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Some compounds along the pathway to unsymmetrically substituted secopentaprismanes

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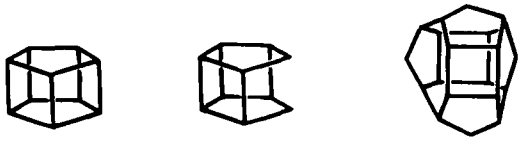
In the preparation of an unsymmetric, polyfunctional [5]-secoprismane hexachlorocyclopentadiene and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene were added sequentially to benzoquinone via Diels-Alder reactions. At one point oxidation of the hydroquinone of the diadduct is necessary, and cerium (IV) ammonium nitrate (CAN) is a common oxidizing agent. Oxidation of the diadduct with CAN led to cleavage of the dimethoxy bridge forming a substituted naphthoquinone. The structures of five Diels-Alder adducts and two reaction products of the naphthoquinone are discussed.

KEY WORDS: Diels-Alder adducts; quinones; norbornenes.

Introduction

Cage compounds such as prismanes and secoprismanes are inherently interesting because of high strain energies, unusual rearrangements, and the potential for practical applications.[1] Polyfunctional [5]-prismanes (**1**) and secoprismanes (**2**) have formed the basis for numerous studies, and recently functionalized **2** has been synthesized via *bis*-norbornenenobenzoquinones (*syn* and *anti*).[1c,d] The $C_{20}H_{24}$ hydrocarbon golcondane (**3**) was synthesized by a similar route.[2] Because of our interest in highly strained cage compounds and their properties, we wished to synthesize unsymmetric polyfunctional [5]-secoprismanes. In this paper we present data on seven intermediate and by-product compounds whose structure were determined during the synthesis of the secoprismane. The starting materials benzoquinone and hexachlorocyclopentadiene, and the reaction scheme is shown below. Compounds **4–9** lie along the normal pathway to [5]-secoprismane; however, compounds **10** and **11** were unexpected oxidation side products while **12** arises from the Diels-Alder addition of dimethylclobutadiene with **10**.



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Experimental

1,4,5a,8a-Tetrahydro-1,2,3,4-tetrachloro-1,4-dichloromethanonaphthalene-4,8-dione (4)

Excess hexachlorocylopentadiene (272 g, 1 mol) was added to a solution of benzoquinone (54 g, 0.5 mol recrystallized from benzene) in 500 mL of dry benzene, and the mixture was refluxed overnight. The solution was concentrated on a rotary evaporator, hexane was added, and the mixture was allowed to crystallize. After filtration the solid was washed with hexane affording 153 g of pure compound **4** (yield 80%), m.p. 174–175°C (lit. 188[3a], 184[3b,c] °C from EtOH): ^{1}H NMR ($CDCl_3$) δ 3.84 (s,2H), 6.75 (s,2H); ^{13}C NMR ($CDCl_3$) δ 53.9 (5a,8a), 60.2 (1,4), 81.7 (CCl_2), 131.3 (2,3),

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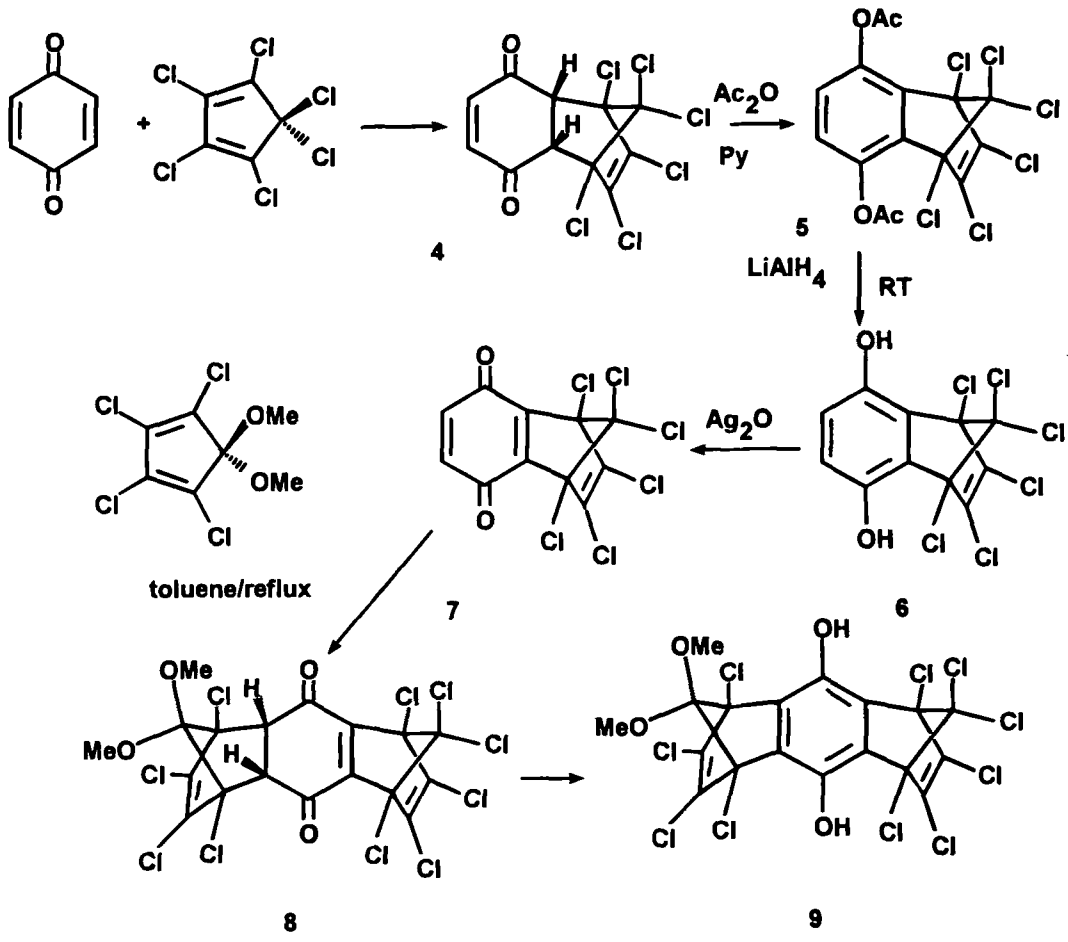


