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The Crystal Structure of 1,4-Ethyleno-2,8-dichloro-2,4,6,8-tetramethyloctahydronaphthal-5-ene-3,7-dione

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The crystal structure of the title compound, $C_{16}H_{18}Cl_2O_2$, has been determined in three dimensions by X-ray diffraction, from 2093 independent intensities. The crystals belong to the triclinic space group $P\bar{1}$ with two molecules per unit cell of dimensions $a = 8.848$ Å, $b = 9.215$ Å, $c = 10.115$ Å, $\alpha = 98.03°$, $\beta = 92.86°$, and $\gamma = 113.80°$. The structure was solved by a combination of heavy-atom and direct methods and refined by full-matrix least-squares to a final R value of 0.052.

The Diels-Alder product 1,4-ethyleno-2,8-dichloro-2,4,6,8-tetramethyloctahydronaphthal-5-ene-3,7-dione is a dimer of 6-chloro-2,6-dimethylcyclohexa-2,4-dien-1-one, formed upon oxidation of 2,6-dimethylphenol by chlorine dioxide. Two molecules with the same absolute configuration about the tertiary carbon atom have dimerised. The structure is rather strained with $C(sp^3) - C(sp^3)$ bond lengths of 1.589 and 1.560 Å for the bonds C(4) – C(4a) and C(4a) – C(8a), respectively.

Oxidation of 2,6-xylenol in carbon tetrachloride solution by chlorine dioxide gives in a low yield the Diels-Alder product 1,4-ethyleno-2,8-dichloro-2,4,6,8-tetramethyloctahydronaphthal-5-ene-3,7-dione which is a dimer of 6-chloro-2,6-dimethylcyclohexa-2,4-dien-1-one.

Table 1. Crystal data.

Lattice constants	$a = 8.848(2)$ Å
	$b = 9.215(3)$ Å
	$c = 10.115(4)$ Å
	$\alpha = 98.03(1)°$
	$\beta = 92.86(1)°$
	$\gamma = 113.80(1)°$
Cell volume	$V = 742.08$ Å^3
Density (calculated)	$d = 1.40$ g cm^{-3}
Molecules per unit cell	$Z = 2$
Space group	$P\bar{1}$

The steric orientation of the chloro group in the cyclohexenone moiety was established [1] from the high value (1700 cm^{-1}) of the stretching frequency of the conjugated carbonyl group.

The purpose of this investigation, in a program of crystal structure studies of oxidation products of phenols, was to establish the steric configuration at carbon atom C(2) and to confirm the structure of the dimer.

EXPERIMENTAL

Two crystals of the approximate volumes 0.0044 and 0.0014 mm^3 were mounted arbitrarily on the computer-controlled Philips diffractometer PW 1100 equipped with a graphite monochromator to reflect Cu$K\alpha$ radiation. Preceding the measurement of the reflexion intensities, the least-squares unit cell parameters, and crystal-orientation parameters were determined, through measurement of the angular positions of 25 accurately centered reflexions by the "Peak-Hunting Program". Table 1 contains the refined cell parameters.

The intensities of 2562 independent reflexions out to $\theta = 65°$ were measured by the moving-crystal, moving-counter technique ($\theta - 2\theta$ scan). Backgrounds were estimated by stationary counting at $\pm 0.75°$ 2θ from the peak maxima. The scan speed was 1.2° min^{-1}. Three monitor reflexions were measured every 90 min, which showed that the crystals were not stable to X-rays. Two crystals were used, each with a decrease in intensity of about 10 to 15 % during the period of data collection. Lorentz and polarization factors were applied but not correction for absorption. Only the 2093 reflexions for which $\sigma(I)/I \leq 0.25$ were used in refinement of the structure. $\sigma(I)$ is the estimated standard

Table 2. Observed and calculated structure amplitudes. The columns use the running index l, $10|F_o|$, and $10|F_c|$, respectively.

