ACTA CHEMICA SCANDINAVICA 27 (1973) 2955–2964

The Crystal Structure of 1,4-Ethyleno-2,8-dihydroxy-2,4a,8,9-tetramethyl-octahydronaphthal-5-en-3,7-dione

BENGT KARLSSON, ANNE-MARIE PILOTTI and ANNE-CHARLOTTE WIEHAGER

Institute of Inorganic and Physical Chemistry, University of Stockholm, S-104 05 Stockholm 50, Sweden

The crystal structure of 1,4-ethyleno-2,8-dihydroxy-2,4a,8,9-tetramethyl-octahydronaphthal-5-en-3,7-dione, $C_{16}H_{20}O_4$, has been determined by single crystal X-ray diffraction analysis. The crystals are monoclinic, space group $P2_1/c$, with $a=12.421$, $b=7.142$, $c=16.412$ Å, $\beta=103.03°$, $Z=4$. The structure was solved by direct methods. The parameters were refined by a full-matrix least-squares method using 1540 observed intensities collected on the computer controlled Philips diffractometer PW 1100. The final R value is 0.044.

The compound is a Diels-Alder dimer of 2,4-dimethyl-*o*-quinol, obtained by periodate oxidation of 2,4-dimethylphenol. Two molecules of 2,4-dimethyl-*o*-quinol with the same absolute configuration about the tertiary carbon atom C(2) have dimerised. The structure is rather strained with $C(sp^3)-C(sp^3)$ bond lengths of 1.578 and 1.567 Å for the bonds C(4) – C(4a) and C(4a) – C(8a), respectively.

1,4-Ethyleno-2,8-dihydroxy-2,4a,8,9-tetramethyl-octahydronaphthal-5-en-3,7-dione is a dimer of 2,4-dimethyl-*o*-quinol, obtained by periodate oxidation of 2,4-dimethylphenol. Structures and steric orientations of Diels-Alder dimers of *o*-quinols have been discussed by Adler *et al.*[1,2] and X-ray structure determinations [3,4] have confirmed proposed structures based on chemical and spectral analysis.

The X-ray investigation of the title compound has been undertaken as part of a program concerning crystal structure studies of Diels-Alder dimerisation of *o*-quinols.

EXPERIMENTAL

Three-dimensional intensities were collected on the computer-controlled Philips diffractometer PW 1100, with monochromatized Cu$K\alpha$ radiation. A crystal of approximate volume 0.0047 mm³ was mounted arbitrarily on the diffractometer. Then 25 reflexions were found by the "Peak Hunting Program" and used by it to calculate the orientation matrix of the crystal relative to the coordinate system of the goniometer. The unit cell dimensions (Table 1) were derived from the matrix, the reflexions indexed, and the cell

dimensions then refined by the least-squares method. The moving crystal, moving counter method ($\omega/2\theta$) was used to measure the intensity data, 1.5° scans at 0.025°/sec, and background counts were recorded for 30 sec at the beginning and end of each scan. Three standard reflexions were monitored at intervals of approximately 1½ h. Of the 2673 reflexions with $2\theta < 130°$, 1540 had $\sigma(I)/I \leq 0.25$ and were used in the crystal structure refinements. The estimated standard deviation, $\sigma(I)$, of the net intensity, I, is based on counter statistics. Corrections were made for Lorentz and polarization factors, but not for absorption. An absolute scale factor and a mean isotropic temperature factor were estimated by Wilson's method [5] and normalized structure factor magnitudes $|E|$ were calculated.

Table 1. Crystal unit cell data. Figures in parentheses are calculated standard deviations.

Lattice constants	$a = 12.421(2)$ Å
	$b = 7.142(2)$ Å
	$c = 16.412(3)$ Å
	$\beta = 103.03(3)°$
Cell volume	$V = 1418.5$ Å^3
Calculated density	$d = 1.292$ g cm^{-3}
Molecules per unit cell	$Z = 4$
Space group	$P2_1/c$

STRUCTURE DETERMINATION AND REFINEMENTS

The structure was solved by using "variance-weighted" $\sum_2$-relationships, described by Norrestam.[6] Signs were determined for the 196 reflexions having $|E| \geq 1.75$. The starting set (Table 2) consisted of four variables and three origin-specifying reflexions. The E map corresponding to the solution with the highest "reliability index" displayed all the non-hydrogen atoms.