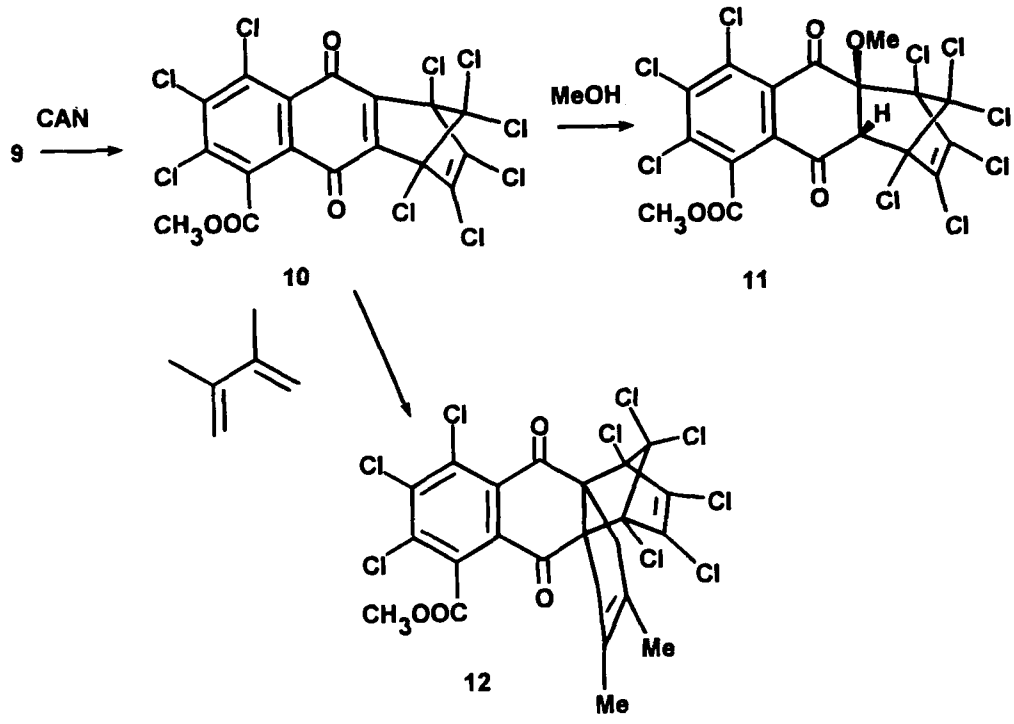
141.6 (6,7), 190.2 (5,8). Anal. Calcd for $C_{11}H_4Cl_6O_2$: C, 35.68; H, 1.08. Found: C, 35.82; H, 1.09.

1,4-Dihydro-5,8-acetoxy-1,2,3,4-tetrachloro-1,4-dichloromethanonaphthalene (5)

To a cooled solution (<20°C) of 60.3 g of **4** (0.157 mol) in 30 mL of pyridine was added dropwise 15 mL of acetic anhydride. After the mixture stood at rt for 7 days it was poured into several times its volume of cold water with vigorous agitation. The crude product was filtered and washed thoroughly with water, dissolved in $CHCl_3$, and washed several times with aqueous sodium hydroxide. After drying over sodium sulfate, the $CHCl_3$ was removed yielding a crystalline solid (65.7% yield). The material was recrystallized from hexane-ethylacetate giving colorless prisms, mp 246.5–247°C: ^{1}H NMR ($CDCl_3$) δ 2.36 (s,6H), 6.97 (s,2H); ^{13}C NMR ($CDCl_3$) δ 20.7 (CH_3), 63.9 (1,4), 82.2 (s), 125.7(S), 132.9(s), 138.4(S), 144.0(s), 169.1(C–O). Anal. Calcd for $C_{15}H_8Cl_6O_4$: C, 38.70; H, 1.72; Cl, 45.80. Found: C, 38.90; H, 1.69; Cl, 45.66.

1,4-Dihydro-1,2,3,4-tetrachloro-1,4-dichloromethanonaphthalene-2,8-diol (6)

To a solution of 5 (16 g, 0.0344 mol) in anhydrous THF (500 mL) was added $LiAlH_4$ (3.1 g, 0.0826 mol) under nitrogen, and the mixture stirred at rt for 4 hrs. The mixture was poured cautiously into 500 mL of 10% sulfuric acid over ice, and the solution was extracted several times with dichloromethane. The dichloromethane extracts were washed with aqueous sodium bicarbonate followed by water. After drying over Na_2SO_4 the solvent was removed yielding a viscous oil which crystallized (with difficulty) from ethyl acetate–hexane as white prisms (7.5 g, 57% yield), m.p. 187–189°C (lit.[3a,b] 184–186°C): ^{1}H NMR ($CDCl_3$) δ 5.93 (s,2H), 6.71 (s,2H); ^{13}C NMR δ 61.9 (1,4), 82.8 (CCl_2), 121.2 (5a,8a), 121.8 (6,7), 137.8 (5,8), 146.5



(2,3). Anal. Calcd. for $C_{11}H_4Cl_6O_2$: C, 35.68; H, 1.08. Found: C, 34.92; H, 1.12.

1,4-Dihydro-1,2,3,4-tetrachloro-1,4-dichloromethanonaphthalene-5,8-dione (7)

A 2.8 g sample of **6** was dissolved in dry benzene and agitated with 9 g of dry, finely divided Ag_2O plus 9 g of Na_2SO_4. The solution turned bright yellow, and after 0.5 hr the mixture was filtered and the solvent evaporated yielding yellow crystals (94% yield). The sample was recrystallized from ethyl acetate, m.p. 117–118°C (lit.[4] 119°C): ^1H NMR ($CDCl_3$) δ 6.75 (s,2H); ^{13}C NMR δ 64.0, 80.9, 136.3, 138.2, 146.8, 179.8. Anal. Calcd. for $C_{11}H_2Cl_6O_2$: C, 34.87; H, 0.53; Cl, 56.15; O, 8.45. Found: C, 367.52; H, 0.48; Cl, 54.62; O, 8.06.

1,4,5a,6,9,9a-Hexahydro-1,2,3,4,6,7,8,9-octachloro-1,4-dichloromethano-7,9-dimethoxymethanoanthracene-5,10-dione (8)

A solution of 7 (7.58 g, 20 mmol) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (7.92 g, 60 mmol) in dry toluene was refluxed overnight. Removal of the solvent under vacuum followed by washing with hexane gave a 91% yield of the *endo,syn*-adduct **8**, m.p. 208°C (dec): ^1H NMR ($CDCl_3$) δ 3.58 (s,3H), 3.65 (s,3H), 3.76 (s,2H); ^{13}C NMR δ 52.3, 53.3, 57.5, 63.0, 82.0, 111.0, 134.3, 138.1, 151.6, 184.9. Anal. Calcd for $C_{18}H_8Cl_{10}O_4$: C, 33.68; H, 1.24. Found: C, 34.46; H, 1.24.

