methiodide derivative of the trans-annular cyclization product of dihydrocleavamine. The compound is $N(a)$-acetyl-7-ethyl-5-desethyl-aspidospermidine $N(b)$-methiodide (Figs. 1, 2, 3), and the parent $N(a)$-acetyl compound is (III). The structure of the *Aspidosperma* skeleton was first established conclusively by X-ray analysis of (−)-aspidospermine $N(b)$-methiodide (Mills & Nyburg, 1960). This alkaloid possesses four asymmetric carbon centres, and the relative configuration at each centre is the same as that in the *Aspidosperma* skeleton in the molecule described in the present paper. Mills & Nyburg did not determine the absolute configuration of (−)-aspidospermine.

The general shape of the $N(a)$-acetyl-7-ethyl-5-desethyl-aspidospermidine molecule (III) is clear from Figs. 1 and 2. The molecule contains five asymmetric centres; H at C(2), and the C(12)–C(11) bond are β; the H atoms at C(5), C(7), C(19) are all α (so that the 7-ethyl group is β); the N-CH$_3$ in the methiodide derivative is α. The six-membered aromatic ring is planar; the indole five-membered ring and the other five-membered ring are each significantly non-planar; the ring C(2)(3)(4)(5)(19)(12) has a chair conformation, but the other six-membered ring has a boat conformation with atoms C(6), C(7), N(9), C(19) approximately in a plane, with C(5) and C(8) displaced in the same direction from this plane; the –CO . CH$_3$ group lies approximately in the aromatic plane. All these features are clear from Fig. 2.

The bond distances and valency angles in the molecule (Table 3) are all quite normal, and require no special comment. The intermolecular distances (Table 4) all correspond to normal van der Waals interactions; the shortest distance is a C $\cdots$ O separation of 3·17 Å, and the shortest C $\cdots$ C contact is 3·46 Å. The I$^-$ ion is situated between the N$^+$(9) atoms of molecules separated by translation a, but the distances are quite large, I$^-$ $\cdots$ N$^+$ =4·63 and 4·84 Å; the shortest distance involving I$^-$ is an I$^-$ $\cdots$ C separation of 3·87 Å.

References

BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature, Lond.* 168, 271.
CAMERMAN, N. & TROTTER, J. (1964). *Acta Cryst.* 17, 384.
FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual.* Milwaukee: General Electric Company.
International Tables for X-Ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
KUTNEY, J. P. & PIERS, E. (1964). *J. Amer. Chem. Soc.* 86, 953.
KUTNEY, J. P., TROTTER, J., TABATA, T., KERIGAN, A. & CAMERMAN, N. (1963). *Chem. & Ind.* p. 648.
MILLS, J. F. D. & NYBURG, S. C. (1960). *J. Chem. Soc.* p. 1458.

The Crystal Structure of the Triclinic Modification of Quinhydrone

BY TOSIO SAKURAI

The Institute of Physical and Chemical Research, Komagome Bunkyoku, Tokyo, Japan

A new triclinic modification of quinhydrone $C_6H_4O_2$. $C_6H_4(OH)_2$, stable at room temperatures, was found to exist. The lattice parameters are $a=7\cdot652$, $b=5\cdot956$, $c=6\cdot770$ Å, $\alpha=107°$ 37′, $\beta=121°$ 56′ and $\gamma=90°$ 17′. In its crystal structure determination, the use of the P_0 function (K. Sakurai, 1958) was especially successful.

Hydroquinone and quinone molecules are linked by hydrogen bonds to form zigzag molecular chains. These chains are packed side by side by the charge transfer force to form a molecular sheet. The structure of each molecular sheet is similar to that in the monoclinic form, although the remarkable deformation of the hydroquinone molecule, which was reported for monoclinic quinhydrone, does not exist in the triclinic modification. From the direct integration of the charge density, the upper limit of the charge transfer from the hydroquinone molecule to the quinone molecule is estimated to be 0·21 in electron units.

Introduction

Quinhydrone is the well known aromatic molecular complex, consisting of p-benzoquinone $C_6H_4O_2$ and hydroquinone $C_6H_4(OH)_2$ with 1:1 molecular ratio. Its structure has been known to be monoclinic (Foz & Palacios, 1932; Palacios & Foz, 1935, 1936). The space group is $P2_1/c$ with two quinhydrone molecular

units in the cell. The crystal structure of monoclinic quinhydrone was solved by Matsuda, Osaki & Nitta (1958).

Very recently, a new triclinic modification of quinhydrone was found to exist, in the course of attempts made in the author's laboratory to prepare several molecular complexes of chloranil and hydroquinone, bromanil and hydroquinone, and p-benzoquinone and tetrachlorohydroquinone. Each pair of components was dissolved in ethyl acetate. The crystals were obtained from these solutions, and all of them were proved to be triclinic with the same crystallographic data. The results of chemical analyses were in conformity with the chemical formula $C_6H_4O_2 . C_6H_4(OH)_2$.

Quinhydrone crystals obtained from an acetone solution of p-benzoquinone and hydroquinone, grown at temperatures between $-2\,^{\circ}C$ and $35\,^{\circ}C$ and under conditions leading to varied growth rates, were also found to be triclinic. The monoclinic modification was only exceptionally obtained, when the acetone solution was evaporated very slowly.

The present study deals with the crystal structure analysis of the new triclinic modification of quinhydrone, and as a result, the magnitude of the charge transfer from hydroquinone molecule to quinone molecule is estimated.

Crystal data

The unit-cell dimensions were determined by a Weissenberg camera with a specially designed Straumanis type cassette. The crystallographic data are

$a = 7\cdot652 \pm 0\cdot022, b = 5\cdot956 \pm 0\cdot013, c = 6\cdot770 \pm 0\cdot020 \text{ Å}$
$\alpha = 107\,^{\circ}37' \pm 7', \beta = 121\,^{\circ}56' \pm 3', \gamma = 90\,^{\circ}17' \pm 9';$
$V = 244\cdot3 \pm 0\cdot5 \text{ Å}^3, Z = 1,$
$D_x = 1\cdot48, D_m = 1\cdot45 \text{ g.cm}^{-3}.$

Considering the shape of the molecules and the external morphology of the crystal (cf. Appendix), the analysis was performed assuming the space group $P\bar{1}$. This assumption was verified at the final stage by the good agreement between observed and calculated structure factors.

Experimental

The triclinic crystals gradually decompose on exposure to the atmosphere, leaving white skeletons. To avoid decomposition, they were sealed into thin-walled glass capillaries. A set of intensity data was obtained up to 6th layers around the a axis, and up to 10th layers around [120], on a Weissenberg camera using Cu $K\alpha$ radiation. The cross section of these crystals, having a needle shape, was approximately rectangular, with diameter about 0·3 mm. The intensities were estimated visually and were corrected for Lorentz and polarization factors. No absorption correction was applied, but the α_1, α_2 resolution was corrected by the method of Sakurai (1962). The scale factor of each layer was determined by the method of Rollett & Sparks (1960). The correlation matrices were separated into two blocks

with even h reflections and odd h reflections, and the correlation between these blocks was obtained by using double slit Weissenberg photographs (Stadler, 1950). At a later stage of analysis, a crystal suitable for taking photographs around the c axis was obtained, and the even–odd correlation was further substantiated through zero layer photographs around the c axis. 848 reflections were observed from about 1050 possible reflections.

Structure determination

A characteristic feature of the X-ray pattern from this crystal is that all reflections with odd h are very weak. This suggests, as in the case of the monoclinic form, that quinone and hydroquinone molecules are almost parallel in orientation and that the latter is shifted by $\frac{1}{2}a$ with respect to the former.

Let us suppose a mean structure which consists of $\frac{1}{2}$(hydroquinone + quinone) molecules at the origin and $\frac{1}{2}, 0, 0$. For this structure, odd h reflections are zero and the even h reflections have exactly the same intensity as those of the real crystal. Similarly, let us suppose a difference structure, which consists of $\frac{1}{2}$(hydroquinone − quinone) molecule at the origin and $\frac{1}{2}$(quinone − hydroquinone) molecule at $\frac{1}{2}, 0, 0$. For this structure, even h reflections vanish and odd h reflections possess exactly the same intensities as those of the real crystal. Therefore, the P_e function, a Patterson function obtained by using even h reflections only, and the P_o function, that using odd h reflections only (Sakurai, 1958), give information of the mean structure and of the difference structure respectively.

The P_e function was very easily solved and gave the mean molecular position. The P_o function contains two characteristic patterns as shown schematically in Fig. 1(a).

