best crystals for X-ray work were obtained by very slow evaporation of a solution in 60–80° petroleum ether,

Table 5. *Observed and calculated structure factors*

hkl	sin θ ($\lambda = 1{\cdot}54$ A.)	$F_{\text{obs.}}$	$F_{\text{calc.}}$
200	0·211	96·5	96·5
400	0·422	8·5	9·0
600	0·633	1·5	−3·0
800	0·845	5·5	5·0
020	0·245	27·0	−25·0
040	0·489	36·5	−35·5
060	0·733	4·0	6·0
080	0·977	2·5	−2·0
002	0·093	34·0	37·5
004	0·186	25·0	−26·5
006	0·279	33·0	31·5
008	0·372	24·0	−23·0
0,0,10	0·465	22·0	−20·5
0,0,12	0·558	26·5	27·0
0,0,14	0·651	11·5	11·5
0,0,16	0·744	1·5	−1·0
0,0,18	0·837	2·0	2·0
0,0,20	0·930	2·5	−1·0
021	0·249	2·5	2·5
022	0·262	3·0	3·0
023	0·282	11·5	−11·0
024	0·308	8·0	−7·0
025	0·338	16·5	12·5
026	0·371	36·5	−37·0
027	0·407	3·0	6·5
028	0·445	10·0	−12·5
029	0·485	10·0	−12·5
0,2,10	0·526	< 2·0	0·5
0,2,11	0·567	4·0	−1·5
0,2,12	0·610	< 2·5	−3·5
0,2,13	0·652	6·0	−6·0
0,2,14	0·696	5·5	3·0
0,2,15	0·739	16·0	−17·5
0,2,16	0·783	3·5	3·0
0,2,17	0·828	< 2·5	−2·0
0,2,18	0·872	< 2·0	−1·0
0,2,19	0·917	< 2·0	2·5
0,2,20	0·962	< 1·5	−0·5
041	0·491	< 2·0	0
042	0·498	2·0	−2·5
043	0·508	3·0	0·5
044	0·523	10·0	9·5
045	0·541	3·0	−2·0
046	0·563	4·0	−3·5
047	0·587	7·0	8·0
048	0·614	11·0	12·5
049	0·643	15·0	17·0
0,4,10	0·675	10·5	10·0
0,4,11	0·708	< 2·5	3·5
0,4,12	0·742	8·5	−6·5
0,4,13	0·778	< 2·5	−0·5
0,4,14	0·814	3·5	−3·5
0,4,15	0·852	4·5	3·5
0,4,16	0·890	< 2·0	0
0,4,17	0·930	< 1·5	−0·5
0,4,18	0·969	< 1·5	−1·0
061	0·735	< 2·5	−1·5
062	0·739	4·5	−6·0
063	0·746	2·5	−4·5
064	0·757	< 2·5	−1·0
065	0·769	5·5	−6·0
066	0·785	14·5	15·5
067	0·802	3·5	−3·0
068	0·822	6·5	5·0
069	0·845	< 2·5	0·5
0,6,10	0·868	< 2·0	−1·5
0,6,11	0·894	< 2·0	0
0,6,12	0·922	< 2·0	1·5
0,6,13	0·950	< 1·5	0
0 6,14	0·980	< 1·0	−1·5
081	0·978	< 1·0	−1·0
082	0·982	< 1·0	−1·0
083	0·987	< 1·0	−0·5
084	0·995	< 1·0	−1·0
102	0·141	3·5	4·5
104	0·215	23·0	−23·0
106	0·300	6·5	4·5
108	0·390	13·5	14·0
1,0,10	0·479	5·5	6·5
1,0,12	0·570	12·5	12·5
1,0,14	0·662	7·0	7·5
1 0,16	0·752	1·0	1·0
1,0,18	0·844	2·5	1·5
1,0,20	0·936	< 0·5	0
202	0·231	7·5	5·0
204	0·282	26·5	−26·5
206	0·351	13·0	11·0
208	0·429	15·0	−15·0
2,0,10	0·514	15·0	−15·0
2,0,12	0·599	18·0	18·5
2,0,14	0·687	10·0	9·0
2,0,16	0·774	4·0	−3·5
2,0,18	0·864	< 0·5	0
2,0,20	0·954	1·5	−0·5
302	0·330	4·0	−2·0
304	0·368	20·0	−24·5
306	0·423	3·5	2·0
308	0·489	7·0	11·5
3,0,10	0·564	7·5	7·0
3,0,12	0·643	18·0	18·0
3,0,14	0·727	8·5	9·5
3,0,16	0·809	1·0	0·5
3,0,18	0·895	3·5	2·5
3,0,20	0·982	< 0·5	0
402	0·433	14·0	−16·0
404	0·461	24·0	−27·0
406	0·506	2·0	−2·5
408	0·563	2·5	−2·0
4,0,10	0·629	7·0	−7·5
4,0,12	0·702	8·0	7·0
4,0,14	0·778	6·0	5·0
4,0,16	0·858	7·0	−5·5
4,0,18	0·938	3·5	−2·0
502	0·536	2·0	−1·0
504	0·560	2·0	−6·5
506	0·597	1·5	1·0
508	0·646	1·0	1·0
5,0,10	0·704	< 1·0	−0·5
5,0,12	0·769	4·0	4·0
5,0,14	0·838	< 0·5	0
5,0,16	0·913	< 0·5	−1·5
5,0,18	0·990	< 0·5	0·5
602	0·639	7·5	−6·5
604	0·659	11·5	−12·5
606	0·693	4·5	−4·5
608	0·735	< 1·0	2·0
6,0,10	0·786	1·5	−3·0
6,0,12	0·845	3·5	2·0
6,0,14	0·908	3·0	3·0
6,0,16	0·977	4·0	−3·0
702	0·745	1·5	−2·5
704	0·762	4·0	3·5
706	0·790	2·0	1·0
708	0·828	3·5	−3·5
7,0,10	0·873	2·5	−2·0
7,0,12	0·926	4·5	−2·0
7,0,14	0·984	4·0	−3·0
802	0·850	1·5	2·0
804	0·865	2·5	−2·5
806	0·889	2·0	−0·5
808	0·923	2·0	0
8,0,10	0·964	< 0·5	−1·0
902	0·955	< 0·5	−1·5
904	0·968	2·0	2·0
906	0·991	< 0·5	0·5
210	0·244	54·5	57·0
220	0·323	2·5	−2·0
230	0·423	9·5	8·0
240	0·532	21·0	−21·0
250	0·646	8·5	−8·5
260	0·763	1·5	3·0
270	0·881	< 1·0	0·5
280	0·999	< 0·5	−1·0
410	0·440	15·0	18·5
420	0·488	5·5	7·0
430	0·559	5·0	4·0
440	0·646	4·0	−3·0
450	0·743	2·5	−4·5
460	0·846	3·0	−0·5
470	0·954	< 1·0	0
610	0·645	6·5	−7·0
620	0·679	5·0	5·0
630	0·732	1·5	−2·0
640	0·800	< 1·5	0·5
650	0·880	1·5	1·0
660	0·969	2·5	−0·5
810	0·854	8·0	−7·5
820	0·879	1·5	0·5
830	0·921	2·0	−2·0
840	0·975	2·0	−1·5