Table 2. Assignments of starting phases.

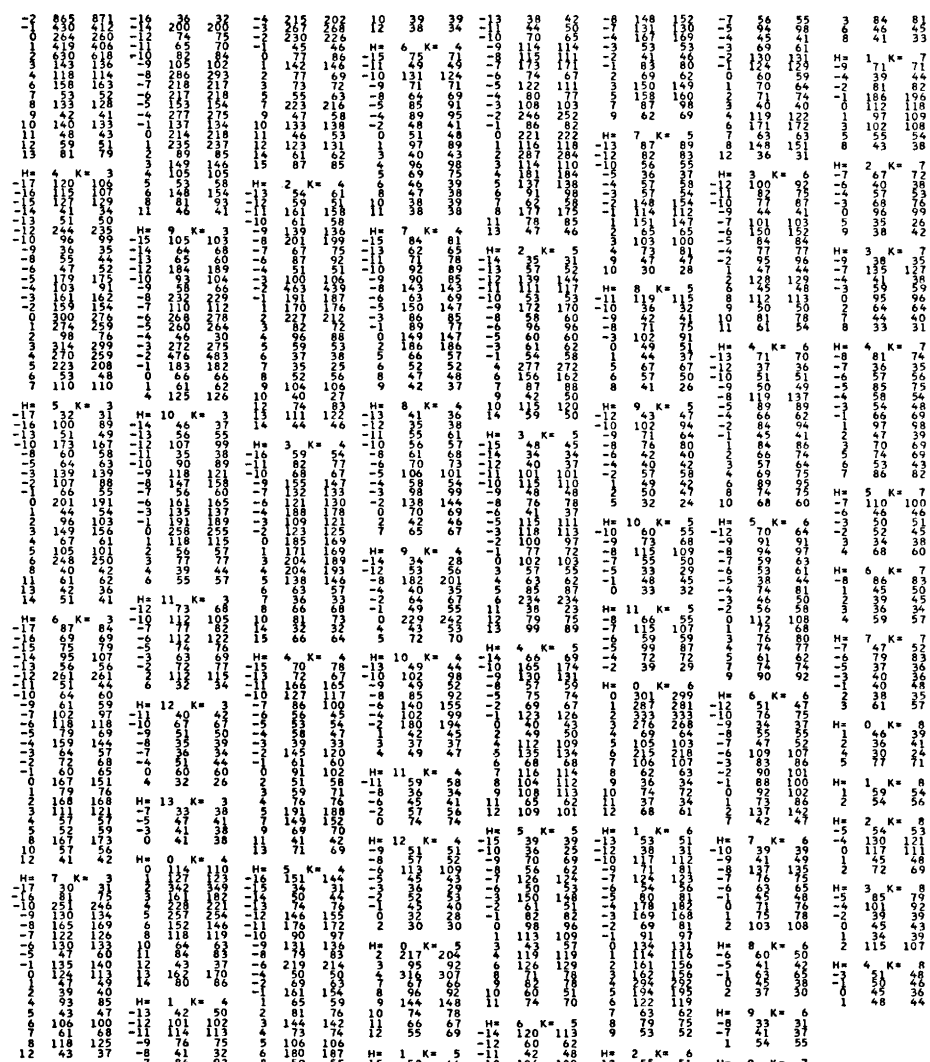
h			$\|E_h\|$	Starting phase value	Correct phase value
9	3	−2	4.97	0	0
3	3	−2	3.73	0,π	0
5	2	−13	3.40	0	0
10	3	0	3.37	0,π	0
6	3	−12	3.23	0	0
9	2	−6	3.10	0,π	0
0	6	1	3.03	0,π	π

Least-squares refinement was started with isotropic temperature factors, subsequent anisotropic cycles reduced R to 0.091. At this stage a difference Fourier synthesis revealed all the non-hydrogen atoms. After introduction of the hydrogen atoms with isotropic temperature factors, equal to those of the final isotropic values of their parent atoms, further refinement reduced the R value to 0.044.