One of them has two minima near the origin peak and another has a minimum which is sandwiched by two positive peaks. Since the position of the sandwiched minimum was found to correspond to the mean O–O vector in the P_e function, these characteristic distributions were easily explained in terms of the vectors between oxygen positions in hydroquinone and quinone molecules, as follows. In Fig. 1(b) and (c), $-O_q$ and $-O_{\bar{q}}$ denote negative oxygen ions belonging to the negative quinone molecule. If the oxygen position in the difference structure near the origin is as shown in Fig. 1(b), the corresponding Patterson function turns out to be as shown in Fig. 1(c). Therefore, two vectors

$-\overrightarrow{O_qO_h}$ and $-\overrightarrow{O_{\bar{q}}O_{\bar{h}}}$ will give the negative peaks near

the origin, and two identical vectors $-\overrightarrow{O_{\bar{h}}O_q}$ and

$-\overrightarrow{O_{\bar{q}}O_h}$ will give the minimum sandwiched by two

positive peaks corresponding to $\overrightarrow{O_{\bar{h}}O_h}$ and $\overrightarrow{O_qO_q}$. Although the structure near the origin in the P_o function is deformed by superposition of many other Patterson peaks, the structure near the sandwiched minimum,
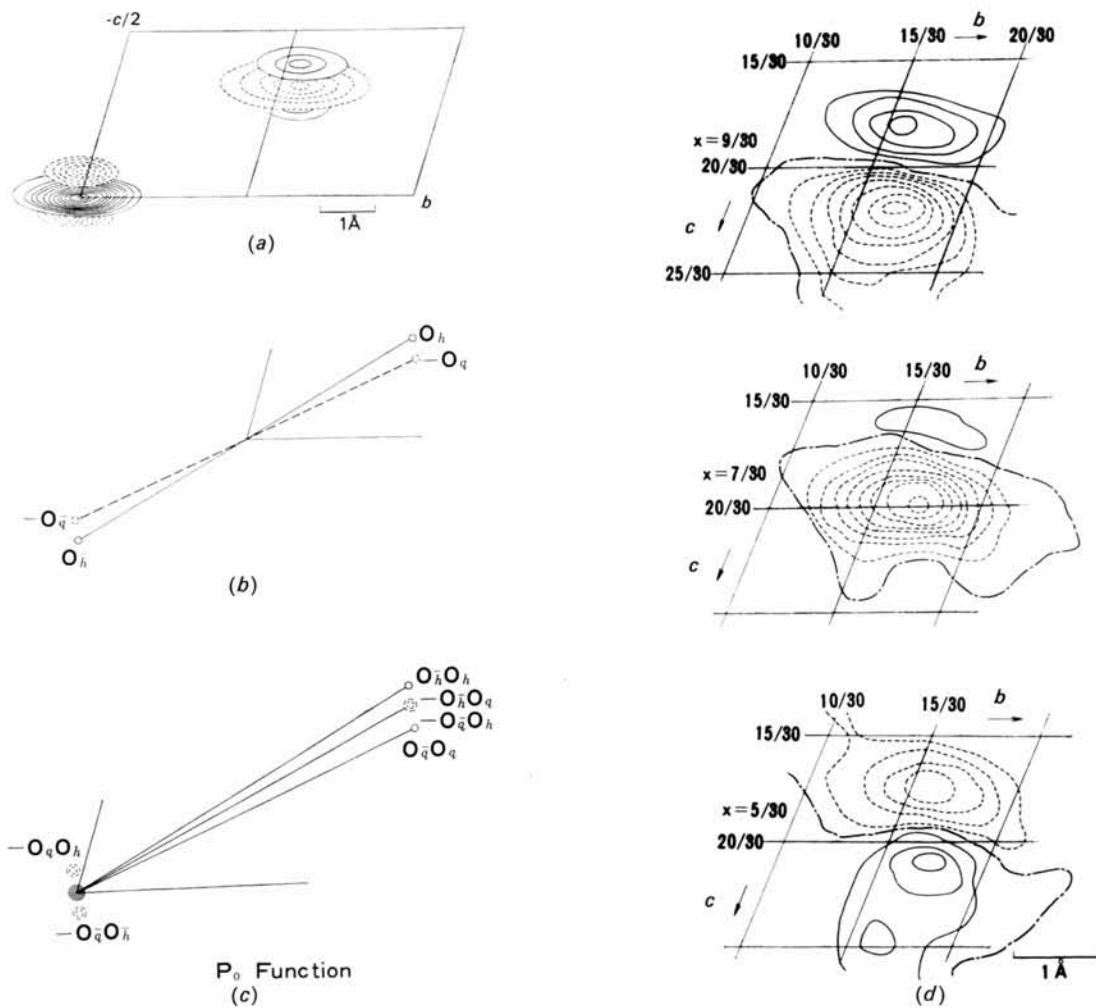
Table 1. *Structure factors*