1,4,6,9-Tertrahydro-1,2,3,4,6,7,8,9-octachloro-1,4-dichloromethano-7,9-dimethoxymethanoanthracene-5,10,-diol (9)

Quinone **8** (7 g) was dissolved in 300 mL of methanol, and 10 mL of 10% KOH in methanol was added. The solution became blood red immediately and was allowed to stand at rt for 2 hr. After neutralization with dilute HCl, the addition of water yielded a white precipitate. The material was filtered, dried and recrystallized from dichloromethane-hexane to give 6.8 g of colorless prismatic rods, m.p. 242°C: ^1H NMR ($CDCl_3$) δ 3.52 (s,3H), 3.64 (s,3H), 6.30 (s,2H); ^{13}C NMR δ 53.3, 78.0, 82.1, 112.0, 127.1, 128.8, 136.3, 138.4, 143.0. Anal. Calcd for $C_{18}H_8Cl_{10}O_4$: C, 33.68; H, 1.24; Cl, 55.18. Found: C, 34.63; H, 1.31; Cl, 54.81.

Table 1. Crystal, data collection, and refinement data

Compound	4	5	6	8	9	11	12
Formula	$C_{11}H_4O_2Cl_6$	$C_{15}H_8O_4Cl_6$	$C_{11}H_4O_2Cl_6$	$C_{18}H_8O_4Cl_{10}$	$C_{18}H_8O_4Cl_{10}$	$C_{18}H_7O_5Cl_8$	$C_{23}H_{13}O_4Cl_9$
F.W.	380.87	464.94	380.87	642.79	642.79	622.33	672.43
Color	Yellow	Colorless	Colorless	Yellow	Colorless	Pale yellow	Colorless
Habit	Prismatic	Prismatic	Prismatic	Prismatic	Prismatic	Prismatic	Prismatic
Dimensions (mm)	.20 × .30 × .30	.20 × .15 × .12	.20 × .30 × .20	.30 × .40 × .30	.20 × .20 × .30	.20 × .20 × .40	.20 × .10 × .50
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*C2/c*	*Pnma*	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a(Å)	23.592(3)	7.640(3)	13.065(3)	21.918(7)	11.741(6)	11.538(4)	12.199(8)
b(Å)	17.770(3)	16.164(2)	11.305(2)	12.358(7)	12.628(5)	11.886(4)	7.526(3)
c(Å)	17.393(2)	14.738(2)	18.851(8)	26.68(1)	15.930(8)	9.204(3)	28.13(1)
α(°)	90	90	90	90	90	110.84(2)	90
β(°)	129.938(5)	90	90.95(2)	101.20(3)	93.49(6)	104.20(3)	90.78(4)
γ(°)	90	90	90	90	90	92.96(3)	90
V(Å^3)	5991(1)	1829(1)	2784(3)	7088(10)	2356(3)	1130.1(7)	2582(4)
Z	16	4	8	12	4	2	4
$D_{calc.}$(g-cm^{-3})	1.810	1.696	1.817	1.807	1.812	1.829	1.730
λ(Å)	0.71069	1.54178	0.71069	0.71069	0.71069	0.71069	0.71069
μ(cm^{-1})	12.28	90.12	12.33	12.14	12.17	11.53	10.13
Transmission factors	.87–1.00	0.72–1.00	.90–1.00	.83–1.00	.62–1.00	.87–1.00	.88–1.00
$2\theta_{max}$(°)	55.2	158.0	55.2	55.2	55.1	55.2	55.1
Total reflections	6849	2213	7000	17564	5979	5308	5601
Unique reflections	6688	1875	6751	17140	5710	5068	5336
hkl range	0,30;0,23;−22,23	0,9;0,20;0,18	0,17;0,13;−24,24	0,28;0,15;−34,34	0,12;0,12;−20,20	0,15;−15,15;−11,11	0,13;0,9;−36,36
Observed reflections	3478	1341	3359	6232	2683	3527	2367
R;R_w	0.059;0.048	0.060;0.072	0.067;0.074	0.097;0.087	0.085;0.096	0.059;0.048	0.120;0.109
Parameters	344	119	344	865	290	290	326
$(\Delta/\sigma)_{max}$	0.005	0.005	0.005	0.02	0.007	0.01	0.06
ρ_{min};ρ_{max}	−0,63;0.97	−0.51;0.47	−0.66;0.74	−0.69;0.74	−0.67;0.81	−0.65;0.97	−0.77;0.89

Table 2. Atomic positional parameters and *B*(eq) values for compound **4**

Atom	*x*	*y*	*z*	*B*(eq)
Cl (1)	−0.0794 (1)	0.4077 (1)	0.4817 (1)	5.44 (9)
Cl (2)	−0.0527 (1)	0.4208 (1)	0.3183 (1)	4.92 (8)
Cl (3)	0.0953 (1)	0.3124 (1)	0.3990 (1)	4.99 (9)
Cl (4)	0.15880 (9)	0.2329 (1)	0.6117 (1)	4.81 (8)
Cl (5)	0.1086 (1)	0.4033 (1)	0.6330 (1)	4.68 (8)
Cl (6)	0.0487 (1)	0.2833 (1)	0.6694 (1)	4.85 (8)
O (1)	−0.1858 (2)	0.2869 (3)	0.3081 (4)	6.0 (2)
O (2)	0.0399 (3)	0.1172 (3)	0.4198 (4)	6.7 (3)
C (1)	−0.1283 (3)	0.2576 (4)	0.3362 (5)	3.8 (3)
C (2)	−0.1225 (4)	0.2249 (4)	0.2670 (5)	4.8 (3)
C (3)	−0.0658 (5)	0.1832 (4)	0.2946 (6)	5.0 (4)
C (4)	−0.0021 (4)	0.1663 (4)	0.4008 (6)	4.0 (3)
C (5)	0.0058 (3)	0.2092 (3)	0.4825 (5)	3.1 (2)
C (6)	−0.0613 (3)	0.2590 (4)	0.4470 (4)	2.8 (2)
C (7)	−0.0277 (3)	0.3398 (3)	0.4771 (4)	2.9 (2)
C (8)	−0.0051 (4)	0.3599 (3)	0.4153 (4)	3.4 (3)
C (9)	0.0519 (3)	0.3167 (3)	0.4454 (4)	2.9 (2)
C (10)	0.0692 (3)	0.2685 (3)	0.5301 (4)	2.7 (2)
C (11)	0.0499 (3)	0.3238 (3)	0.5779 (4)	3.0 (2)
Cl (31)	0.4072 (1)	0.6724 (1)	0.6240 (1)	4.53 (8)
Cl (32)	0.2435 (1)	0.6863 (1)	0.4009 (1)	5.58 (9)
Cl (33)	0.1331 (1)	0.5464 (1)	0.3759 (1)	5.29 (9)
Cl (34)	0.2311 (1)	0.4470 (1)	0.5858 (1)	4.67 (8)
Cl (35)	0.2942 (1)	0.6230 (1)	0.6747 (1)	4.08 (7)
Cl (36)	0.4097 (1)	0.5174 (1)	0.7476 (1)	4.87 (8)
O (31)	0.4076 (3)	0.5848 (3)	0.4605 (4)	6.9 (3)
O (32)	0.2380 (3)	0.3665 (3)	0.4246 (4)	6.1 (3)
C (31)	0.3652 (4)	0.5426 (4)	0.4545 (5)	3.9 (3)
C (32)	0.3066 (4)	0.5068 (4)	0.3592 (5)	4.6 (3)
C (33)	0.2643 (4)	0.4516 (4)	0.3496 (5)	4.7 (3)
C (34)	0.2708 (4)	0.4223 (4)	0.4327 (5)	3.7 (3)
C (35)	0.3205 (3)	0.4630 (3)	0.5328 (5)	3.0 (2)
C (36)	0.3701 (3)	0.5270 (3)	0.5439 (4)	3.1 (2)
C (37)	0.3458 (3)	0.5963 (3)	0.5715 (4)	2.7 (2)
C (38)	0.2663 (3)	0.6141 (3)	0.4788 (4)	2.9 (2)
C (39)	0.2249 (3)	0.5602 (4)	0.4701 (4)	3.0 (3)
C (40)	0.2742 (3)	0.5044 (3)	0.5554 (4)	2.8 (2)
C (41)	0.3311 (3)	0.5618 (3)	0.6379 (4)	2.9 (2)