The full-matrix least-squares refinements were performed by a modified version of program LALS.[7] Hughes' weighting scheme [8] was applied with $F_{o,min} = 3.3$. The atomic scattering factors for oxygen and carbon were taken from Freeman [9] and that for hydrogen from Stewart, Davidson and Simpson.[10]

Table 3. Observed and calculated structure amplitudes. The columns contain the index *l*, $10|F_o|$ and $10|F_c|$.

Table 3. Continued.



The observed and calculated structure factors are given in Table 3. The positional and thermal parameters of the non-hydrogen atoms with estimated standard deviations are listed in Tables 4 and 5, those for the hydrogen atoms in Table 6.

Table 4. Fractional atomic coordinates ($\times 10^4$) for non-hydrogen atoms with estimated standard deviations in parentheses.

	x	*y*	*z*
C(1)	2218(2)	5095(4)	3200(2)
C(2)	3164(2)	5571(4)	2768(2)
C(3)	3766(2)	3729(4)	2702(2)
C(4)	3260(2)	2065(4)	3044(2)
C(4a)	3323(2)	2411(4)	4003(2)
C(5)	2740(3)	744(4)	4272(2)
C(6)	1781(3)	790(4)	4487(2)
C(7)	1204(3)	2556(4)	4542(2)
C(8)	1932(3)	4293(4)	4664(2)
C(8a)	2743(2)	4330(4)	4082(2)
C(9)	1514(2)	3625(4)	2676(2)
C(10)	2071(2)	2075(4)	2593(2)
C(11)	2749(3)	6425(5)	1906(2)
O(12)	3905(2)	6811(3)	3291(2)
O(13)	4567(2)	3681(3)	2402(2)
C(14)	4545(3)	2423(6)	4465(3)
O(15)	234(2)	2647(4)	4554(2)
C(16)	2575(5)	4265(7)	5578(3)
O(17)	1294(3)	5939(3)	4503(2)
C(18)	329(3)	3979(6)	2273(3)

Table 5. Thermal parameters of the non-hydrogen atoms, with estimated standard deviations in parentheses. The β values refer to the temperature factor expression $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$. Values are $\times 10^4$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	49(2)	108(5)	32(1)	29(5)	35(2)	5(4)
C(2)	54(2)	118(5)	35(1)	0(5)	39(2)	1(4)
C(3)	52(2)	160(6)	38(1)	12(5)	43(3)	−8(4)
C(4)	58(2)	105(5)	41(2)	42(5)	36(3)	−8(4)
C(4a)	61(2)	126(5)	32(1)	1(5)	12(2)	18(4)
C(5)	87(3)	136(6)	35(1)	4(6)	17(3)	28(4)
C(6)	108(3)	132(6)	41(2)	−59(7)	56(3)	5(4)
C(7)	115(3)	188(6)	47(2)	−61(7)	106(4)	−27(5)
C(8)	135(3)	145(6)	40(2)	−55(7)	100(4)	−37(5)
C(8a)	70(2)	113(5)	26(1)	−44(5)	32(2)	−16(4)
C(9)	50(2)	153(6)	31(1)	−7(5)	19(2)	15(4)
C(10)	66(2)	142(5)	26(1)	−37(6)	28(2)	−23(4)
C(11)	96(3)	209(8)	46(2)	27(8)	58(4)	70(5)
O(12)	75(2)	176(4)	53(1)	−80(4)	71(2)	−25(3)
O(13)	95(2)	226(5)	91(2)	52(5)	135(3)	14(4)
C(14)	77(3)	241(8)	58(2)	8(8)	−18(4)	57(7)
O(15)	139(3)	254(6)	107(2)	−57(6)	180(4)	−59(5)
C(16)	246(8)	335(11)	39(2)	−261(15)	105(6)	−76(8)
O(17)	188(3)	173(5)	102(2)	10(6)	230(4)	−29(5)
C(18)	63(3)	231(8)	75(3)	−15(8)	−11(4)	37(7)

Table 6. Positional and isotropic thermal parameters of the hydrogen atoms, with estimated standard deviations in parentheses.