h	k	l	|Fo|	Fc
0	1	-7	0.90	-1.23
0	2	-7	1.24	-0.61
0	4	-7	1.76	-2.01
0	1	-6	3.79	-4.39
0	2	-6	4.76	-4.83
0	3	-6	3.90	3.67
0	4	-6	7.58	8.99
0	5	-6	1.01	0.69
0	6	-6	1.50	-1.59
0	2	-5	3.83	-4.13
0	3	-5	6.41	6.67
0	4	-5	13.35	13.97
0	5	-5	1.43	1.17
0	6	-5	5.70	-6.63
0	7	-5	1.58	-2.13
0	1	-4	1.20	1.67
0	3	-4	1.84	-1.80
0	4	-4	3.75	4.27
0	5	-4	1.24	1.52
0	6	-4	5.29	-6.36
0	7	-4	2.89	-3.46
0	1	-3	10.16	-9.35
0	2	-3	6.38	6.04
0	3	-3	12.68	-13.60
0	4	-3	11.48	-11.46
0	5	-3	5.63	5.87
0	6	-3	6.19	6.19
0	1	-2	19.84	-20.44
0	2	-2	5.81	5.14
0	3	-2	7.73	-7.27
0	4	-2	10.01	-11.09
0	5	-2	9.79	9.99
0	6	-2	15.90	15.93
0	7	-2	1.80	1.55
0	1	-1	3.34	3.47
0	2	-1	3.71	-3.30
0	3	-1	7.65	7.05
0	4	-1	0.98	-1.01
0	5	-1	2.85	2.50
0	6	-1	7.61	6.95
0	1	0	19.88	21.74
0	2	0	24.12	-26.55
0	3	0	5.70	-4.51
0	4	0	2.14	2.35
0	5	0	6.04	-6.62
0	6	0	5.14	-5.08
0	7	0	1.31	1.78
0	0	1	32.93	33.82
0	1	1	7.39	7.00
0	2	1	23.37	-23.56
0	3	1	13.84	-11.47
0	4	1	3.19	2.35
0	5	1	3.83	-5.05
0	6	1	4.61	-5.24
0	0	2	25.13	-22.75
0	1	2	8.74	7.75
0	2	2	6.15	5.98
0	3	2	2.70	-2.33
0	0	3	20.70	-18.86
0	1	3	7.91	7.85
0	2	3	19.47	19.25
0	3	3	5.18	4.55
0	4	3	4.50	-4.62
0	5	3	1.35	-0.52
0	0	4	3.08	-2.45
0	1	4	3.45	3.54
0	2	4	11.25	10.42
0	3	4	1.95	2.43
0	4	4	5.63	-5.00
0	0	5	1.54	1.63
0	1	5	2.66	-2.56
0	2	5	2.59	-2.67
0	0	6	1.16	-0.61
0	1	6	3.56	-3.14
1	0	-7	1.09	-1.00
1	1	-7	0.83	-0.52
1	4	-7	0.94	0.73
1	5	-7	0.64	0.58
1	-2	-6	0.30	0.33
1	-1	-6	1.05	1.01
1	0	-6	1.05	-1.16
1	1	-6	1.01	-0.86
1	2	-6	1.16	1.38
1	3	-6	1.16	1.19
1	6	-6	0.26	0.29
1	-2	-5	0.53	0.35
1	-1	-5	1.46	1.35
1	1	-5	1.28	-1.12
1	2	-5	0.41	0.57
1	3	-5	0.79	0.92
1	4	-5	0.75	-0.55
1	6	-5	1.24	1.20
1	-4	-4	1.39	1.14
1	-3	-4	1.88	1.57
1	-2	-4	0.53	-0.70
1	-1	-4	0.45	-0.27
1	0	-4	0.86	0.97
1	1	-4	0.30	-0.60
1	2	-4	1.80	-1.78
1	3	-4	0.14	-0.18
1	4	-4	1.80	0.47
1	6	-4	0.94	0.99
1	-4	-3	0.86	0.82
1	-3	-3	1.54	1.33
1	-2	-3	1.01	-1.87
1	-1	-3	2.96	-2.40
1	0	-3	1.58	1.43
1	1	-3	2.21	1.63
1	2	-3	2.85	-2.39
1	3	-3	1.91	-1.63
1	4	-3	0.75	0.83
1	-4	-2	0.94	-0.77
1	-3	-2	0.26	0.27
1	-2	-2	0.26	-0.36
1	-1	-2	1.61	-1.31
1	1	-2	2.59	2.35
1	2	-2	1.01	-0.62
1	3	-2	2.39	-2.69
1	4	-2	0.23	-0.21
1	6	-2	0.53	0.70
1	7	-2	0.98	0.87
1	-6	-1	0.79	-0.37
1	-5	-1	0.38	0.39
1	-4	-1	1.13	-1.04
1	-2	-1	2.29	1.89
1	-1	-1	1.84	1.50
1	0	-1	3.08	-2.06
1	1	-1	0.41	0.02
1	2	-1	1.91	1.74
1	3	-1	1.05	-1.16
1	4	-1	0.19	-0.23
1	6	-1	0.79	0.85
1	7	-1	0.56	0.53
1	-7	0	0.64	-0.52
1	-6	0	-0.	-0.43
1	-5	0	0.56	0.54
1	-4	0	-0.	-0.20
1	-3	0	0.26	-0.11
1	-2	0	1.09	1.06
1	-1	0	2.25	2.12
1	0	0	-0.	-0.33
1	1	0	-0.	-0.15
1	2	0	2.21	2.18
1	3	0	0.34	0.09
1	4	0	-0.	0.15
1	5	0	-0.	-0.09
1	6	0	0.60	-0.56
1	-7	1	0.60	0.44
1	-6	1	0.64	-0.41
1	-1	1	2.51	7.36
1	0	1	2.63	2.26
1	1	1	0.52	-0.59
1	2	1	0.30	-0.10
1	3	1	0.75	-0.58
1	5	1	0.64	-0.67
1	-7	2	0.90	0.94
1	-6	2	0.38	-0.22
1	-5	2	0.49	-0.68
1	-4	2	0.45	-0.69
1	-3	2	0.30	-0.22
1	-1	2	1.31	1.50
1	0	2	0.41	0.41
1	1	2	1.69	-1.82
1	2	2	0.83	-0.91
1	3	2	0.41	-0.37
1	0	3	0.90	-0.86
1	1	3	1.20	-1.30
1	2	3	0.60	0.57
1	3	3	0.83	0.87
1	-3	3	0.60	-0.77
1	-7	3	0.75	0.83
1	-5	3	0.38	-0.24
1	-4	3	0.86	-1.02
1	-6	4	0.56	0.55
1	-7	4	0.79	0.73
1	-4	4	0.90	-0.89
1	-3	4	0.53	-0.64
1	-1	4	0.26	-0.15
1	1	4	0.45	0.43
1	2	4	1.35	1.46
1	3	4	0.75	0.71
1	-5	5	0.34	0.36
1	0	5	0.90	0.94
1	1	5	0.86	0.60
1	-5	6	0.49	0.59
1	-4	6	0.68	0.86
1	-3	6	1.13	0.46
1	-2	6	0.45	-0.32
1	-1	6	0.56	-0.72
1	0	6	0.26	0.26
2	2	-8	0.79	0.59
2	3	-8	4.95	-5.53
2	4	-8	2.74	-3.07
2	0	-7	2.29	-2.76
2	1	-7	2.51	-2.07
2	2	-7	0.53	-0.60
2	3	-7	1.16	-1.23
2	4	-7	2.59	-2.21
2	-3	-6	4.28	-4.49
2	-2	-6	4.39	-3.90
2	-1	-6	0.75	-0.32
2	0	-6	4.58	-4.57
2	1	-6	7.13	-7.83
2	2	-6	5.93	6.02
2	3	-6	14.55	13.77
2	4	-6	1.69	1.43
2	5	-6	4.13	-3.95
2	6	-6	0.83	0.76
2	-4	-5	0.60	-0.34
2	-3	-5	0.94	-1.08
2	-2	-5	1.95	-2.11
2	-1	-5	1.65	1.76
2	0	-5	1.73	1.44
2	1	-5	5.10	-5.09
2	2	-5	7.35	7.03
2	3	-5	19.95	19.41
2	4	-5	2.93	2.73
2	5	-5	11.63	-11.58
2	6	-5	4.54	-3.64
2	7	-5	0.98	1.01
2	-5	-4	5.14	-4.74
2	-4	-4	1.76	2.80
2	-3	-4	12.73	12.37
2	-2	-4	5.40	5.24
2	-1	-4	4.13	-4.99
2	0	-4	0.53	0.88
2	1	-4	1.61	2.21
2	2	-4	6.53	-6.15
2	3	-4	1.28	1.62
2	4	-4	4.35	3.81
2	5	-4	6.94	-6.92
2	6	-4	4.95	-5.21
2	-5	-3	3.30	-3.44
2	-4	-3	3.75	3.51
2	-3	-3	17.07	17.00
2	-2	-3	8.70	8.41
2	-1	-3	24.23	-21.02
2	0	-3	16.43	-14.59
2	1	-3	10.95	8.97
2	2	-3	20.70	-18.10
2	3	-3	22.32	-19.06
2	4	-3	9.58	9.08
2	5	-3	13.01	12.65
2	7	-3	2.93	-2.63
2	-6	-2	0.86	-1.04
2	-4	-2	2.59	-2.68
2	-3	-2	0.53	0.52
2	-2	-2	6.64	6.08
2	-1	-2	17.37	-15.07
2	0	-2	20.33	-20.37
2	1	-2	5.29	4.15
2	2	-2	6.04	-5.07
2	3	-2	13.50	-12.91
2	4	-2	10.80	11.17
2	5	-2	21.27	20.89
2	6	-2	2.03	2.46
2	7	-2	8.14	-7.34
2	-6	-1	4.13	-4.11
2	-5	-1	1.13	0.94
2	-4	-1	7.84	-7.54
2	-3	-1	15.47	-18.68
2	-2	-1	5.06	5.26
2	-1	-1	37.69	36.63
2	0	-1	8.10	9.23
2	1	-1	7.88	-7.50
2	2	-1	10.13	7.90
2	3	-1	1.09	0.83
2	4	-1	0.23	0.02
2	5	-1	6.79	5.85
2	7	-1	4.50	-5.18
2	-7	0	1.80	-1.99
2	-6	0	3.19	-3.05
2	-5	0	0.53	0.66
2	-4	0	1.73	-1.58
2	-3	0	13.46	-13.52
2	-2	0	11.03	10.92
2	-1	0	56.93	61.93
2	0	0	17.63	18.66
2	1	0	27.15	-26.63
2	2	0	9.17	-8.39
2	3	0	2.85	3.10
2	4	0	6.68	-7.87
2	5	0	6.64	-7.09
2	6	0	2.06	2.66
2	-7	1	6.90	6.06
2	-6	1	3.75	4.03
2	-5	1	0.79	-1.25
2	-4	1	2.14	2.14
2	-3	1	0.38	0.04
2	-2	1	2.03	-1.83
2	-1	1	12.00	12.16
2	0	1	5.44	5.21
2	1	1	16.31	-16.27
2	2	1	11.48	-10.98
2	3	1	2.66	1.96
2	4	1	2.59	-4.05
2	5	1	4.43	-5.40
2	6	1	3.11	4.59
2	-7	2	11.29	9.41
2	-6	2	6.94	6.77
2	-5	2	5.93	-6.21
2	-4	2	6.11	-6.16
2	-3	2	2.40	2.28
2	-2	2	10.35	-10.58
2	-1	2	15.86	16.25
2	0	2	5.03	4.60
2	1	2	8.06	8.67
2	2	2	0.94	-1.13
2	5	2	1.01	0.16
2	-7	3	2.78	2.52
2	-6	3	2.69	2.16
2	-5	3	4.50	-4.89
2	-4	3	6.45	-6.83
2	-3	3	1.58	1.49
2	-2	3	4.24	-4.19
2	-1	3	10.69	-10.13
2	0	3	4.99	5.17
2	1	3	15.11	15.92
2	2	3	4.80	4.77
2	3	3	4.39	-4.70
2	4	3	1.99	-1.04
2	-5	4	3.45	3.90
2	-4	4	1.09	1.27
2	-3	4	0.49	-0.35
2	-2	4	0.90	0.54
2	-1	4	0.75	-0.37
2	0	4	2.14	2.23
2	1	4	6.08	6.62
2	2	4	1.13	1.53
2	3	4	4.16	-3.91
2	-6	5	0.79	0.97
2	-5	5	7.24	7.92
2	-4	5	5.78	4.55
2	-3	5	2.21	-2.43
2	-2	5	1.35	-0.49
2	-1	5	0.68	0.80
2	0	5	2.06	-1.47
2	1	5	2.78	-2.73
2	-1	6	0.53	-0.48
2	-2	6	2.70	-2.69
2	-3	6	2.14	-2.76
2	-4	6	1.99	1.79
3	1	-8	0.71	-0.66
3	2	-8	1.09	-1.07
3	3	-8	0.98	1.01
3	4	-8	0.83	0.98
3	-1	-7	1.39	-1.44
3	0	-7	0.71	-0.24
3	1	-7	0.75	0.84
3	3	-7	1.13	0.89
3	6	-7	1.16	-1.72
3	-3	-6	0.86	0.30
3	-2	-6	1.24	1.53
3	-1	-6	1.13	-1.26
3	0	-6	1.61	-1.58
3	1	-6	1.95	2.25
3	2	-6	1.73	1.83
3	3	-6	1.50	-1.60
3	5	-6	1.54	1.45
3	6	-6	0.49	-0.77
3	-2	-5	1.43	1.36
3	-1	-5	0.53	0.50
3	0	-5	1.95	-2.03
3	1	-5	0.53	0.33
3	2	-5	2.59	2.54
3	3	-5	0.83	-0.86
3	4	-5	1.20	-1.33
3	5	-5	2.03	1.99
3	6	-5	0.64	0.59
3	7	-5	1.28	-1.75
3	-5	-4	1.16	1.22
3	-4	-4	1.73	1.80
3	-3	-4	1.28	-1.38
3	-2	-4	1.09	-0.98
3	-1	-4	2.10	2.13
3	0	-4	0.45	-0.18
3	1	-4	3.60	-3.21
3	2	-4	0.83	0.89
3	3	-4	2.14	1.97
3	4	-4	1.39	-1.24
3	6	-4	0.94	0.83
3	7	-4	0.71	-0.89
3	-6	-3	0.30	-0.31
3	-5	-3	0.45	0.47
3	-4	-3	1.76	1.67
3	-3	-3	1.16	-1.27
3	-2	-3	3.38	-3.17
3	-1	-3	1.54	1.68
3	0	-3	3.90	3.34
3	1	-3	3.94	-3.58
3	2	-3	3.41	-2.72
3	3	-3	2.18	2.39
3	4	-3	0.49	-0.23
3	5	-3	1.09	-1.24
3	6	-3	0.75	0.52
3	7	-3	0.68	0.64
3	-5	-2	0.90	-0.81
3	-4	-2	0.75	0.70
3	-3	-2	1.09	1.05
3	-2	-2	2.10	-2.00
3	-1	-2	1.84	-1.69
3	0	-2	3.30	3.19
3	1	-2	0.49	-0.26
3	2	-2	4.76	-4.50
3	3	-2	1.13	1.34
3	4	-2	0.45	0.25
3	5	-2	0.71	0.67
3	7	-2	0.71	0.99
3	-6	-1	0.38	0.56
3	-5	-1	0.79	-0.84
3	-4	-1	0.38	-0.39
3	-3	-1	2.10	2.30
3	-2	-1	0.60	0.90
3	-1	-1	4.35	-4.12
3	1	-1	3.04	3.34
3	2	-1	1.35	-1.30
3	3	-1	0.45	-0.50
3	4	-1	1.43	1.64
3	5	-1	1.01	1.11
3	-7	0	0.49	-0.53
3	-6	0	0.30	0.47
3	-5	0	-0.	-0.13
3	-4	0	1.05	-0.95
3	-3	0	1.09	0.88
3	-2	0	3.00	2.85
3	-1	0	0.98	-0.74
3	0	0	2.21	-1.33
3	1	0	2.59	2.68
3	2	0	0.68	0.75
3	3	0	0.79	-0.52
3	4	0	-0.	-0.05
3	5	0	-0.	-0.33