Table 3. Atomic positional parameters and *B*(eq) values for compound **5**

Atom	*x*	*y*	*z*	*B*(eq)
Cl (3)	−0.1949 (3)	0.1439 (1)	−0.0621 (2)	4.0 (1)
Cl (4)	0.1565 (3)	0.0797 (1)	0.0474 (1)	3.26 (8)
Cl (5)	0.0432 (5)	1/4	0.1698 (2)	4.4 (1)
Cl (6)	0.4009 (4)	1/4	0.1135 (2)	3.9 (1)
O (2)	0.3917 (7)	0.0782 (3)	−0.1258 (3)	2.8 (2)
O (2B)	0.167 (1)	0.0529 (4)	−0.2115 (6)	9.9 (5)
C (2A)	0.291 (1)	0.0278 (4)	−0.1725 (6)	3.8 (4)
C (2B)	0.345 (1)	−0.0586 (4)	−0.1674 (6)	4.4 (4)
C (3)	0.458 (1)	0.2077 (4)	−0.1978 (4)	2.5 (3)
C (4)	0.3672 (9)	0.1638 (3)	−0.1324 (4)	2.0 (3)
C (5)	0.2675 (8)	0.2063 (3)	−0.0706 (4)	1.5 (2)
C (9)	−0.0391 (9)	0.2084 (4)	−0.0250 (4)	2.2 (3)
C (10)	0.1434 (9)	0.1796 (3)	0.0058 (4)	1.9 (3)
C (11)	0.181 (1)	1/4	0.0744 (6)	2.1 (4)

*1,4-Dihydro-9-carbomethoxy-1,2,3,4,6,7,8-hexachloro-1,4- dichloromethanoanthracene-5,10-dione (**10**)*

The hydroquinone **9** (500 mg) was dissolved in acetone (20 mL), and 20 mL of 5% cerium(IV) ammonium nitrate (CAN) was added. An off-white precipitate was filtered, washed with water, dissolved in CH_2Cl_2, and dried over Na_2SO_4. Evaporation yielded a yellow crystalline solid in 75% yield, m.p. 229°C: ^{1}H NMR ($CDCl_3$) δ 4.06 (s,3H); ^{13}C NMR δ 53.8, 64.0, 128.0, 129.3, 136.0, 137.6, 138.2, 141.9, 147.8, 165.0, 175.4, 188.3. Anal. Calcd for $C_{17}H_3O_4Cl_9$: C, 34.55; H, 0.51. Found: C, 350.04, H, 0.53.

*1,4,4a,9a-Tetrahydro-9-carbomethoxy-1,2,3,4,6,7,8-heptachloro-4a-methoxy-1,4-dichloromethanoanthracene-5,10-dione (**11**)*

Compound **10** (100 mg) was dissolved in 20 mL of methanol for recrystallization, and after several days 53 mg of compound **11** was recovered (53% yield), m.p. 197°C (dec): 1H NMR ($CDCl_3$) δ 33.7 (s,3H), 4.00 (s,3H), 4.16 (s,1H); ^{13}C NMR δ 53.7, 55.0, 61.2, 80.2, 87.1, 102.4, 132.4, 132.7, 133.1, 134.6, 135.5, 137.9, 142.0, 164.1, 185.4, 187.2. Anal. Calcd for $C_{18}H_7O_5Cl_9$: C, 34.70; H, 1.12. Found: C, 34.82; H, 1.22.

*Diels-Alder adduct (**12**)*

To a solution of quinone **10** (640 mg, 1.08 mmol) in acetone at rt was added with stirring 2,3-dimethyl-1,3-butadiene (400 mg, 8 mmol), and the resulting mixture stirred overnight. The solvent and unreacted 2,3-dimethyl-1,3-butadiene were removed by evaporation giving 720 mg of an off-white solid **12** (yield 99%), m.p. 225°C (dec): ^{1}H NMR ($CDCl_3$) δ 1.49 (s,6H), 2.49 (m,4H), 4.04 (s,3H); ^{13}C NMR δ 18.2, 38.9, 53.5, 59.2, 83.5, 126.4, 127.0, 132.5, 133.0, 134.0, 136.5, 140.2, 165.0, 188.0, 188.5. Anal. Calcd

for $H_{13}O_4Cl_9$: C, 41.04; H, 1.92. Found: C, 41.00; H, 1.76.