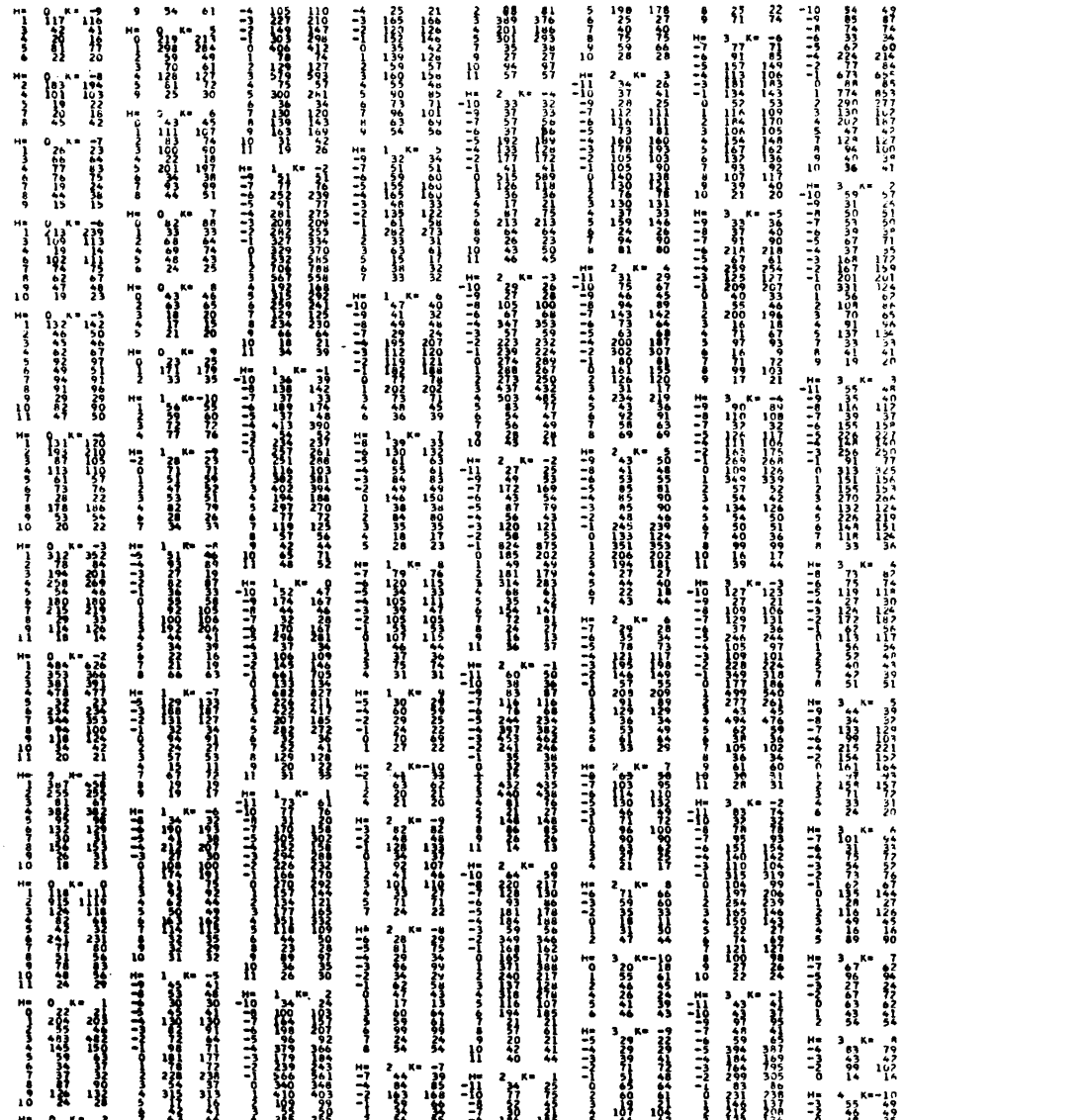

Table 2. Continued.