Table 1 (cont.)

h	k	l	|Fo|	Fc
3	6	0	0.71	-0.86
3	-7	1	0.64	-0.51
3	-4	1	0.38	-0.44
3	-3	1	0.23	-0.30
3	-2	1	2.70	2.76
3	-1	1	2.18	2.01
3	0	1	2.10	-1.79
3	1	1	0.79	-0.80
3	4	1	0.90	-1.01
3	5	1	0.79	-0.87
3	-6	2	0.49	-0.41
3	-5	2	0.30	-0.20
3	-3	2	0.49	-0.42
3	-2	2	0.79	0.84
3	-1	2	0.98	0.92
3	0	2	1.61	-1.68
3	1	2	1.61	-1.62
3	3	2	0.56	0.43
3	-6	3	0.38	-0.31
3	-5	3	0.79	-1.00
3	-3	3	0.75	-0.35
3	-2	3	0.64	-0.51
3	0	3	0.38	-0.32
3	2	3	0.64	0.48
3	3	3	0.56	0.49
3	-5	4	0.98	-0.94
3	-4	4	0.34	-0.20
3	-2	4	0.49	-0.42
3	0	4	0.94	0.60
3	1	4	0.98	1.20
3	2	4	0.26	0.25
3	-1	5	0.49	0.41
3	0	5	0.68	0.73
4	0	-8	4.61	4.24
4	1	-8	0.68	0.64
4	2	-8	6.98	-6.84
4	3	-8	5.55	-4.44
4	-1	-7	3.19	-3.40
4	0	-7	3.94	-3.72
4	1	-7	0.83	0.31
4	2	-7	1.01	0.98
4	3	-7	2.36	-2.17
4	-3	-6	4.24	-3.90
4	-1	-6	3.86	-3.73
4	0	-6	7.80	-8.02
4	1	-6	7.09	6.64
4	2	-6	17.67	18.09
4	3	-6	3.28	2.74
4	4	-6	6.56	-6.50
4	6	-6	1.20	1.20
4	-4	-5	0.64	0.69
4	-3	-5	0.79	-0.13
4	-2	-5	0.83	0.92
4	-1	-5	1.54	1.66
4	0	-5	3.41	-3.29
4	1	-5	5.93	5.58
4	2	-5	19.73	19.06
4	3	-5	4.31	3.92
4	4	-5	13.99	-14.15
4	5	-5	6.26	-5.80
4	6	-5	1.54	1.91
4	-5	-4	1.76	1.75
4	-4	-4	10.50	11.14
4	-3	-4	6.64	5.93
4	-2	-4	6.19	-5.18
4	-1	-4	2.48	-1.62
4	0	-4	3.00	2.90
4	1	-4	7.43	-7.27
4	2	-4	3.64	-3.20
4	3	-4	5.74	4.46
4	4	-4	4.24	4.46
4	5	-4	5.63	-5.69
4	-5	-3	2.51	2.76
4	-4	-3	10.46	10.60
4	-3	-3	6.41	5.81
4	-2	-3	14.89	-13.76
4	-1	-3	12.45	-12.36
4	0	-3	5.59	5.42
4	1	-3	14.74	-13.55
4	2	-3	22.40	-18.82
4	3	-3	9.23	8.94
4	4	-3	16.46	16.94
4	5	-3	1.65	1.44
4	-6	-3	1.76	-1.54
4	6	-3	4.24	-4.23
4	-6	-2	0.86	-0.24
4	-5	-2	1.88	-1.56
4	-4	-2	2.10	-2.04
4	-3	-2	1.84	1.96
4	-2	-2	4.80	-4.19
4	-1	-2	9.00	-9.59
4	0	-2	0.60	1.02
4	1	-2	1.35	-1.31
4	2	-2	8.55	-8.06
4	3	-2	9.71	9.23
4	4	-2	17.22	19.86
4	5	-2	2.21	2.96
4	6	-2	8.21	-8.29
4	-5	-1	4.35	-4.18
4	-4	-1	10.91	-10.14
4	-3	-1	2.78	2.55
4	-2	-1	21.83	21.32
4	-1	-1	8.40	8.04
4	0	-1	6.11	-6.47
4	1	-1	2.96	2.74
4	2	-1	2.03	2.02
4	3	-1	1.35	-1.15
4	4	-1	2.14	2.45
4	6	-1	3.86	-4.06
4	-7	0	0.60	-1.04
4	-5	0	1.13	-1.22
4	-4	0	5.14	-4.90
4	-3	0	4.84	4.99
4	-2	0	24.83	24.67
4	-1	0	9.04	9.68
4	0	0	14.59	-14.66
4	1	0	8.44	-8.02
4	2	0	1.65	1.55
4	3	0	5.51	-6.32
4	4	0	6.80	-7.35
4	5	0	2.70	2.47
4	-7	1	3.15	3.51
4	-5	1	0.45	-0.52
4	-3	1	1.09	-0.82
4	-2	1	2.21	2.13
4	-1	1	2.10	1.71
4	0	1	6.19	-6.60
4	1	1	6.41	-6.33
4	2	1	0.83	0.34
4	3	1	3.30	-2.65
4	4	1	3.30	-3.58
4	-6	2	3.00	-2.75
4	-5	2	3.56	-4.93
4	-3	2	3.64	-4.72
4	-2	2	7.84	-8.40
4	-1	2	1.43	1.52
4	0	2	6.19	7.21
4	1	2	1.43	2.04
4	2	2	1.31	-1.71
4	-6	3	1.76	-1.66
4	-5	3	2.36	-2.66
4	-3	3	1.61	-2.34
4	-2	3	4.05	-4.08
4	-1	3	2.66	3.13
4	0	3	8.51	9.19
4	1	3	2.74	4.11
4	2	3	3.00	-3.00
4	-5	4	1.80	1.90
4	-1	4	1.24	1.31
4	0	4	2.74	2.73
4	1	4	0.41	0.41
5	0	-8	0.34	-0.30
5	1	-8	1.35	-1.59
5	2	-8	0.75	0.90
5	3	-8	1.24	1.87
5	4	-8	1.31	-1.91
5	-2	-7	1.16	-1.43
5	-1	-7	0.60	-0.48
5	0	-7	1.24	1.41
5	2	-7	1.05	-1.22
5	4	-7	0.49	0.85
5	5	-7	1.65	-2.47
5	-1	-6	1.60	-1.92
5	0	-6	1.99	2.27
5	3	-7	1.16	1.22
5	-3	-6	1.39	1.35
5	-2	-6	0.83	-1.22
5	1	-6	2.78	2.45
5	2	-6	2.51	-2.57
5	3	-6	0.56	-0.78
5	4	-6	2.93	3.13
5	6	-6	1.46	-2.16
5	-5	-5	0.60	-0.55
5	-3	-5	0.68	0.99
5	-2	-5	0.79	0.84
5	-1	-5	1.69	-1.84
5	0	-5	0.53	-0.18
5	1	-5	3.90	-3.39
5	2	-5	0.71	-0.33
5	3	-5	2.59	-2.54
5	4	-5	2.14	2.16
5	5	-5	1.46	1.53
5	6	-5	1.73	-2.28
5	-5	-4	1.39	1.35
5	-4	-4	0.90	-1.42
5	-3	-4	1.28	-1.30
5	-2	-4	1.76	1.96
5	-1	-4	0.75	0.58
5	0	-4	3.41	-3.06
5	1	-4	1.09	1.02
5	2	-4	3.56	2.91
5	3	-4	2.44	-2.05
5	4	-4	1.13	-1.26
5	5	-4	1.05	1.28
5	-5	-3	1.46	1.46
5	-3	-3	2.44	-2.46
5	-2	-3	0.53	0.69
5	-1	-3	2.74	2.84
5	0	-3	2.48	-2.63
5	1	-3	2.85	-2.92
5	2	-3	2.59	2.47
5	4	-3	1.65	-2.22
5	6	-3	1.28	1.47
5	-6	-2	0.71	-0.43
5	-5	-2	0.56	0.79
5	-4	-2	1.16	1.13
5	-3	-2	1.28	-1.30
5	-2	-2	2.18	-2.06
5	-1	-2	1.50	1.74
5	0	-2	0.41	0.32
5	1	-2	3.11	-3.57
5	2	-2	0.23	0.22
5	3	-2	1.69	2.22
5	6	-2	0.49	1.21
5	-6	-1	0.71	-0.45
5	-5	-1	0.49	-0.13
5	-4	-1	1.31	1.39
5	-3	-1	0.49	0.70
5	-2	-1	2.51	-2.60
5	-1	-1	0.30	-0.47
5	0	-1	2.33	2.58
5	1	-1	0.38	-0.39
5	2	-1	0.49	-0.52
5	3	-1	1.35	1.92
5	4	-1	0.79	1.25
5	5	-1	0.49	-0.79
5	-5	0	0.90	-0.43
5	-4	0	0.38	0.51
5	-3	0	2.21	2.03
5	-2	0	-0.	-0.02
5	-1	0	1.13	-1.13
5	0	0	1.84	1.40
5	1	0	0.86	0.90
5	2	0	0.79	-0.65
5	-3	1	1.76	1.75
5	-2	1	1.31	1.36
5	-1	1	1.13	-1.36
5	0	1	1.28	-1.16
5	2	1	0.23	-0.06
5	3	1	0.64	-1.01
5	-4	2	0.34	-0.41
5	-3	2	0.19	0.50
5	-2	2	0.71	0.56
5	-1	2	0.90	-1.01
5	0	2	1.24	-1.20
5	1	2	0.56	-0.21
5	2	2	0.53	0.44
5	1	3	0.34	0.37
5	-3	3	0.64	-0.49
6	0	-8	0.26	0.31
6	1	-8	5.70	-6.16
6	2	-8	4.76	-4.83
6	4	-8	2.14	-2.74
6	-2	-7	2.29	-2.72
6	-1	-7	3.86	-4.33
6	0	-7	0.90	-0.27
6	1	-7	3.60	3.67
6	2	-7	0.64	-0.53
6	-3	-6	0.71	-0.28
6	-2	-6	2.44	-2.37
6	-1	-6	4.58	-5.22
6	0	-6	4.69	5.65
6	1	-6	16.76	16.95
6	2	-6	4.46	4.20
6	3	-6	7.10	-7.51
6	4	-6	0.71	-1.66
6	5	-6	1.20	1.53
6	-4	-5	0.94	1.09
6	-1	-5	1.09	-0.98
6	0	-5	3.38	3.94
6	1	-5	11.80	12.59
6	2	-5	2.96	3.23
6	3	-5	11.20	-11.99
6	4	-5	6.50	-6.65
6	5	-5	1.00	1.39
6	6	-5	4.30	-4.54
6	-5	-4	7.20	7.28
6	-4	-4	4.05	4.57
6	-3	-4	2.96	-3.45
6	-2	-4	2.70	-3.17
6	-1	-4	1.35	1.35
6	0	-4	3.15	-4.81
6	1	-4	4.31	-5.31
6	2	-4	2.48	2.48
6	3	-4	2.10	-2.73
6	4	-4	4.46	5.39
6	-5	-3	2.59	2.90
6	-4	-3	6.30	-6.88
6	-3	-3	6.98	-7.53
6	-2	-3	0.56	0.74
6	-1	-3	7.31	-7.03
6	0	-3	9.45	-11.43
6	1	-3	6.75	6.27
6	2	-3	16.28	15.64
6	3	-3	2.74	3.86
6	4	-3	4.69	-4.55
6	5	-3	2.10	-1.95
6	-5	-2	0.41	0.14
6	-4	-2	2.48	-2.11
6	-2	-2	2.68	-0.63
6	-1	-2	0.86	-0.88
6	0	-2	2.55	-2.70
6	1	-2	7.39	6.36
6	2	-2	16.61	13.57
6	3	-2	2.74	2.48
6	4	-2	7.13	-6.95
6	5	-2	2.10	-2.29
6	-6	-1	5.63	-4.61
6	-5	-1	1.43	0.88
6	-4	-1	12.80	11.13
6	-3	-1	6.90	6.25
6	-2	-1	4.13	-3.91
6	-1	-1	1.13	-0.99
6	0	-1	1.50	1.30
6	1	-1	2.71	-0.80
6	2	-1	0.71	-1.06
6	-6	0	0.75	-1.06
6	-5	0	2.33	-1.54
6	-4	0	3.41	2.97
6	-3	0	12.45	9.88
6	-2	0	5.78	4.49
6	-1	0	7.50	-6.44
6	0	0	6.60	-5.49
6	1	0	6.70	-6.34
6	2	0	3.98	-3.31
6	3	0	6.64	-5.21
6	2	1	1.95	-1.80
6	1	1	0.23	0.22
6	0	1	3.19	-2.40
6	-1	1	2.51	-1.79
6	-2	1	0.75	-0.47
6	-4	1	0.41	-0.22
6	-4	2	3.34	-2.33
6	-3	2	5.63	-3.79
6	-2	2	0.60	0.95
6	-1	2	6.04	4.57
6	0	2	3.04	2.45
6	1	2	1.13	-0.82
6	-3	3	0.49	-1.41
6	-2	3	1.73	1.95
7	0	-8	0.90	-1.58
7	-2	-7	0.45	-0.72
7	-1	-7	1.24	1.59
7	0	-7	0.38	0.14
7	1	-7	1.69	-1.88
7	-3	-6	0.45	-0.47
7	-2	-6	1.54	-1.52
7	-1	-6	1.28	1.33
7	0	-6	2.10	2.38
7	1	-6	1.76	-2.01
7	-3	-5	0.71	0.61
7	-2	-5	0.94	-0.68
7	-1	-5	0.23	-0.27
7	0	-5	2.44	2.73
7	1	-5	0.23	0.40
7	-4	-4	1.01	-1.08
7	-3	-4	1.05	0.74
7	-2	-4	0.64	0.83
7	-1	-4	1.54	-1.73
7	0	-4	0.45	0.43
7	1	-4	2.25	2.28
7	-4	-3	1.39	-1.30
7	-2	-3	1.39	1.47
7	-1	-3	1.09	-1.26
7	0	-3	1.91	-2.08
7	1	-3	1.31	1.36
7	-5	-2	0.71	0.71
7	-4	-2	0.60	-0.41
7	-3	-2	1.43	-1.50
7	-2	-2	0.49	0.39
7	-1	-2	0.34	0.34
7	0	-2	1.73	-1.75
7	-5	-1	0.64	0.66
7	-4	-1	0.45	0.59
7	-3	-1	1.20	-1.24
7	-2	-1	0.38	-0.51
7	-1	-1	1.35	1.32
7	-4	0	1.39	1.24
7	-3	0	0.26	0.42
7	-2	0	0.79	-0.72
7	-1	0	0.38	0.66
7	0	0	0.53	-0.34
7	1	0	0.53	0.16
7	-4	1	0.86	0.93
7	-3	1	0.94	0.76
7	-2	1	0.98	-0.82
7	-1	1	1.24	-0.99
8	-1	-7	0.53	0.48
8	0	-7	3.90	4.25
8	1	-7	1.20	1.09
8	-2	-6	2.81	-2.85
8	-1	-6	4.20	4.20
8	0	-6	11.33	12.68
8	1	-6	4.80	3.35
8	-3	-6	0.79	-0.64
8	-1	-5	2.70	2.51
8	0	-5	5.21	5.73
8	1	-5	1.58	1.35
8	-4	-4	1.28	-1.89
8	-3	-4	2.96	-3.14
8	-2	-4	2.40	-2.39
8	0	-4	3.34	-4.11
8	1	-4	0.45	1.09
8	-4	-3	2.59	-3.03
8	-2	-3	0.94	0.16
8	-1	-3	3.38	-4.47
8	0	-3	4.88	-5.22
8	1	-3	4.24	3.32
8	-3	-3	3.56	-3.76
8	-4	-2	0.90	1.04
8	-2	-2	0.71	-1.20
8	-1	-2	1.01	-1.58
8	0	-2	0.41	0.31
8	1	-2	4.28	4.27
8	-4	-1	3.94	5.62
8	-3	-1	4.09	4.04
8	-2	-1	1.43	-1.33
8	-1	-1	1.80	-1.48
8	0	-1	0.45	0.03
8	1	-1	0.41	-0.44
8	-3	0	1.99	1.82
8	-2	0	2.44	-2.68
8	-1	0	3.15	-3.01
8	0	0	0.64	-1.00
9	0	-6	1.35	1.70
9	0	-6	0.86	-1.08
9	-1	-6	1.73	1.62
9	0	-5	0.75	0.62
9	0	-4	0.71	-0.65
9	-2	-4	1.24	1.20
9	-3	-3	0.38	0.47
9	-1	-3	0.45	-0.51
9	0	-3	1.16	-1.12
9	0	-3	0.53	0.49
9	-1	-2	0.71	-0.57