X-ray analysis

All data were collected on a Rigaku AFC-6S diffractometer using the θ-2θ mode at a fixed scan rate with multiple scans for weak reflections. Cu $K\alpha$ (λ = 1.54178 Å) was used for compound **5** while Mo $K\alpha$ (λ = 0.71073 Å) was used for the rest. All structures were solved by direct methods[5] and refined and analyzed using TEXSAN[6] and PLATON.[7] Compound **6**

Table 4. Atomic positional parameters and B(eq) values for compound **6**

Atom	x	y	z	B(eq)
Cl (1)	0.7236 (2)	0.1515 (3)	0.1344 (2)	4.8 (2)
Cl (2)	0.5705 (3)	−0.0702 (3)	0.0888 (2)	5.7 (2)
Cl (3)	0.3231 (2)	0.0153 (3)	0.1146 (2)	6.0 (2)
Cl (4)	0.3251 (2)	0.2930 (3)	0.1734 (2)	5.4 (2)
Cl (5)	0.5330 (3)	0.1681 (3)	0.2562 (2)	5.6 (2)
Cl (6)	0.5776 (3)	0.3871 (3)	0.1908 (1)	4.8 (2)
O (1)	0.7208 (5)	0.2641 (6)	−0.0175 (4)	3.7 (4)
O (2)	0.3127 (5)	0.3931 (6)	0.0201 (3)	2.9 (3)
C (1)	0.6190 (7)	0.2899 (8)	−0.0091 (5)	2.5 (5)
C (2)	0.5662 (8)	0.3549 (9)	−0.0584 (5)	2.8 (5)
C (3)	0.4662 (8)	0.3890 (8)	−0.0503 (4)	2.5 (5)
C (4)	0.4126 (7)	0.3567 (8)	0.0125 (5)	2.1 (4)
C (5)	0.4641 (7)	0.2900 (8)	0.0610 (5)	2.3 (4)
C (6)	0.5662 (7)	0.2551 (8)	0.0518 (5)	2.3 (4)
C (7)	0.5947 (7)	0.1769 (8)	0.1147 (5)	2.6 (5)
C (8)	0.5257 (9)	0.0674 (9)	0.1108 (6)	3.8 (6)
C (9)	0.4311 (8)	0.1002 (9)	0.1201 (6)	3.4 (5)
C (10)	0.4323 (8)	0.2338 (9)	0.1318 (5)	3.1 (5)
C (11)	0.5343 (8)	0.2428 (9)	0.1761 (5)	3.1 (5)
Cl (31)	0.7390 (2)	0.6847 (2)	0.1576 (1)	3.5 (1)
Cl (32)	0.8230 (2)	0.8510 (2)	0.0256 (1)	4.0 (1)
Cl (33)	1.0782 (2)	0.9025 (3)	0.0532 (2)	4.6 (2)
Cl (34)	1.1522 (2)	0.7691 (3)	0.2010 (2)	4.4 (2)
Cl (35)	0.9098 (2)	0.8701 (3)	0.2379 (2)	4.6 (2)
Cl (36)	0.9412 (2)	0.6273 (3)	0.2744 (1)	4.4 (2)
O (31)	0.7894 (5)	0.4517 (5)	0.0737 (4)	3.2 (3)
O (32)	1.2050 (5)	0.5481 (6)	0.1146 (4)	3.6 (4)
C (31)	0.8915 (7)	0.4735 (8)	0.0886 (5)	2.3 (5)
C (32)	0.9636 (8)	0.3892 (8)	0.0714 (5)	2.6 (5)
C (33)	1.0669 (8)	0.4139 (9)	0.0814 (5)	2.8 (5)
C (34)	1.1033 (7)	0.5218 (9)	0.1068 (5)	2.5 (5)
C (35)	1.0309 (7)	0.6032 (8)	0.1280 (5)	2.2 (4)
C (36)	0.9266 (7)	0.5797 (8)	0.1172 (5)	2.1 (4)
C (37)	0.8707 (7)	0.6921 (8)	0.1410 (5)	2.5 (5)
C (38)	0.9042 (7)	0.7913 (8)	0.0861 (5)	2.7 (5)
C (39)	1.0017 (8)	0.8097 (8)	0.0985 (5)	2.9 (5)
C (40)	1.0400 (7)	0.7270 (8)	0.1570 (5)	2.4 (4)
C (41)	0.9407 (8)	0.7292 (8)	0.2039 (5)	3.0 (5)

Table 5. Atomic positional parameters and B(eq) values for compound **8**

Atom	x	y	z	B(eq)
Cl (1)	0.8693 (2)	0.5612 (4)	0.1691 (2)	5.8 (2)
Cl (2)	0.7737 (2)	0.4905 (4)	0.2442 (2)	6.4 (3)
Cl (3)	0.6295 (2)	0.4552 (4)	0.1701 (2)	6.3 (3)
Cl (4)	0.6384 (2)	0.4841 (4)	0.0496 (2)	5.3 (2)
Cl (5)	0.7310 (2)	0.6839 (4)	0.1163 (2)	5.2 (2)
Cl (6)	0.7877 (2)	0.5715 (4)	0.0443 (2)	5.9 (2)
Cl (7)	0.9239 (2)	0.0994 (4)	0.1790 (2)	5.2 (2)
Cl (8)	0.8247 (2)	0.2256 (4)	0.2360 (2)	5.8 (2)
Cl (9)	0.6767 (2)	0.1872 (4)	0.1667 (2)	5.6 (2)
Cl (10)	0.6831 (2)	0.0210 (4)	0.0736 (2)	5.5 (2)
O (1)	0.9096 (4)	0.3440 (9)	0.1313 (4)	5.0 (6)
O (2)	0.6852 (5)	0.265 (1)	0.0239 (4)	6.1 (7)
O (3)	0.8409 (5)	−0.0168 (8)	0.0852 (4)	3.9 (5)
O (4)	0.7954 (5)	−0.0632 (9)	0.1520 (4)	4.1 (5)
C (1)	0.8562 (6)	0.313 (1)	0.1185 (5)	3.1 (7)
C (2)	0.8421 (6)	0.200 (1)	0.1008 (5)	2.9 (7)
C (3)	0.7747 (7)	0.177 (1)	0.0699 (5)	3.3 (7)
C (4)	0.7315 (7)	0.271 (1)	0.0573 (6)	3.5 (8)
C (5)	0.7458 (6)	0.365 (1)	0.0899 (5)	2.6 (7)
C (6)	0.8023 (6)	0.382 (1)	0.1180 (5)	2.6 (7)
C (7)	0.8012 (6)	0.498 (1)	0.1424 (6)	3.9 (8)
C (8)	0.7538 (7)	0.479 (1)	0.1796 (5)	4.4 (8)
C (9)	0.6983 (6)	0.468 (1)	0.1530 (6)	4.1 (8)
C (10)	0.7060 (7)	0.465 (1)	0.0950 (5)	3.6 (7)
C (11)	0.7561 (7)	0.554 (1)	0.0999 (5)	3.7 (8)
C (12)	0.8472 (6)	0.116 (1)	0.1484 (5)	3.0 (7)
C (13)	0.8023 (7)	0.160 (1)	0.1794 (6)	3.4 (7)
C (14)	0.7457 (7)	0.143 (1)	0.1534 (6)	3.6 (8)
C (15)	0.7509 (7)	0.088 (1)	0.1025 (5)	3.9 (8)
C (16)	0.8102 (6)	0.019 (1)	0.1203 (6)	3.4 (7)
C (21)	0.8141 (9)	−0.100 (1)	0.0507 (7)	7 (1)
C (22)	0.8437 (8)	−0.129 (1)	0.1789 (6)	6 (1)
Cl (31)	0.5250 (2)	0.2576 (4)	0.0704 (2)	5.8 (2)
Cl (32)	0.5193 (2)	0.2583 (4)	0.1931 (2)	5.8 (2)
Cl (33)	0.3683 (2)	0.2116 (4)	0.2041 (2)	5.9 (2)
Cl (34)	0.2823 (2)	0.1846 (4)	0.0900 (2)	5.0 (2)
Cl (35)	0.3852 (2)	0.3834 (4)	0.0754 (2)	5.8 (3)
Cl (36)	0.3762 (2)	0.2177 (4)	−0.0004 (2)	5.7 (2)
Cl (37)	0.5874 (2)	−0.1943 (4)	0.1238 (2)	6.0 (3)
Cl (38)	0.5449 (2)	−0.0262 (4)	0.2038 (2)	7.2 (3)
Cl (39)	0.3950 (2)	−0.0774 (4)	0.2129 (2)	6.8 (3)
Cl (40)	0.3431 (2)	−0.2828 (4)	0.1368 (2)	6.1 (3)
O (31)	0.5367 (5)	0.015 (1)	0.0518 (4)	5.3 (6)
O (32)	0.3036 (5)	−0.059 (1)	0.0759 (5)	6.4 (7)
O (33)	0.4526 (5)	−0.343 (1)	0.0829 (4)	4.7 (6)
O (34)	0.4991 (5)	−0.335 (1)	0.1688 (4)	5.4 (6)
C (31)	0.4894 (7)	−0.007 (1)	0.0671 (6)	3.8 (8)
C (32)	0.4703 (6)	−0.123 (1)	0.0732 (5)	3.3 (7)
C (33)	0.4007 (6)	−0.145 (1)	0.0788 (5)	3.0 (7)
C (34)	0.3595 (7)	−0.049 (1)	0.0807 (5)	3.3 (7)
C (35)	0.3882 (6)	0.058 (1)	0.0856 (5)	3.4 (7)
C (36)	0.4500 (7)	0.081 (1)	0.0822 (5)	3.8 (8)
C (37)	0.4622 (7)	0.200 (1)	0.0906 (5)	3.8 (8)
C (38)	0.4585 (7)	0.218 (1)	0.1475 (7)	5 (1)
C (39)	0.4000 (7)	0.201 (1)	0.1521 (5)	4.3 (8)
C (40)	0.3640 (6)	0.171 (1)	0.0996 (5)	3.2 (7)