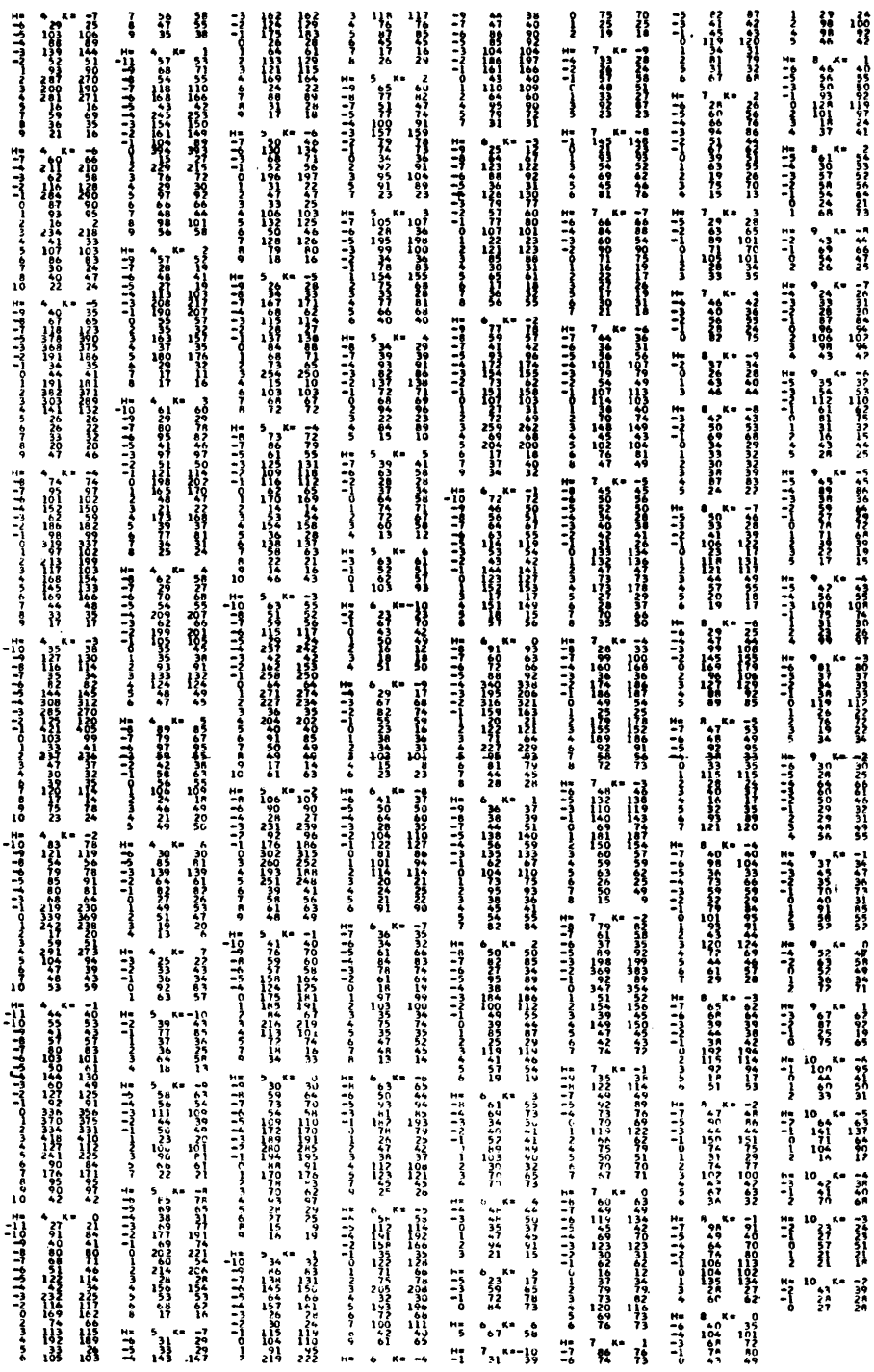

Table 3. Positional and anisotropic thermal parameters of the non-hydrogen atoms. The β-values refer to the temperature factor expression exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$. Estimated standard deviations are given in parentheses. Values are $\times 10^4$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	3375(3)	2821(3)	3005(3)	93(4)	101(4)	81(3)	92(6)	−2(5)	21(5)
C(2)	3265(4)	1096(4)	2602(3)	132(5)	125(4)	85(3)	149(7)	19(6)	24(6)
C(3)	1431(4)	−41(3)	2254(3)	148(5)	102(4)	79(3)	112(7)	3(6)	30(5)
C(4)	262(3)	769(3)	2583(3)	106(4)	101(4)	88(3)	67(7)	23(5)	47(5)
C(4a)	612(3)	2065(3)	1621(3)	98(4)	100(4)	60(3)	80(6)	3(5)	16(5)
C(5)	−553(3)	2848(4)	1878(3)	85(4)	129(4)	95(3)	90(7)	22(5)	57(6)
C(6)	−132(4)	4318(4)	2563(3)	133(5)	138(4)	78(3)	139(7)	62(6)	64(6)
C(7)	1642(4)	5379(3)	2947(3)	165(5)	101(4)	79(3)	135(7)	6(6)	36(5)
C(8)	2760(3)	5001(3)	1987(3)	86(4)	99(4)	99(3)	45(6)	3(5)	70(5)
C(8a)	2498(3)	3223(3)	1833(3)	90(4)	110(4)	65(3)	94(6)	32(5)	33(5)
C(9)	2425(4)	2781(4)	4198(3)	147(5)	121(4)	65(3)	144(7)	−7(6)	11(5)
C(10)	865(4)	1731(4)	3990(3)	150(5)	147(5)	69(3)	150(8)	57(6)	65(6)
C(11)	4108(5)	596(5)	3699(4)	178(6)	150(5)	134(4)	197(10)	−43(8)	44(8)
Cl(12)	4268(1)	956(1)	1103(1)	206(2)	213(2)	129(1)	271(3)	124(2)	31(2)