Fig. 1. P_o function. (a) Schematic representation. (b) Oxygen positions in the difference structure. (c) Patterson peaks corresponding to (b). (d) Three sections of the P_o function near the sandwiched minimum. Sections are parallel to the bc plane, with x coordinates 9/30, 7/30 and 5/30.
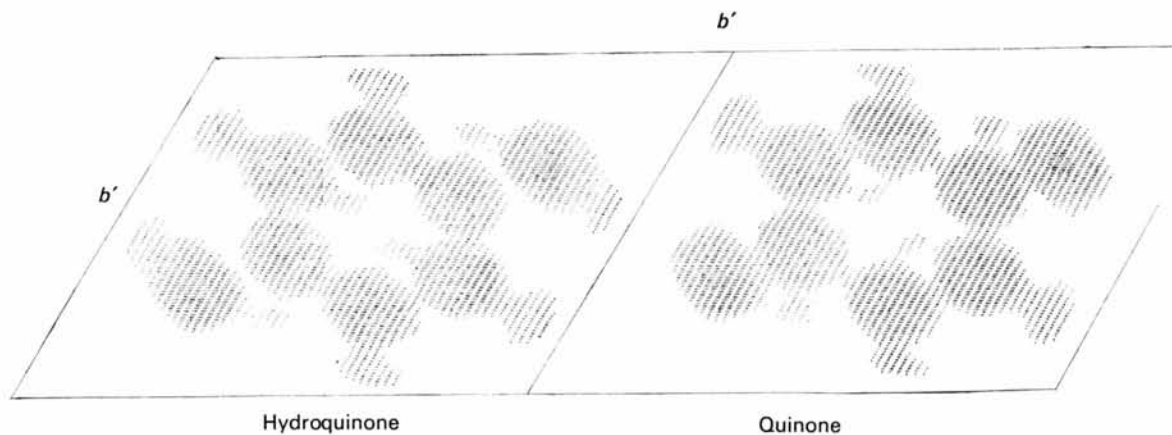
Fig. 2. $(2\bar{1}0)$ section of the electron density. Direct computer output.

shown in Fig. 1(*d*), is consistent with the above explanation, and the approximate molecular orientation was easily determined. A similar consideration was used by Osaki & Nakai (1963) independently for a more general case containing substructures.