	$x \times 10^3$	$y \times 10^3$	$z \times 10^3$	$B \times 10^2$ Å^2
H(C1)	183(2)	618(4)	324(2)	240
H(C4)	363(2)	105(4)	297(2)	250
H(C5)	314(2)	−46(4)	422(2)	356
H(C6)	143(2)	−25(4)	457(2)	397
H(C8a)	331(2)	521(4)	431(2)	285
H(C10)	178(2)	108(4)	226(2)	276
H1(C11)	221(3)	572(4)	155(2)	419
H2(C11)	332(3)	666(4)	165(2)	419
H3(C11)	237(3)	762(5)	194(2)	419
H(012)	435(3)	719(4)	305(2)	322
H1(C14)	488(3)	129(5)	441(2)	521
H2(C14)	455(3)	258(5)	505(3)	521
H3(C14)	492(3)	349(5)	426(2)	521
H1(C16)	202(3)	435(6)	587(3)	728
H2(C16)	291(4)	316(6)	570(3)	728
H3(C16)	308(3)	472(6)	569(3)	728
H(O17)	92(3)	604(3)	480(2)	588
H1(C18)	30(3)	513(5)	190(2)	508
H2(C18)	0(3)	288(5)	194(2)	508
H3(C18)	−1(3)	420(5)	271(2)	508

RESULTS AND DISCUSSION

Fig. 1 is a perspective view of the molecule [11] with the atom numbering scheme. The Diels-Alder dimerisation of 2,4-dimethyl-*o*-quinol follows the *endo* addition rule.[12] The relative position of the two keto groups is such that

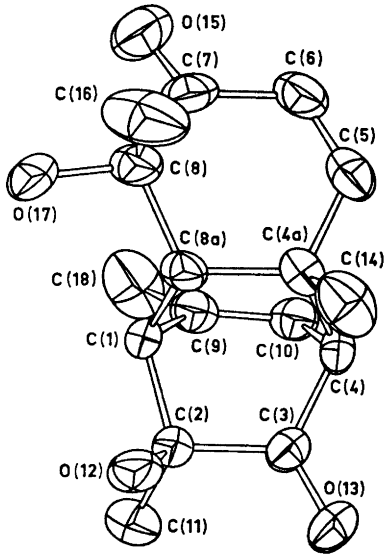


Fig. 1. A perspective view of the molecule.

the dipole moment of the transition state is lower than for any other structural isomers. This arrangement is favored according to Horner and Dürckheimer.[13] The configurations of the tertiary carbon atoms C(2) and C(8) reveal that the two molecules of 2,4-dimethyl-*o*-quinol which undergo dimerisation have the same configuration about the tertiary carbon atom C(2); this is probably a steric requirement.[14] The crystal structures of 1,4-ethyleno-2,8-dihydroxy-2,4,6,8-tetramethyl-octahydronaphthal-5-en-3,7-dione [15] and 1,4-ethyleno-2,8-dichloro-2,4,6,8-tetramethyl-octahydronaphthal-5-en-3,7-dione [16] have also been found upon X-ray investigation to follow the above mentioned rules.

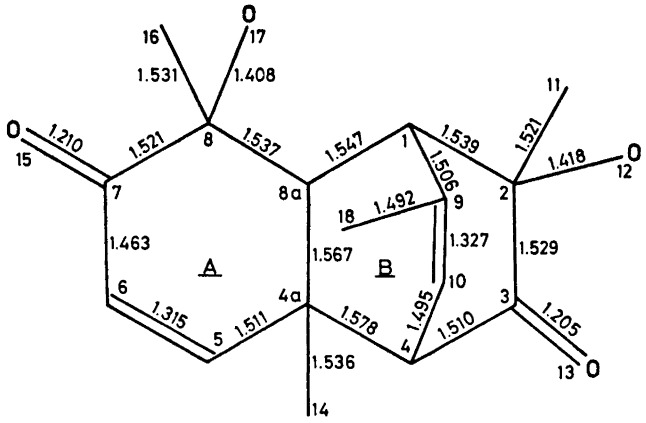


Fig. 2. Bond distances in the molecule.

Table 7. Bond distances (Å) involving the non-hydrogen atoms, with estimated standard deviations in parentheses.