O(13)	961(3)	−1438(3)	1759(3)	208(5)	112(4)	157(3)	132(6)	−35(6)	−15(5)
C(14)	−1535(4)	−454(4)	2403(4)	122(5)	136(5)	148(5)	43(8)	21(7)	90(8)
C(15)	−1381(5)	4958(5)	2985(4)	206(7)	196(6)	130(4)	280(11)	127(9)	82(9)
O(16)	2134(4)	6503(3)	3870(3)	266(5)	137(4)	118(3)	162(7)	−34(6)	−37(5)
C(17)	2429(5)	5412(5)	610(4)	165(6)	186(6)	117(4)	173(10)	77(8)	164(8)
Cl(18)	4896(1)	6312(1)	2594(1)	107(2)	132(2)	233(2)	5(2)	−62(3)	122(2)

Table 4. Positional and isotropic thermal parameters of the hydrogen atoms, with estimated standard deviations in parentheses.

	$x\times 10^3$	$y\times 10^3$	$z\times 10^3$	$B\times 10^2$
H(C1)	445(4)	350(4)	319(3)	283
H(C4a)	35(4)	142(4)	77(3)	242
H(C5)	−158(4)	220(4)	160(3)	287
H(C8a)	295(4)	299(3)	110(3)	230
H(C9)	295(4)	352(4)	505(3)	281
H(C10)	13(4)	166(4)	464(3)	311
H1(C11)	526(5)	133(4)	385(4)	378
H2(C11)	354(4)	54(4)	449(4)	378
H3(C11)	405(4)	−41(4)	347(4)	378
H1(C14)	−193(5)	−84(5)	157(4)	441
H2(C14)	−164(4)	−134(5)	287(4)	441
H3(C14)	−226(5)	8(5)	274(4)	441
H1(C15)	−254(5)	420(5)	252(4)	432
H2(C15)	−134(5)	508(5)	383(4)	432
H3(C15)	−115(5)	596(5)	257(4)	432
H1(C17)	244(4)	631(5)	65(4)	362
H2(C17)	328(5)	541(4)	9(4)	362
H3(C17)	129(5)	458(4)	16(3)	362

deviation, based on counter statistics, of the net intensity I.