(*a*)

(*b*)
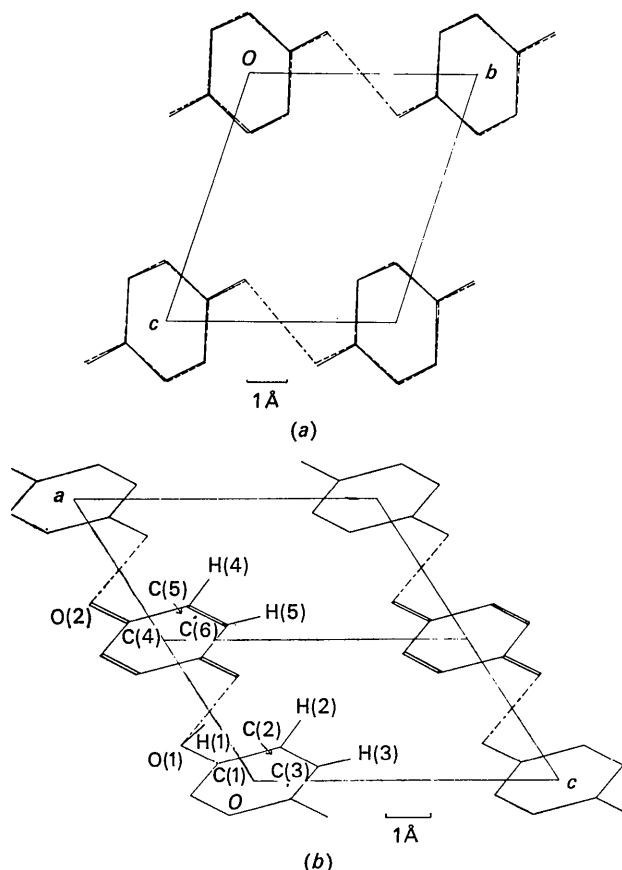
Fig. 3. Configuration of molecules in the crystal. (*a*) projection along the *a* axis. (*b*) Projection along the *b* axis.

At the stage of the above approximation, the R index was 36% and the agreement between F_o and F_c was generally good. The structure was further refined by successive applications of least-squares and Fourier syntheses. The molecular plane is found to be almost parallel to $(2\bar{1}0)$. A Fourier synthesis on this plane is shown in Fig. 2. Positions of hydrogen atoms were obtained from this Figure. Their coordinates were refined by one cycle of least squares at the final stage of calculation. The final R value becomes 10·1% excluding unobserved reflections.

The main part of these calculations was carried out on an IBM 7090 computer with programs ERBR1 (diagonal, isotropic least-squares by Van den Hende, 1961), ERFR2 (Fourier summation by Sly, Shoemaker & Van den Hende, 1962), and ORFLS (full-matrix, anisotropic least-squares by Busing, Martin & Levy, 1962). Structure factors are shown in Table 1, and atomic parameters are listed in Table 2. F_o and F_c values in Table 1 are the direct output from ORFLS, and they must be multiplied by a scale factor 1·16 to give absolute values of F_o and F_c.

Discussion of the structure

Crystal structure

The arrangement of the molecules in the crystal is shown in Fig. 3(*a*) and (*b*) and Fig. 4(*a*).
The molecules are planar within the experimental error, and the mean planes for hydroquinone and quinone are expressed by

$$0\cdot8106x - 0\cdot5246y - 0\cdot0550z = 0$$
$$\text{and} \quad 0\cdot8364x - 0\cdot4979y - 0\cdot1002z = 3\cdot190$$

respectively, where x, y, z are coordinates with respect to the crystal axes abc in Å. The maximum deviation of atoms from the planes is 0·01 Å for both carbon and oxygen atoms. The angle between these planes is 2·0°.

Table 2. *Atomic parameters*

The expression of the temperature factor is $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2klB_{23}+2lhB_{31})\}$
The positions of the atoms are shown in Fig. 3(*b*).

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12} $\times 10^{-2}$	B_{23}	B_{31}
Hydroquinone									
O(1)	0·1302	0·2796	−0·1756	2·76	1·64	2·84	−0·17	0·98	2·18
C(1)	0·0659	0·1419	−0·0846	1·51	1·27	2·63	0·17	1·00	1·43
C(2)	0·1239	0·2278	0·1623	1·64	1·44	2·52	0·04	0·63	1·41
C(3)	0·0560	0·0818	0·2441	1·53	1·64	2·09	0·07	0·61	1·27
H(1)	0·214	0·419	−0·040						
H(2)	0·213	0·405	0·270						
H(3)	0·080	0·138	0·412						
Quinone									
O(2)	0·6115	0·2834	−0·1665	2·51	1·69	2·96	−0·07	1·11	2·02
C(4)	0·5610	0·1490	−0·0897	1·47	1·34	2·77	0·10	0·80	1·41
C(5)	0·6279	0·2327	0·1751	1·69	1·48	2·44	−0·05	0·59	1·38
C(6)	0·5666	0·0897	0·2551	1·64	1·69	2·17	0·05	0·69	1·40
H(4)	0·718	0·410	0·278						
H(5)	0·588	0·144	0·412						
Standard deviations									
O	0·0006	0·0006	0·0007	0·12	0·12	0·15	0·10	0·11	0·12
C	0·0008	0·0008	0·0009	0·13	0·15	0·18	0·11	0·14	0·13
H	0·007	0·008	0·008						
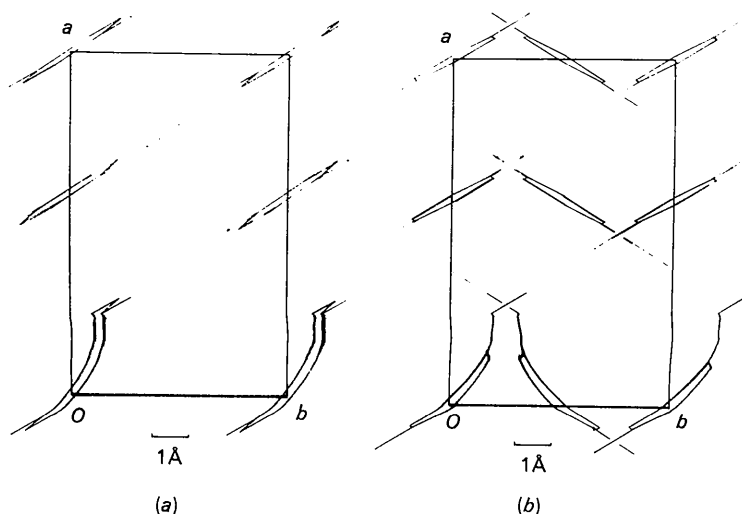
Fig. 4. Structure of the molecular sheet. (a) (0 0 1) plane of the triclinic form. Projection along the c axis. (b) (0 0 1) plane of the monoclinic form. Projection along [1 0 1].

Hydroquinone and quinone molecules are linked by O–H · · · O hydrogen bonds to form a zigzag molecular chain along the [120] direction. These chains are packed side by side to form a molecular sheet parallel to the (001) plane. The structure of the molecular sheet is similar to that found in the monoclinic form.

The cell dimensions of the monoclinic form are $a = 7 \cdot 674$, $b = 6 \cdot 001$, $c = 11 \cdot 590$ Å; $\beta = 109° 58'$. a and b of this form are almost equal to a and b respectively of the triclinic form. The arrangement of molecular sheets in both forms is shown in Fig. 4. The perpendicular projection of the quinone molecule on the hydroquinone molecule in the molecular sheet in both forms is shown in Fig. 5. All the intermolecular atomic distances shorter than 3·6 Å are shown in this Figure. There are several distances of the order of 3·2 Å. These distances, being considerably shorter than the ordinary van der Waals distance of 3·4 Å, are consistent with those in many other similar molecular complexes (Wallwork, 1961; Brown, Wallwork & Wilson, 1964; Hanson, 1963), and indicate the charge transfer interaction between these molecules.

The only difference between the triclinic and monoclinic forms is that in the former all the molecular sheets are identical, while in the latter the direction of the molecular chain in the successive sheets varies from the [120] direction to the [1$\bar{2}$0] direction according to the glide mirror operation. No particularly short atomic distance was found between these molecular sheets. Therefore, they are packed by ordinary van der Waals forces. Since the van der Waals force is not sensitive to the orientation of the molecular chain, these two forms may have nearly equal lattice energy.

A similar polymorphism was found in hexadecanamide (Sakurai & Yabe, 1958). In that case, both triclinic and monoclinic forms were obtained at room temperatures, depending on the method of crystallization. In those forms too, long chain molecules are linked by hydrogen bonds to form molecular sheets. While the molecular axes are all parallel in the triclinic form,

those in the successive sheets in the monoclinic form vary according to the glide mirror operation.

Molecular structure

Bond distances and angles are shown in Fig. 6(a). Standard deviations of these distances are 0·008 Å for C–O and C–C and 0·06 Å for C–H and O–H bonds, and those of bond angles are 0·5° for

$$\underset{C \quad\quad C}{\overset{C}{\diagup \diagdown}} \quad \text{and} \quad \underset{C \quad\quad O}{\overset{C}{\diagup \diagdown}}$$

and 3° for

$$\underset{C \quad\quad H}{\overset{O}{\diagup \diagdown}} \quad \text{and} \quad \underset{C \quad\quad H}{\overset{C}{\diagup \diagdown}} \quad .$$
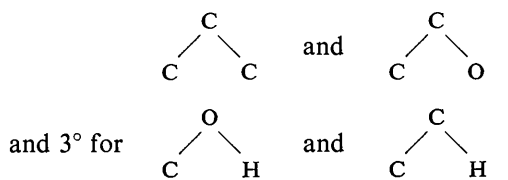
Fig. 5. Interatomic distances between molecular chains. (a) Triclinic modification. (b) Monoclinic modification.