Table 5. Continued.

Atom	*x*	*y*	*z*	*B*(eq)
C (41)	0.3963 (7)	0.248 (1)	0.0645 (5)	3.7 (8)
C (42)	0.5075 (6)	−0.178 (1)	0.1215 (6)	3.8 (8)
C (43)	0.4958 (7)	−0.113 (1)	0.1678 (5)	4.3 (8)
C (44)	0.4365 (8)	−0.133 (1)	0.1710 (5)	4.3 (8)
C (45)	0.4097 (6)	−0.210 (1)	0.1293 (6)	3.6 (8)
C (46)	0.4688 (7)	−0.280 (1)	0.1280 (7)	4.0 (8)
C (51)	0.5015 (8)	−0.407 (2)	0.0684 (7)	6 (1)
C (52)	0.4696 (9)	−0.420 (2)	0.1885 (8)	8 (1)
Cl (61)	0.0702 (2)	−0.3192 (4)	−0.0136 (1)	6.5 (3)
Cl (62)	−0.0359 (2)	−0.3504 (4)	0.0562 (2)	6.9 (3)
Cl (63)	0.0351 (2)	−0.4312 (4)	0.1753 (2)	6.4 (3)
Cl (64)	0.1862 (2)	−0.4437 (4)	0.1803 (2)	6.2 (3)
Cl (65)	0.1212 (2)	−0.5410 (4)	0.0608 (2)	6.6 (3)
Cl (66)	0.2154 (2)	−0.3822 (4)	0.0600 (2)	6.7 (3)
Cl (67)	0.0765 (2)	0.1407 (4)	0.0494 (1)	5.2 (2)
Cl (68)	−0.0158 (2)	−0.0551 (4)	0.0736 (2)	5.7 (2)
Cl (69)	0.0345 (2)	−0.1460 (4)	0.1949 (2)	5.3 (2)
Cl (70)	0.1557 (2)	−0.0014 (4)	0.2493 (1)	4.9 (2)
O (61)	0.1292 (5)	−0.094 (1)	0.0134 (4)	5.8 (6)
O (62)	0.2190 (5)	−0.207 (1)	0.2032 (4)	6.1 (7)
O (63)	0.1732 (4)	0.1691 (8)	0.1524 (4)	4.0 (5)
O (64)	0.0779 (4)	0.1639 (9)	0.1774 (4)	4.0 (5)
C (61)	0.1355 (7)	−0.113 (1)	0.0592 (6)	4.1 (8)
C (62)	0.1548 (6)	−0.023 (1)	0.0975 (5)	3.5 (7)
C (63)	0.1801 (6)	−0.057 (1)	0.1545 (5)	2.9 (7)
C (64)	0.1860 (7)	−0.175 (1)	0.1647 (6)	3.7 (8)
C (65)	0.1509 (6)	−0.248 (1)	0.1265 (5)	3.0 (7)
C (66)	0.1241 (6)	−0.217 (1)	0.0788 (5)	3.4 (8)
C (67)	0.0932 (7)	−0.317 (2)	0.0535 (5)	4.8 (9)
C (68)	0.0412 (7)	−0.354 (1)	0.0825 (7)	4.6 (9)
C (69)	0.0693 (7)	−0.381 (1)	0.1277 (6)	4.3 (8)
C (70)	0.1395 (7)	−0.367 (1)	0.1323 (6)	4.1 (8)
C (71)	0.1416 (8)	−0.402 (2)	0.0744 (7)	5 (1)
C (72)	0.0980 (7)	0.057 (1)	0.1015 (5)	3.8 (7)
C (73)	0.0491 (6)	−0.021 (1)	0.1159 (6)	4.2 (8)
C (74)	0.0683 (7)	−0.053 (1)	0.1618 (6)	3.6 (8)
C (75)	0.1315 (6)	−0.001 (1)	0.1815 (5)	3.7 (8)
C (76)	0.1221 (6)	0.107 (1)	0.1550 (5)	3.4 (8)
C (81)	0.2025 (7)	0.226 (1)	0.1962 (6)	6 (1)
C (82)	0.0567 (8)	0.266 (1)	0.1561 (7)	6 (1)

contains three independent molecules per cell, but no added symmetry, expanded lattice or cell reduction could be found. Table 1 contains crystal, data collection and refinement data on the seven structures reported. Tables 2–8 report atomic positional parameters while Table 9 and 10 contain selected bond distances and Tables 11 and 12 selected valence angles.