when thick but soft plates, tabular on {001}, were obtained. These were cut to a size suitable for the X-ray photographs.

(2) *Refractive indices*

These were determined by the Becke-line method of immersion in solutions of potassium mercuri-iodide as described by Wherry (1918). The vibration directions corresponding to the various refractive indices were correlated with the crystallographic axes by X-ray photographs.

(3) *X-ray work*

As the compound is rather volatile, crystals less than 0·5 mm. in thickness did not last longer than 24 hr. at room temperature. Hence to preserve them for axis measurements, etc., they were surrounded by small gelatine capsules. For intensity measurements, however, too much scattering from the capsules occurred and they were abandoned. Hence, with very small crystals only 60 % of the {0*kl*} reflexions and still fewer {*h*0*l*} and {*hk*0} planes could be recorded. Larger crystals were therefore used to obtain the weak reflexions in the {*h*0*l*} and {*hk*0} zones; 86 and 88 % respectively of the possible reflexions in these zones were eventually measured.

Intensities were estimated by the multiple-moving-film technique (Robertson, 1943), using crystals cut to approximate cubic shape, and the measured intensities were corrected for absorption of the incident Cu $K\alpha$ radiation, and for the Lorentz and polarization factors. Where appreciable difference was recorded for the intensity of a given plane as measured for large and small crystals, that from the small crystals was used. Measurements were made on six different crystals. The observed structure factors were put on an absolute scale by correlation with the values finally calculated from the atomic positions. These are compared in Table 5, where the contributions of the hydrogen atoms are included. Table 6 shows, for certain planes, the effect on $F_{\text{calc.}}$ of the omission of the contributions of the hydrogen atoms.

Table 6. *Effect of hydrogen atoms on calculated structure factors*

hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$ including hydrogens	$F_{\text{calc.}}$ excluding hydrogens
020	27·0	−25·0	−21·5
002	34·0	37·5	40·0
004	25·0	−26·5	−22·5
008	24·0	−23·0	−27·5
021	2·5	2·5	− 7·0
022	3·0	3·0	5·0
029	10·0	−12·5	−14·0
102	3·5	4·5	1·5
104	23·0	−23·0	−20·0
106	6·5	4·5	1·0
108	13·5	14·0	10·0
202	7·5	5·0	9·5
206	13·0	11·0	13·5
208	15·0	−15·0	−16·5
210	54·5	57·0	48·0
220	2·5	− 2·0	− 7·5
410	15·0	18·5	20·5

(4) *Atomic scattering factors* (*f*)

By the well-known method of plotting the variation of the ratio $F_{\text{calc.}}/F_{\text{obs.}}$ against $\sin\theta$ it was found necessary to modify Robertson's (1935) scattering curve per electron to obtain agreement between $F_{\text{calc.}}$ and $F_{\text{obs.}}$. The resulting *f* values (per electron) are shown in Table 7. The figures for the aromatic carbon atoms and oxygen were weighted in the ratio 6 : 8.

(5) *Thermometric measurements*

At one time it was thought that evidence had been obtained of rotation of the methoxy group about the bond O–C(1). Had this been so, a discontinuity would have been expected in the cooling curve of the substance at the temperature at which rotation ceases. Measurements were made from room temperature to that of liquid air, but no such discontinuity was observed.

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Table 7. *f values per electron*

Atoms \ $\sin\theta$	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
O and ring C	1·000	0·740	0·574	0·446	0·338	0·245	0·176	0·122	0·079	0·047
C of CH_3	1·000	0·870	0·606	0·430	0·307	0·221	0·156	0·105	0·063	0·032
H	1·000	0·83	0·58	0·36	0·20	0·09	0·03	0	0	0