Both quinone and hydroquinone molcules deviate slightly from *mmm* symmetry. Differences of the bond distances and angles related by the *mmm* operation are shown in Table 3.

According to the ordinary statistical significance test, the difference between two experimentally determined values is significant if $\delta/(\sigma_1^2+\sigma_2^2)^{\ddagger} > 2\cdot5$, where δ is the difference between two values and σ_1, σ_2 are their standard deviations. The differences between C(4')–C(6) and C(4')–C(5'), C(3')–C(1) and C(1)–C(2), angle C(3)–C(1')–O(1') and angle C(2')–C(1')–O(1') thereby proved to be significant. Since the quinoid rings in *p*-benzoquinone (Trotter, 1960) and in tetrachloro-*p*-benzoquinone (Chu, Jeffrey & Sakurai, 1962) were shown to have *mmm* symmetry, the deviation from this

symmetry in quinhydrone will be due to the effect of hydrogen bonding between the molecules.

The length of the hydrogen bond is 2·739 Å, and the hydrogen atom deviates about 10° from the line joining oxygen atoms.

The dimensions of the quinone molecule found in the triclinic and in the monoclinic modification [Fig. 6(*b*)] are very similar. However, for the hydroquinone molecule, a considerable difference is observed. Especially, the deformation of the benzenoid ring is remarkable in the monoclinic modification. In view of the similar configuration in the molecular sheet, it is hard to believe that the deformation of the molecule in the monoclinic modification is due to the monoclinic crystalline field. To clarify this point, it seems desirable to

Table 3. *Differences between the dimensions related by the mmm operation*

Difference between distances	δ	$(\sigma_1{}^2+\sigma_2{}^2)^{\ddagger}$	$\delta/(\sigma_1{}^2+\sigma_2{}^2)^{\ddagger}$
C(3')–C(1) and C(1)–C(2)	0·031 Å	0·011	2·8
C(4')–C(5') and C(4')–C(6)	0·040	0·011	3·6
Difference between angles			
C(1')–C(2')–C(3') and C(2')–C(3')–C(1)	1·3°	0·7	1·9
C(3) –C(1')–O(1') and C(2')–C(1')–O(1')	3·4	0·7	4·9
C(4')–C(5')–C(6') and C(5')–C(6')–C(4)	1·3	0·7	1·9
C(6')–C(4) –O(2) and C(5) –C(4) –O(2)	0·9	0·7	1·3

(*a*)

(*b*)

Hydroquinone   Quinone
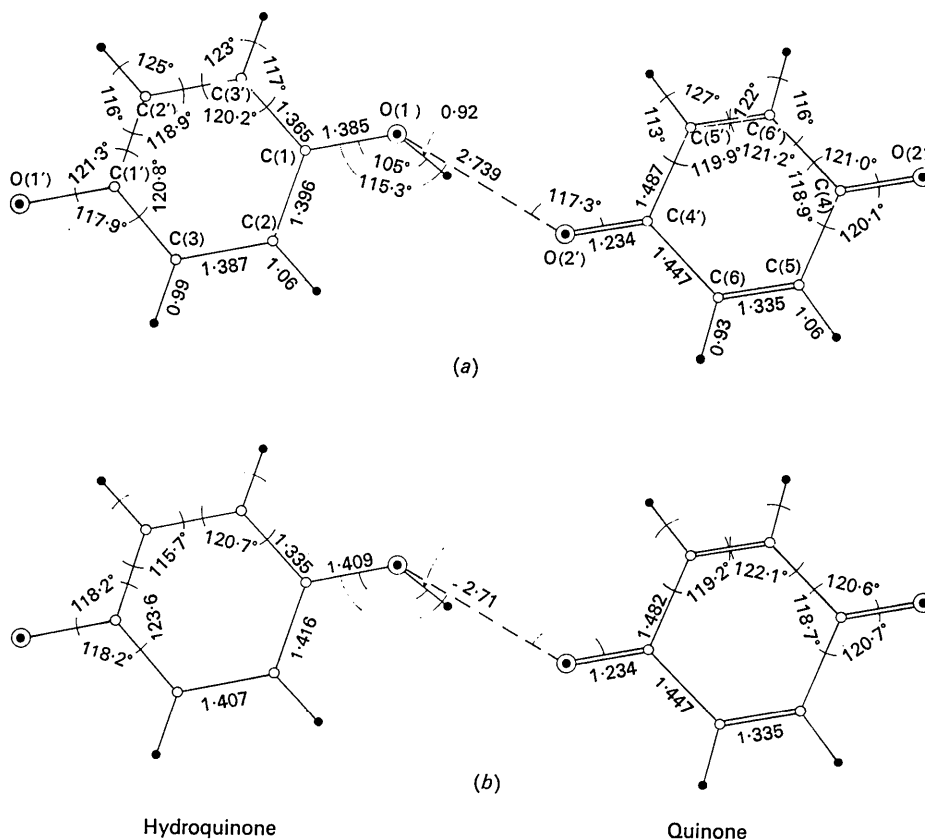
Fig. 6. Interatomic distances and bond angles in the molecule. (*a*) Triclinic modification. (*b*) Monoclinic modification. Circles with black dots: oxygen; open circles: carbon; black dots: hydrogen.

reinvestigate the structure of monoclinic quinhydrone with complete three-dimensional data.

Charge transfer

A most interesting point to be pursued will be the problem of the charge transfer which may take place between molecules. According to the general theory of molecular complexes (Mulliken, 1952), the electronic state of the quinhydrone molecule is expressed by

$$\psi = a\psi_0(Q,H) + b\psi_1(Q^-,H^+) \tag{1}$$

where Q and H represent the state of quinone and hydroquinone molecules respectively, and $\psi_0(Q,H)$ is the neutral and $\psi_1(Q^-,H^+)$ is the ionic state of quinhydrone. Then the quantity

$$I = b/(a + b) \tag{2}$$

gives the contribution of the ionic part if the overlapping integral $\int\psi_0 \cdot \psi_1 d\tau$ can be neglected. The quantity I can be obtained from the optical absorption coefficient (Briegleb, 1961), with several assumptions to simplify the analysis. On the other hand, I can be obtained directly if the charge distribution is known. In the present accuracy of the X-ray intensity measurement, it is impossible to discuss the electron distribution in individual atoms. However, the total electronic charge of a molecule can be obtained with reasonable accuracy by direct integration of the charge density.

In order to integrate the charge density over a molecule, it is convenient to transform the crystal axes into an $\mathbf{a'}$, $\mathbf{b'}$, $\mathbf{c'}$ system as shown in Fig. 7. The relation between these two systems is expressed by $\mathbf{a'} = \mathbf{a} - \mathbf{b}$, $\mathbf{b'} = \mathbf{a} + 2\mathbf{b}$ and $\mathbf{c'} = \mathbf{c}$. Then, $\mathbf{b'}$ and $\mathbf{c'}$ are nearly on the plane of the molecule and $\mathbf{a'}$ is almost perpendicular to it. In this new system, the charges of hydroquinone and quinone molecules are given by

$$Q_h = \int_{-1/6a'}^{1/6a'} \int_{-1/4b'}^{1/4b'} \int_{-1/2c'}^{1/2c'} \varrho \, d\tau$$

and $\hspace{6cm}$ (3)

$$Q_q = \int_{-1/6a'}^{1/6a'} \int_{1/4b'}^{3/4b'} \int_{-1/2c'}^{1/2c'} \varrho \, d\tau$$

respectively, where

$$\varrho = \frac{2}{V'} \sum_{k'}\sum_{k'}\sum_{l'} F_{h'k'l'} \cos 2\pi(h'x' + k'y' + l'z') \,.$$

The range of integration is shown by the shaded area in Fig. 7, and corresponds to the left half and the right half of Fig. 2. After integration, (3) becomes

$$Q = \tfrac{1}{2}F_{000} + \frac{3\sqrt{3}}{4\pi} \sum_{h'} \frac{F_{h'00}}{h'} A_{h'} + \frac{1}{\pi} \sum_{k'} \frac{F_{0k'0}}{k'} C_{k'}$$
$$+ \frac{3\sqrt{3}}{2\pi^2} \sum_{h'}\sum_{k'} \frac{F_{h'k'0}}{h'k'} A_{h'}C_{k'} \tag{4}$$

where $h' = h - k$, $k' = h + 2k$ and $l' = l$, and $A_{h'}$ and $C_{k'}$ are the constants given in Table 4.

Table 4. Values of $A_{h'}$ and $C_{k'}$

h'	$A_{h'}$	k'	$C_{k'}$ Hydroquinone	Quinone
$6n+0$	0	$4n$	0	0
$6n+1$	1	$4n+1$	1	-1
$6n+2$	1	$4n+2$	0	0
$6n+3$	0	$4n+3$	-1	1
$6n+4$	-1			
$6n+5$	-1			

Since $h' = -3k$ for $k' = 0$, the second term in (4) is identically zero. The third and fourth terms have opposite signs for hydroquinone and quinone molecules. Since all of these reflections belong to weak odd h reflections, the extinction effect will be negligible. Because of the presence of k' or $h'k'$ in the denominator of each term, the higher order terms are not important. Accordingly the errors due to the absorption and α_1, α_2 resolution are small. White radiation background due to some strong even h reflections may superpose on some low order odd h reflections such as 110 or 100. This effect was eliminated by the use of monochromatic radiation, and all required terms were obtained on zero layer photographs of c axis rotation. By virtue of these favorable circumstances, the error accompanying the total charge in a molecule obtained in the above way is conceived to be fairly small. The result of calculation shows that

$$Q_h = \tfrac{1}{2}F_{000} + 0.79$$

and $\hspace{3cm} Q_q = \tfrac{1}{2}F_{000} - 0.79 \,.$ $\hspace{2cm}$ (5)

Since F_{000} is the total charge in the unit cell of the crystal, $Q_h = \tfrac{1}{2}F_{000} + 1.0$ and $Q_q = \tfrac{1}{2}F_{000} - 1.0$ in the $\psi_0(Q,H)$ state, while in the $\psi_1(Q^-,H^+)$ state $Q_h = Q_q = \tfrac{1}{2}F_{000}$. The above result means that I defined in (2) is 21%.