Structure determination and refinement

The structure was solved by a combination of heavy-atom and direct methods. The positional parameters of the two chlorine atoms were found from a 3-D Patterson synthesis. The structure factors were converted to normalized $|E|$'s using an approximate absolute scale and average temperature factor determined by Wilson's [2] method. The atomic positions of the chlorine atoms were used to calculate structure factors. The phases of 10 reflexions with $|F_c| \geq 0.2|F_o|$, where $|F_c|$ and $|F_o|$ are calculated and observed structure factor magnitudes, respectively, were used as starting phases together with two reflexions as variables. These

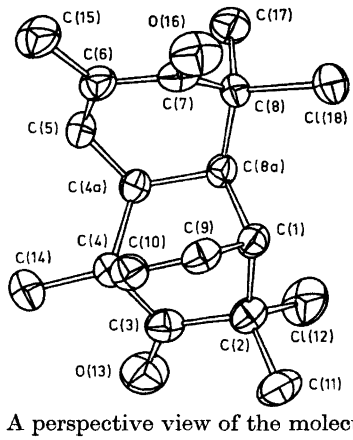

Fig. 1. A perspective view of the molecule.

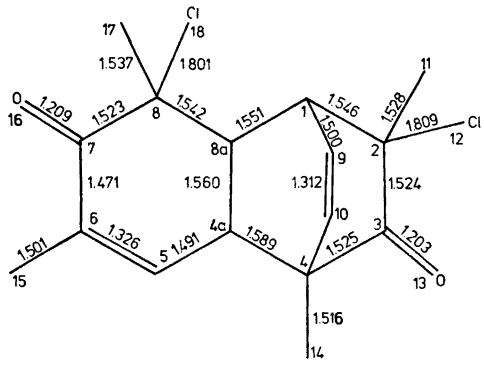

Fig. 2. Bond distances in the molecule.

Table 5. Interatomic angles (°) with estimated standard deviations in parentheses.

C(2) – C(1) – C(8a)	108.9(2)
C(2) – C(1) – C(9)	105.9(2)
C(8a) – C(1) – C(9)	108.8(2)
C(1) – C(2) – C(3)	107.6(2)
C(1) – C(2) – C(11)	112.6(3)
C(1) – C(2) – Cl(12)	110.2(2)
C(3) – C(2) – C(11)	111.7(3)
C(3) – C(2) – Cl(12)	107.2(2)
C(11) – C(2) – Cl(12)	107.4(2)
C(2) – C(3) – C(4)	113.4(2)
C(2) – C(3) – O(13)	123.0(3)
C(4) – C(3) – O(13)	123.6(3)
C(3) – C(4) – C(4a)	105.4(2)
C(3) – C(4) – C(10)	106.8(2)
C(3) – C(4) – C(14)	111.3(3)
C(4a) – C(4) – C(10)	105.5(2)
C(4a) – C(4) – C(14)	113.3(3)
C(10) – C(4) – C(14)	113.9(3)
C(4) – C(4a) – C(5)	107.1(2)
C(4) – C(4a) – C(8a)	109.6(2)
C(5) – C(4a) – C(8a)	115.7(2)
C(4a) – C(5) – C(6)	125.2(3)
C(5) – C(6) – C(7)	118.9(3)
C(5) – C(6) – C(15)	123.2(3)
C(7) – C(6) – C(15)	117.9(3)
C(6) – C(7) – C(8)	113.0(2)
C(6) – C(7) – O(16)	122.8(3)
C(8) – C(7) – O(16)	124.0(3)
C(7) – C(8) – C(8a)	112.0(2)
C(7) – C(8) – C(17)	109.3(3)
C(7) – C(8) – Cl(18)	109.0(2)
C(8a) – C(8) – C(17)	110.3(3)
C(8a) – C(8) – Cl(18)	110.2(2)
C(17) – C(8) – Cl(18)	105.8(2)
C(1) – C(8a) – C(4a)	109.2(2)
C(1) – C(8a) – C(8)	114.8(2)
C(4a) – C(8a) – C(8)	111.4(2)
C(1) – C(9) – C(10)	114.9(3)
C(4) – C(10) – C(9)	116.0(3)