C(1) – C(2)	1.539(3)	C(4a) – C(8a)	1.567(3)
C(1) – C(8a)	1.547(3)	C(4a) – C(14)	1.536(4)
C(1) – C(9)	1.506(3)	C(5) – C(6)	1.315(4)
C(2) – C(3)	1.529(3)	C(6) – C(7)	1.463(4)
C(2) – C(11)	1.521(4)	C(7) – C(8)	1.521(4)
C(2) – O(12)	1.418(3)	C(7) – O(15)	1.210(4)
C(3) – C(4)	1.510(3)	C(8) – C(8a)	1.537(4)
C(3) – O(13)	1.205(3)	C(8) – C(16)	1.531(5)
C(4) – C(4a)	1.578(4)	C(8) – O(17)	1.408(4)
C(4) – C(10)	1.495(3)	C(9) – C(10)	1.327(3)
C(4a) – C(5)	1.511(4)	C(9) – C(18)	1.492(4)

The bond distances for the molecule are displayed in Fig. 2. Corrections for thermal motion were not applied in the calculation of bond lengths or angles (Tables 7 and 8). The average estimated standard deviations in bond lengths and angles involving non-hydrogen atoms are 0.0036 Å and 0.3°. Most

Table 8. Bond angles (°) involving non-hydrogen atoms, with estimated standard deviations in parentheses.

C(2) – C(1) – C(8a)	107.7(2)	C(7) – C(8) – C(8a)	112.6(3)
C(2) – C(1) – C(9)	107.1(2)	C(7) – C(8) – C(16)	106.4(3)
C(8a) – C(1) – C(9)	110.8(2)	C(7) – C(8) – O(17)	111.3(3)
C(1) – C(2) – C(3)	106.2(2)	C(8a) – C(8) – C(16)	109.8(4)
C(1) – C(2) – C(11)	112.6(3)	C(8a) – C(8) – O(17)	106.8(3)
C(1) – C(2) – O(12)	108.5(2)	C(16) – C(8) – O(17)	110.0(3)
C(3) – C(2) – C(11)	110.3(3)	C(1) – C(8a) – C(4a)	109.7(2)
C(3) – C(2) – O(12)	108.6(2)	C(1) – C(8a) – C(8)	113.0(3)
C(11) – C(2) – O(12)	110.5(3)	C(4a) – C(8a) – C(8)	114.4(2)
C(2) – C(3) – C(4)	113.6(2)	C(1) – C(9) – C(10)	113.1(3)
C(2) – C(3) – O(13)	121.0(3)	C(1) – C(9) – C(18)	121.4(3)
C(4) – C(3) – O(13)	125.4(3)	C(10) – C(9) – C(18)	125.4(3)
C(3) – C(4) – C(4a)	108.5(2)	C(4) – C(10) – C(9)	115.6(3)
C(3) – C(4) – C(10)	105.0(2)		
C(4a) – C(4) – C(10)	108.3(2)		
C(4) – C(4a) – C(5)	104.5(2)		
C(4) – C(4a) – C(8a)	107.4(2)		
C(4) – C(4a) – C(14)	108.4(3)		
C(5) – C(4a) – C(8a)	114.0(2)		
C(5) – C(4a) – C(14)	110.2(3)		
C(8a) – C(4a) – C(14)	112.0(3)		
C(4a) – C(5) – C(6)	125.5(3)		
C(5) – C(6) – C(7)	121.5(3)		
C(6) – C(7) – C(8)	115.3(3)		
C(6) – C(7) – O(15)	123.3(3)		
C(8) – C(7) – O(15)	121.2(3)		