Discussion

A drawing of one of the independent molecules of **4** is shown in Fig. 1 The six-membered diketone

Table 6. Atomic positional parameters and *B*(eq) values for compound **9**

Atom	*x*	*y*	*z*	*B*(eq)
Cl (1)	0.0497 (3)	0.1304 (3)	0.6426 (3)	3.6 (2)
Cl (2)	0.0499 (4)	0.1151 (4)	0.4357 (3)	4.7 (2)
Cl (3)	0.1712 (4)	0.3443 (4)	0.3649 (2)	4.8 (2)
Cl (4)	0.2398 (3)	0.4974 (3)	0.5270 (3)	3.3 (2)
Cl (5)	−0.0106 (3)	0.3842 (4)	0.5785 (3)	4.2 (2)
Cl (6)	0.1684 (3)	0.3719 (3)	0.7096 (2)	3.7 (2)
Cl (7)	0.5267 (3)	−0.0334 (3)	0.7507 (3)	4.0 (2)
Cl (8)	0.6322 (4)	−0.0767 (4)	0.5712 (3)	5.5 (3)
Cl (9)	0.7539 (4)	0.1506 (4)	0.5023 (3)	5.6 (3)
Cl (10)	0.7094 (3)	0.3434 (3)	0.6385 (3)	3.9 (2)
O (1)	0.2883 (8)	0.0296 (8)	0.6742 (6)	3.7 (5)
O (2)	0.4778 (7)	0.4010 (7)	0.5458 (6)	2.9 (5)
O (3)	0.5857 (8)	0.2352 (8)	0.7805 (6)	3.2 (5)
O (4)	0.7319 (8)	0.1210 (8)	0.7604 (6)	3.3 (5)
C (1)	0.338 (1)	0.121 (1)	0.6473 (8)	2.6 (7)
C (2)	0.454 (1)	0.141 (1)	0.6507 (8)	2.2 (6)
C (3)	0.504 (1)	0.235 (1)	0.6205 (8)	2.0 (6)
C (4)	0.435 (1)	0.312 (1)	0.5807 (8)	2.1 (6)
C (5)	0.318 (1)	0.294 (1)	0.5773 (8)	2.1 (6)
C (6)	0.270 (1)	0.202 (1)	0.6092 (9)	2.4 (6)
C (7)	0.138 (1)	0.211 (1)	0.5892 (9)	2.5 (7)
C (8)	0.118 (1)	0.215 (1)	0.4909 (9)	2.6 (7)
C (9)	0.161 (1)	0.302 (1)	0.4646 (9)	2.6 (7)
C (10)	0.216 (1)	0.361 (1)	0.5385 (9)	2.4 (6)
C (11)	0.128 (1)	0.335 (1)	0.6057 (8)	2.3 (6)
C (12)	0.557 (1)	0.074 (1)	0.686 (1)	3.3 (7)
C (13)	0.629 (1)	0.049 (1)	0.613 (1)	3.8 (8)
C (14)	0.675 (1)	0.137 (1)	0.588 (1)	3.6 (8)
C (15)	0.633 (1)	0.225 (1)	0.6397 (9)	2.5 (7)
C (16)	0.632 (1)	0.169 (1)	0.731 (1)	2.7 (7)
C (21)	0.548 (1)	0.193 (1)	0.8595 (9)	3.9 (8)

rings are folded along a C(1)···C(4) axis forming a flattened boat conformation[8] with the two oxygen atoms lying on the same side of the mean plane. The cyclohexene rings and the five-membered rings are almost ideal boat[8] and envelope[9] conformations, respectively. Compound **5** is shown in Fig. 2. The molecule is bisected by a mirror plane with the dichloromethano group lying in the plane. The phenyl ring is planar while the cyclohexene and five-membered rings are again in boat and envelope conformations. The ester groups are in extended conformations with the oxygen atoms lying on the opposite side of the ring from the methano chlorine. One of the two independent molecules of compound **6** is shown in Fig. 3. Both molecules exhibit conformations identical to that of compound **5**. The molecules form an array of intermolecular hydrogen bonds.

A drawing of one of the independent molecules of **8** is shown in Fig. 4. The six-membered diketone

Table 7. Atomic positional parameters and B(eq) values for compound **11**

Atom	x	y	z	B(eq)
Cl (1)	0.3356 (1)	1.0032 (1)	0.4794 (2)	4.63 (5)
Cl (2)	0.4955 (1)	1.2771 (1)	0.6119 (1)	4.71 (4)
Cl (3)	0.4196 (1)	1.3915 (1)	0.3148 (1)	4.19 (4)
Cl (4)	0.2208 (1)	1.1889 (1)	−0.0001 (1)	4.83 (5)
Cl (5)	0.4124 (1)	1.0159 (1)	0.1472 (2)	5.47 (5)
Cl (6)	0.1630 (1)	0.9309 (1)	0.0789 (1)	3.96 (4)
Cl (7)	0.3367 (1)	1.4290 (1)	0.9109 (1)	5.23 (5)
Cl (8)	0.3790 (1)	1.6965 (1)	0.9501 (2)	5.36 (5)
Cl (9)	0.2831 (1)	1.7726 (1)	0.6617 (2)	5.50 (5)
O (1)	0.1796 (3)	1.2158 (3)	0.6764 (3)	4.3 (1)
O (2)	0.0269 (3)	1.3478 (3)	0.2115 (4)	5.7 (1)
O (3)	0.0418 (5)	1.6317 (4)	0.3605 (7)	10.0 (2)
O (4)	0.1877 (5)	1.5722 (5)	0.2565 (6)	9.3 (3)
O (5)	0.0867 (2)	1.0485 (2)	0.3780 (3)	2.8 (1)
C (1)	0.1874 (3)	1.2485 (3)	0.5702 (5)	2.6 (1)
C (2)	0.2178 (4)	1.3786 (4)	0.5956 (5)	2.7 (1)
C (3)	0.1731 (4)	1.4143 (4)	0.4637 (5)	3.0 (1)
C (4)	0.1028 (4)	1.3220 (4)	0.3045 (5)	3.0 (1)
C (5)	0.1341 (4)	1.1946 (3)	0.2573 (4)	2.6 (1)
C (6)	0.1683 (3)	1.1484 (3)	0.3992 (4)	2.4 (1)
C (7)	0.2929 (4)	1.1048 (4)	0.3852 (5)	2.9 (1)
C (8)	0.3851 (4)	1.2162 (4)	0.4345 (5)	3.4 (1)
C (9)	0.3573 (4)	1.2614 (4)	0.3205 (5)	3.5 (1)
C (10)	0.2455 (4)	1.1793 (3)	0.1903 (4)	3.0 (1)
C (11)	0.2773 (4)	1.0570 (4)	0.2001 (5)	3.1 (1)
C (12)	0.2800 (4)	1.4667 (4)	0.7463 (5)	3.1 (1)
C (13)	0.2996 (4)	1.5880 (4)	0.7659 (5)	3.4 (1)
C (14)	0.2534 (4)	1.6221 (4)	0.6349 (6)	3.4 (2)
C (15)	0.1884 (4)	1.5378 (4)	0.4869 (6)	3.5 (2)
C (16)	0.1338 (7)	1.5814 (6)	0.357 (1)	7.5 (3)
C (21)	0.116 (1)	1.649 (1)	0.160 (1)	14.9 (6)
C (22)	−0.0344 (4)	1.0713 (4)	0.3695 (5)	3.6 (2)