phases were extended and refined by use of "variance-weighted" $\sum_2$-relationships.[3] Signs were determined for 178 reflexions ($|E| > 1.8$) without any contradictions in the solution with the highest "reliability index". An E-map based on these phases revealed the complete structure, except for hydrogens. The positional and isotropic thermal parameters of these atoms were refined by full-matrix least-squares computations to an R value of 0.162. Upon assignment of anisotropic thermal parameters to all atoms the value of R fell after three cycles of refinement to 0.075.

The hydrogen atoms were then located from a difference Fourier synthesis. Refinement was continued including all atoms. For the heavy atoms anisotropic temperature factors were used and for the hydrogen atoms isotropic temperature factors equal to those of the final isotropic values of their parent atoms, were applied. The R value converged to 0.052.

The full-matrix least-squares refinements were performed by a modified version of program LALS.[4] Hughes' weighting scheme [5] was applied with $|F_{o,min}| = 1.75$. The atomic scattering factors for oxygen and carbon were taken from Freeman,[6] that for chlorine from *International Tables for X-Ray Crystallography* [7] and that for hydrogen from Stewart, Davidson and Simpson.[8] The observed and calculated structure amplitudes are given in Table 2. The positional and thermal parameters of the non-hydrogen atoms with estimated standard deviations are listed in Table 3 and those for the hydrogen atoms in Table 4.

RESULTS AND DISCUSSION

A perspective view of the molecule together with the numbering of atoms is given in Fig. 1. The stereochemistry of the structure is consonant with considerations given by Adler and Holmberg [9] and agrees with that found through X-ray investigations of related structures by Karlsson, Pilotti and Wiehager.[10,11] Intramolecular bond distances and bond angles involving non-hydrogen atoms are given in Fig. 2 and Table 5, respectively.* No corrections for

* The estimated standard deviations, based solely on least-squares parameters, are about 0.004 Å for for the bonds.