bond lengths are in good agreement with usually observed values.[17] The C–H bond distances range from 0.70 to 1.02 Å, mean value 0.91 Å, in good agreement with values found in some precisely determined X-ray structures.[10] C(sp^3) – C(sp^3) bond lengths, excluding C(4) – C(4a) and C(4a) – C8(a), have a mean value of 1.535 Å. The lengths of the two bonds C(4) – C(4a) and C(4a) – C(8a) are 1.578 Å and 1.567 Å, significantly longer ($> 10\sigma$) than this mean value. This lengthening, probably associated with internal strain in the molecule, has previously been observed in the crystal structure of 1,4-ethyleno-2,8-dihydroxy-2,4,6,8-tetramethyl-octahydronaphthal-5-en-3,7-dione, [15] a Diels-Alder dimer of 2,6-dimethyl-*o*-quinol, where the lengths of C(4) – C(4a) and C(4a) – C(8a) are 1.589 and 1.554 Å, respectively. The methyl group C(14), attached to the carbon atom C(4a) in the dimer of 2,4-dimethyl-*o*-quinol, has probably caused the lengthening of the C(4a) – C(8a) bond in the present structure relative to the structure of the dimer of 2,6-dimethyl-*o*-quinol.

A least-squares plane for ring A (Fig. 2) and the displacements of the atoms from this best plane are listed in Table 9. The conformation of the ring is puckered. Atom C(8) is significantly out of the plane of the other five atoms, as also was observed in the dimer of 2,6-dimethyl-*o*-quinol.[15] The three rings in the rigid B ring system (Fig. 2) are all boat-shaped and least-squares planes with deviations from them are also given in Table 9.

Fig. 3 is a view along the a^* axis of the arrangement of the molecules. The two hydrogen atoms bonded to oxygen participate in hydrogen bonds, forming

Table 9. Least-squares planes and deviations. The planes are described in terms of axes (m,n,p) having $m||a^*$, $n||b$ and $p||c$. The atoms indicated with asterisks were omitted from the calculations of the least-squares planes. Deviation in Å.

Plane A[a]		Plane B1[b]		Plane B2[c]		Plane B3[d]	
Atom	Deviation	Atom	Deviation	Atom	Deviation	Atom	Deviation
C(4a)*	−0.060	C(1)*	−0.779	C(1)*	0.728	C(1)*	0.646
C(5)	0.005	C(2)	−0.012	C(2)	−0.010	C(4)*	0.716
C(6)	−0.008	C(3)	0.012	C(3)	0.011	C(4a)	−0.026
C(7)	0.005	C(4)*	−0.716	C(4)*	0.688	C(8a)	0.025
C(8)*	0.554	C(4a)	−0.012	C(9)	0.012	C(9)	−0.030
C(8a)	−0.002	C(8a)	0.012	C(10)	−0.012	C(10)	0.030

[a] Plane A : $0.4808m+0.1028n+0.8708p=7.080$.
[b] Plane B1: $0.8557m+0.3806n+0.3505p=6.082$.
[c] Plane B2: $0.2119m-0.1041n+0.9717p=3.962$.
[d] Plane B3: $0.6448m+0.4914n-0.5855p=0.1596$.

the three-dimensional network shown in Fig. 3. Two molecules related to each other by a center of symmetry at $0,\frac{1}{2},\frac{1}{2}$ form a hydrogen-bonded dimer (Table 10). The O(15^{ii})···(O17) distance is 2.184 Å and the O(17)−H(O17)··· O(15^{ii}) angle is 158.7°. The hydrogen-bonded dimers are linked by hydrogen bonds along the *b* direction (Table 10). The O(13^{vi})···H(O12) distance is 1.986 Å and the O(12)−H(O12)···O(13^{vi}) angle is 166.1°.

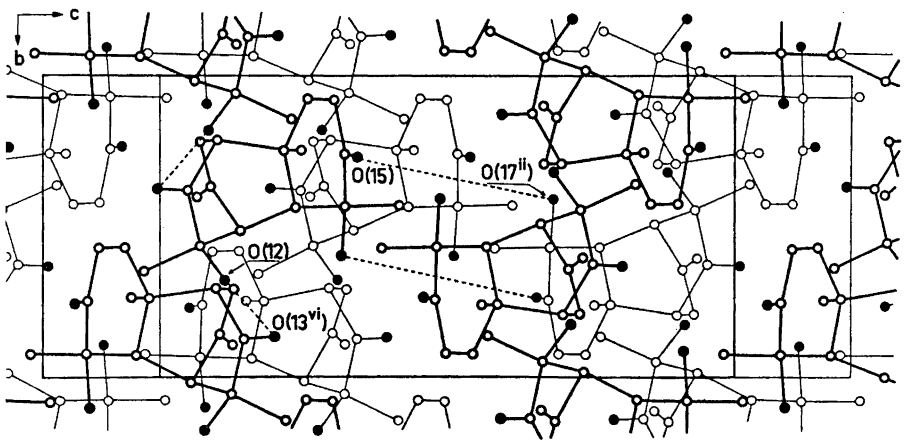


Fig. 3. Packing of molecules in the crystal as viewed along a^*. Molecules lying below the origin are marked with thin lines and hydrogen bonds with broken lines. ○ carbon; ● oxygen.