From the optical absorption spectrum of the monoclinic quinhydrone crystal (Nakamoto, 1952), Suzuki
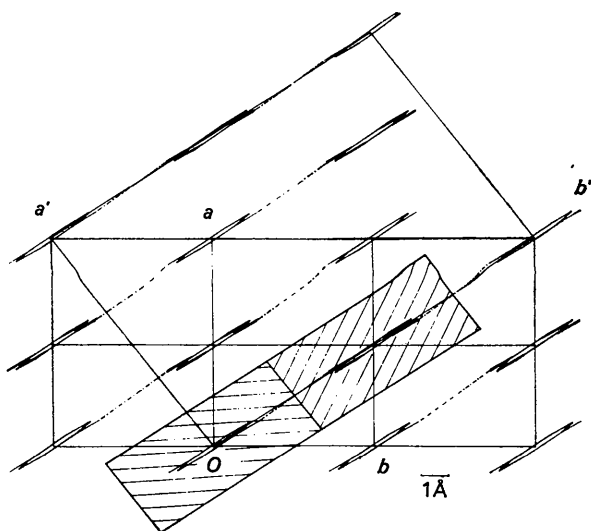
Fig. 7. The relation between crystallographic axes **a b c** and **a' b' c'**. The shaded area represents the range of integration for each molecule.

(1956) calculated that I is 4%. Similar values were obtained for many other molecular complexes (Briegleb, 1961). The value obtained from the present X-ray analysis is considerably larger than that derived from the optical data. Although equation (3) gives the total charge in a shaded area in Fig. 7, without any theoretical assumption or serious experimental error, it is probable that the value obtained does not exactly represent the total electronic charge of a molecule, for the following reason. Since the hydrogen atom forming the hydrogen bond is located near the boundary of the integration (Fig. 2), some fraction of the charge of this hydrogen might be outside the range of integration for Q_h. Thus, in the present stage of the analysis, the value 21%, which corresponds to a charge of 0·21 in electron units, should be regarded as the upper limit of the electronic charge transferred from the hydroquinone to the quinone molecule.

Thermal vibration of the molecule

It is clearly seen from Fig. 2 that each molecule is undergoing libration in its own plane. The anisotropic temperature factors of each atom in Table 2 may be transformed into the rigid body vibration of the molecule, by referring to the molecular axes L, M, N defined in Fig. 8. The components of translational tensor T and rotational tensor Ω obtained by a least-squares method (Cruickshank, 1956) are shown in Table 5.

The two molecules are similar in their thermal vibration. The translational motion is largest along the L direction. Of the rotational motions that around the M axis, which does not include the stretching of the hydrogen bond, is largest. Several diffuse scattering regions were observed. These scatterings are probably due to some phase relations between the molecular vibrations. Further studies of the diffuse scattering are in progress.

APPENDIX
Identification of the two modifications

External shapes of the typical single crystals are shown in Fig. 9. The triclinic crystal is a flat parallelepiped. The flat faces are {001}. The monoclinic crystal is a long prism along the a axis, and the {001} faces are most predominant. Top and bottom of the prism are generally not well defined. Powder diffraction data of both forms are shown in Table 6.
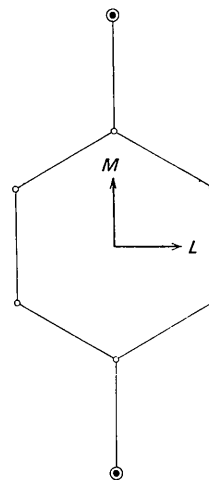
Fig. 8. Axes of the molecule. Axis N is perpendicular to the plane.
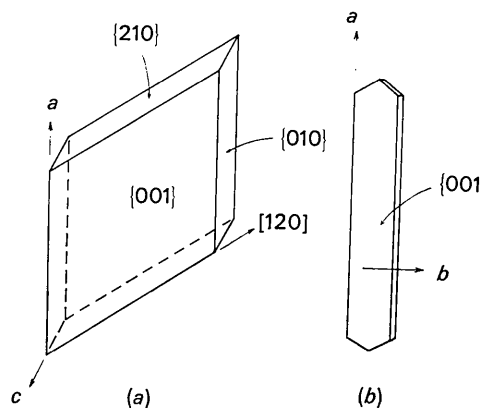
Fig. 9. External shape of single crystal.
(a) Triclinic. (b) Monoclinic.

Table 5. *Rigid body vibration of the molecule*

Hydroquinone

	Translational				Rotational		
$T=$	3·6	−0·2	0·7	$\times 10^{-2}$ Å^2 $\Omega=$	17	0	0	degree^2
	−0·2	2·0	−0·2		0	25	0	
	0·7	−0·2	2·1		0	0	5	

Quinone

$T=$	3·0	−0·4	0·4	$\Omega=$	9	0	0
	−0·4	1·7	−0·3		0	33	0
	0·4	−0·3	2·0		0	0	6

Table 6. *Powder diffraction data of quinhydrone*

Triclinic		Monoclinic	
d	Intensity	d	Intensity
5·44 Å	s	5·34 Å	s
3·77	w	3·98	w
3·12	m	3·58	m
3·06	s	3·22	m
2·78	m	3·08	s
2·66	m	2·87	w
2·54	m	2·72	w
2·32	w	2·59	m
2·16	m	2·42	m
2·01	w	2·30	m
1·90	w	2·15	w
1·82	w	2·09	w
1·76	w	1·80	w
1·75	w	1·69	w
1·66	w	1·59	m
1·60	m		
1·51	w		
1·16	w		

References

Briegleb, G. (1961). *Elektronen-Donator-Acceptor-Komplexe*. Berlin, Gottingen, Heidelberg: Springer-Verlag.

Brown, D. S., Wallwork, S. C. & Wilson, A. (1964). *Acta Cryst.* 17, 168.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). ORFLS: Oak Ridge National Laboratory.

Chu, S. C., Jeffrey, G. A. & Sakurai, T. (1962). *Acta Cryst.* 15, 661.

Cruickshank, D. W. J. (1956). *Acta Cryst.* 9, 754.

Foz, O. R. & Palacios, J. (1932). *Anales Soc. Españ. Fis. Quim.* 30, 421.

Hanson, A. W. (1963). *Acta Cryst.* 16, 1147.

Matsuda, H., Osaki, K. & Nitta, I. (1958). *Bull. Chem. Soc. Japan,* 31, 611.

Mulliken, R. S. (1952). *J. Amer. Chem. Soc.* 74, 811.

Nakamoto, K. (1952). *J. Amer. Chem. Soc.* 74, 1739.

Osaki, K. & Nakai, H. (1963). *Ann. Meeting Crystallographic Soc. Japan.*

Palacios, J. & Foz, O. R. (1935). *Anales Soc. Españ. Fis. Quim.* 33, 627.

Palacios, J. & Foz, O. R. (1936). *Anales Soc. Españ. Fis. Quim.* 34, 779.

Rollett, J. S. & Sparks, R. A. (1960). *Acta Cryst.* 13, 273.

Sakurai, K. (1958). *Acta Cryst.* 11, 840.

Sakurai, T. (1962). *Acta Cryst.* 15, 443.

Sakurai, T. & Yabe, M. (1958). *J. Phys. Soc. Japan,* 13, 5.

Sly, W. G., Shoemaker, D. P. & Van den Hende, J. H. (1962). ERFR2: ESSO Research and Engineering Co.

Stadler, H. P. (1950). *Acta Cryst.* 3, 262.

Suzuki, K. (1956). *Busseiron Kenkyu,* 102, 5.

Trotter, J. (1960). *Acta Cryst.* 13, 86.

Van den Hende, J. H. (1961). ERBR1: ESSO Research and Engineering Co.

Wallwork, S. C. (1961). *J. Chem. Soc.,* p. 494.

The Crystal Structure of α-Keto-1,1′-trimethyleneferrocene*

By Noel D. Jones,† Richard E. Marsh, and John H. Richards

The Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.

The crystal structure of α-keto-1,1′-trimethyleneferrocene has been determined by three-dimensional X-ray diffraction analysis. This compound, $C_{13}H_{12}OFe$, crystallizes in the centrosymmetric monoclinic space group $P2_1/a$. The unit cell contains four molecules and has the dimensions

$$a = 22\cdot981 \pm 0\cdot002, \ b = 7\cdot381 \pm 0\cdot001, \ c = 5\cdot833 \pm 0\cdot001 \ \text{Å}; \ \beta = 93\cdot38 \pm 0\cdot02°.$$

A trial structure was obtained from the locations of the iron–iron vectors in the (001) Patterson projection and was refined in both two and three dimensions by the method of least squares. The final reliability factor, R, was 0·067.

The dihedral angle between the best planes through the two nearly planar cyclopentadienyl rings is about 8·8°. The average ring carbon–carbon bond distance is $1·424 \pm 0·010$ Å and the average iron–carbon bond distance is $2·039 \pm 0·006$ Å. The principal thermal motion is a vibration of the entire molecule in a direction roughly perpendicular to the *ab* plane.

Introduction

The stable bridged 'sandwich' compound α-keto-1,1′-trimethyleneferrocene, $C_{13}H_{12}OFe$ (I), may be prepared by the procedure of Rinehart & Curby (1957).

(I)