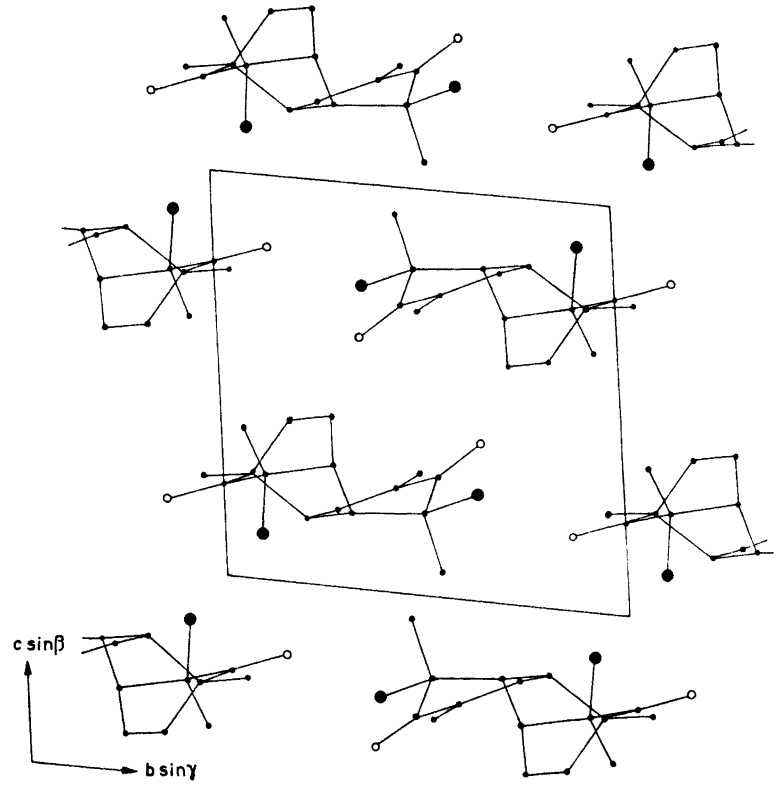

Fig. 3. The unit cell in projection along the *a* axis. •, carbon; ○, oxygen; ●, chlorine.

Table 6. Intermolecular distances (Å) less than 3.8 Å.

Code for symmetry related atoms

Superscript	Coordinates	Superscript	Coordinates
None	$x;\ y;\ z$	iv	$1-x;\ -y;\ -z$
i	$x;\ -1+y;\ z$	v	$1-x;\ -y;\ 1-z$
ii	$-1+x;\ -1+y;\ z$	vi	$-x;\ 1-y;\ -z$
iii	$-x;\ -y;\ -z$	vii	$-x;\ 1-y;\ 1-z$
		viii	$1-x;\ 1-y;\ 1-z$

C(11) – O(16^{i})	3.492(4)	Cl(12) – Cl(12^{iv})	3.285(2)
O(13) – C(7^{i})	3.570(3)	C(11) – C(11^{v})	3.523(7)
O(13) – C(15^{i})	3.565(4)	C(15) – C(17^{vi})	3.641(5)
O(13) – O(16^{i})	3.425(3)	C(9) – C(15^{vii})	3.670(5)
O(13) – C(17^{i})	3.703(4)	C(15) – O(16^{vii})	3.612(5)
C(14) – Cl(18^{ii})	3.393(3)	C(9) – Cl(18^{viii})	3.703(3)
C(4a) – O(13^{iii})	3.503(3)	C(11) – O(16^{viii})	3.797(4)
C(5) – O(13^{iii})	3.673(4)		

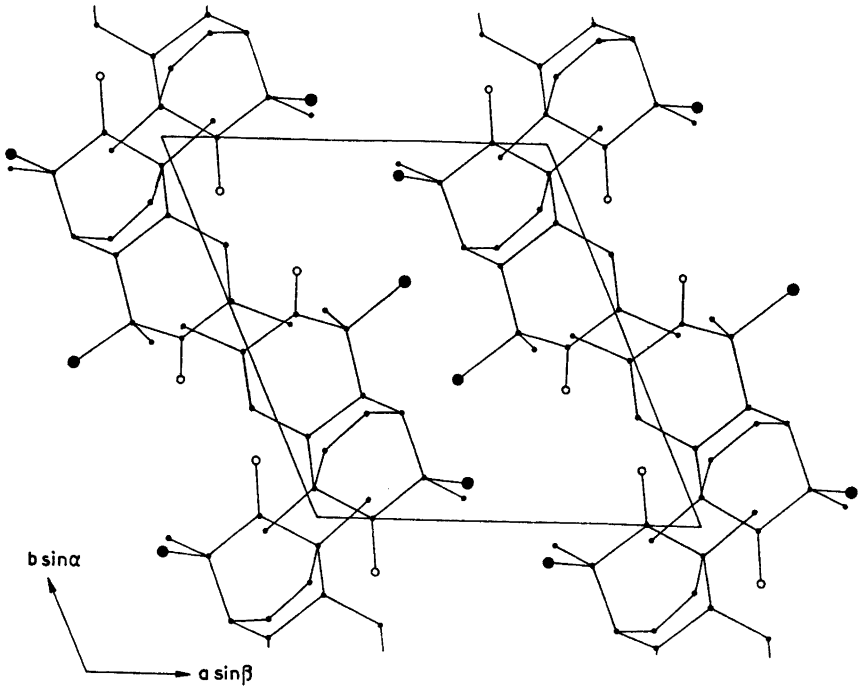

Fig. 4. The unit cell in projection along the *c* axis. •, carbon; ○, oxygen; ●, chlorine.