Table 10. Intermolecular distances (Å) shorter than 3.8 Å, with estimated standard deviations in parentheses.

Superscript	Code for symmetry related atoms. Coordinates	Superscript	Coordinates
none	x,y,z	iv	$x,1/2-y,-1/2+z$
i	$x,-1+y,z$	v	$-x,-1/2+y,1/2-z$
ii	$-x,1-y,1-z$	vi	$1-x,1/2+y,1/2-z$
iii	$1-x,1-y,1-z$	vii	$x,3/2-y,-1/2+z$

C(5) – O(12^{i})	3.691(3)	C(10) – C(18^{v})	3.756(4)
C(6) – O(17^{i})	3.518(4)	C(18) – C(18^{v})	3.775(2)
O(15) – O(15^{ii})	3.764(5)	C(2) – O(13^{iv})	3.647(3)
O(15) – O(17^{ii})	2.887(4)	C(11) – O(13^{vi})	3.644(4)
O(12) – C(14^{iii})	3.790(4)	O(12) – O(13^{vi})	2.765(3)
C(10) – C(16^{iv})	3.631(5)	O(13) – O(13^{vi})	3.722(1)
C(6) – C(18^{v})	3.669(5)	C(11) – C(16^{vii})	3.750(6)

This investigation has received financial support from the *Tri-Centennial Fund of the Bank of Sweden* and from the *Swedish Natural Science Research Council.*

The authors are indebted to Professor Peder Kierkegaard for his encouraging interest in this work and for the facilities placed at their disposal. Thanks are due to Dr. Bengt Lindgren for the supply of crystals used in the work and for valuable comments. Dr. Åke Pilotti is also thanked for valuable discussions and Dr. Don Koenig for his correction of the English of this paper.

REFERENCES

1. Adler, E., Brasen, S. and Miyake, H. *Acta Chem. Scand.* **25** (1971) 2055.
2. Adler, E. and Holmberg, K. *Acta Chem. Scand.* **25** (1971) 2775.
3. Vannerberg, N.-G. and Brasen, S. *Acta Chem. Scand.* **24** (1970) 1894.
4. Karlsson, B., Kierkegaard, P., Pilotti, A.-M., Wiehager, A.-C. and Lindgren, B. *Acta Chem. Scand.* **27** (1973) 1428.
5. Wilson, A. J. C. *Nature* **150** (1942) 151.
6. Norrestam, R. *Acta Cryst.* **A 28** (1972) 303.
7. Gantzel, P. K., Sparks, R. A. and Trueblood, K. N. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., Program 384 (1961).
8. Hughes, E. W. *J. Am. Chem. Soc.* **63** (1941) 1737.
9. Freeman, A. J. *Acta Cryst.* **12** (1959) 261.
10. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
11. Johnson, C. K. *ORTEP* Report *ORNL*-3794 (1965) Oak Ridge National Laboratory, Oak Ridge, Tennessee.
12. Alder, K. and Stein, G. *Angew. Chem.* **50** (1937) 514.
13. Horner, L. and Dürckheimer, W. *Chem. Ber.* **95** (1962) 1219.
14. Kende, A. S. and Mac Gregor, P. *J. Am. Chem. Soc.* **83** (1961) 4197.
15. Karlsson, B., Pilotti, A.-M. and Wiehager, A.-C. *Acta Chem. Scand.* **27** (1973) 2945.
16. Karlsson, B., Pilotti, A.-M. and Wiehager, A.-C. *To be published.*
17. Sutton, L. E. *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London 1965, Supplement 1956 – 1959.

Received April 18, 1973.