Table 7. Least-squares planes and deviations. The planes are described in terms of normalized equations in the orthogonal coordinate system (m,n,p) having $p \parallel c$, n in the bc plane and m in the abc octant.

Plane A	$-0.0307m-0.3701n+0.9285p=0.4227$
Plane B1	$-0.1205m+0.3597n+0.9252p=1.7490$
Plane B2	$0.1245m-0.6029n+0.7880p=2.2637$
Plane B3	$-0.2549m+0.9538n+0.1590p=1.6508$

Plane A		Plane B1	
Atom	Deviation (Å)	Atom	Deviation (Å)
C(4a)[a]	0.198	C(1)[a]	0.742
C(5)	0.001	C(2)	0.034
C(6)	0.001	C(3)	−0.035
C(7)	0.001	C(4)[a]	0.758
C(8)[a]	−0.650	C(4a)	0.034
C(8a)	0.001	C(8a)	−0.033
Plane B2		**Plane B3**	
Atom	Deviation (Å)	Atom	Deviation (Å)
C(1)[a]	−0.740	C(1)[a]	−0.667
C(2)	0.031	C(4)[a]	−0.729
C(3)	−0.031	C(4a)	0.021
C(4)[a]	−0.632	C(8a)	−0.021
C(9)	−0.036	C(9)	0.025
C(10)	0.036	C(10)	−0.025

Angles between the normals to the planes (°).	A ∧ B1	60
	A ∧ B2	77
	A ∧ B3	78

[a] These atoms were omitted from the calculations of the least-squares planes.

thermal motion have been made. The bond lengths and angles are comparable with values observed in similar structures.[10,11] Bonds C(4) – C(4a) (1.589 Å) and C(4a) – C(8a) (1.560 Å) are significantly longer than the average value, 1.532 Å, of the other C(sp^3) – C(sp^3) bonds in the structure, probably in consequence of internal strain in the molecule. Some of the C(sp^2) – C(sp^3) bond lengths significantly exceed the standard value 1.501 ± 0.004 Å;[12] those of C(2) – C(3), C(3) – C(4), and C(7) – C(8) are 1.524, 1.525, and 1.523 Å, respectively, perhaps because each involves a highly substituted carbon atom. The effect of conjugation is apparent in the C(6) – C(7) bond, 1.471 Å, which is adjacent to double bonds. The two C – Cl bond lengths of 1.801 and 1.809 Å agree with the "normal" value of 1.81 Å given by Gade and Glusker.[13]

The arrangement of the molecules as viewed along the *a* and *c* axis is shown in Figs. 3 and 4, respectively. The molecules are held together in three-dimensional space by van der Waals forces. There are, however, some close intermolecular contacts, a C···Cl distance of 3.393 Å and a Cl···Cl distance of 3.285 Å (Table 6).

Parameters of least-squares planes through selected atoms of the molecule are given in Table 7. The four atoms C(5), C(6), C(7), and C(8a) in the cyclohexene ring are coplanar within ± 0.001 Å. Atoms C(4a) and C(8) deviate by 0.198 and – 0.650 Å from the plane, respectively. Atom C(8) is significantly out of the plane as it is in the dimers of 2,4- and 2,6-dimethyl-*o*-quinol.[10,11] The three rings containing the ethyleno moiety are all boat-shaped. This rather strained three-ring system is connected to the cyclohexene ring in accordance with the endo rule; the angle between the normals to the planes containing atoms C(5), C(6), C(7), and C(8a) and atoms C(4a), C(8a), C(9), and C(10), respectively, is 77.7°.

All hydrogen atoms lie in chemically reasonable positions with apparent bond distances ranging from 0.80 to 1.05 Å, mean value 0.93 Å, in good agreement with values found by Stewart, Davidson and Simpson.[8]

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