Table 8. Atomic positional parameters and B(eq) values for compound **12**

Atom	x	y	z	B(eq)
Cl (1)	0.3131 (8)	0.4297 (7)	0.1085 (2)	4.7 (4)
Cl (2)	0.3795 (8)	0.6480 (8)	0.0045 (2)	4.8 (4)
Cl (3)	0.0869 (9)	0.691 (1)	0.1525 (2)	5.2 (5)
Cl (4)	0.1337 (9)	0.5124 (9)	0.0458 (2)	5.3 (5)
Cl (5)	0.233 (1)	1.0039 (9)	−0.0084 (2)	5.8 (5)
Cl (6)	0.053 (1)	1.027 (1)	0.0839 (3)	5.9 (5)
Cl (7)	0.663 (1)	0.672 (1)	0.3073 (2)	6.8 (6)
Cl (8)	0.420 (1)	0.742 (1)	0.2884 (2)	6.2 (5)
Cl (9)	0.825 (1)	0.659 (1)	0.2227 (3)	6.7 (6)
O (1)	0.552 (3)	0.647 (3)	0.0760 (8)	9 (2)
O (2)	0.764 (2)	0.515 (2)	0.1211 (6)	5 (1)
O (3)	0.765 (3)	0.811 (3)	0.1050 (7)	8 (2)
O (4)	0.285 (2)	0.636 (2)	0.2075 (5)	4 (1)
C (1)	0.251 (3)	0.606 (3)	0.0774 (8)	5 (2)
C (2)	0.197 (3)	0.755 (3)	0.117 (1)	6 (2)
C (3)	0.305 (3)	0.819 (3)	0.1388 (7)	3 (1)
C (4)	0.388 (3)	0.811 (3)	0.0975 (7)	3 (1)
C (5)	0.319 (3)	0.737 (3)	0.0533 (8)	3 (1)
C (6)	0.437 (3)	1.004 (3)	0.84 (1)	7 (2)
C (7)	0.472 (3)	1.103 (3)	0.1304 (8)	4 (2)
C (8)	0.404 (3)	1.099 (3)	0.165 (1)	3 (2)
C (9)	0.295 (3)	1.014 (3)	0.1600 (7)	3 (1)
C (10)	0.422 (3)	1.207 (3)	0.2118 (8)	4 (2)
C (11)	0.586 (4)	1.190 (3)	0.126 (1)	6 (2)
C (12)	0.346 (3)	0.710 (3)	0.1822 (8)	3 (1)
C (13)	0.498 (3)	0.708 (3)	0.105 (1)	4 (2)
C (14)	0.540 (3)	0.700 (3)	0.157 (1)	3 (1)
C (15)	0.465 (3)	0.714 (3)	0.1933 (8)	3 (1)
C (16)	0.507 (3)	0.709 (3)	0.2408 (8)	3 (1)
C (17)	0.612 (3)	0.688 (3)	0.2501 (8)	3 (2)
C (18)	0.692 (3)	0.673 (3)	0.2119 (8)	3 (1)
C (19)	0.651 (3)	0.685 (3)	0.1635 (9)	4 (2)
C (20)	0.729 (4)	0.676 (4)	0.1238 (8)	6 (2)
C (21)	0.848 (4)	0.493 (4)	0.0836 (9)	8 (2)
C (22)	0.231 (3)	0.879 (3)	0.0426 (8)	3 (1)
C (23)	0.169 (3)	0.891 (3)	0.0790 (9)	4 (2)

rings are again folded along a C(1)···C(4) axis resulting in a boat conformation for the three independent molecules. The cyclohexene and cyclohexadiene rings are in ideal boat conformations while the five-membered rings exhibit envelope conformations. The three independent molecules are identical except for small differences in the methoxy group orientations. A drawing of compound **9** is shown in Fig. 5. The hydroquinone moiety is planar with the two hydrogen atoms intramolecularly interacting with two chlorine atoms (O(2)···Cl(10) = 3.09(1) Å, O(2)−H(2)···Cl(10) = 145(1)°; O(1)···Cl(2) = 3.09(1) Å, O(1)−H(1)···Cl(2) = 109(1)°). The conformations of the other six- and five-membered rings are the same as in the other compounds.

Figure 6 is a thermal ellipsoid drawing of compound **11**. The six-membered diketone ring is folded along the C(1)··C(4) axis while the attached phenyl ring is planar with the ester in an extended conformation. The double bond of the norbornene moiety is folded back under the cyclohexenedione ring with the separation of the two π-bonds C(2)−C(3) and C(8)−C(9) being less than 3.5 Å. The conformation of the norbornene group is the same as in the previous compounds. Surprisingly, the methoxy group has added stereospecifically at C(6). Any C(5) isomer must be less than the C(13) sensitivity.

Figure 7 is a drawing of compound **12**. Unlike **11** where the addition of the methoxy was from the side of the dichloromethano bridge, the Diels-Alder adduct with 2,3-dimethylcyclobutadiene is formed via

Table 9. Interatomic distances for compounds 4, 5, 6, 8, and 9[a]

	4a	4b	5	6	8	9
C(1)–O(1)	1.225(7)	1.201(7)	1.399(7)	1.38(1)	1.22(2)	1.37(2)
C(1)–C(2)	1.421(9)	1.456(9)	1.383(9)	1.37(1)	1.51(2)	1.39(2)
C(1)–C(6)	1.517(8)	1.509(8)	1.372(8)	1.40(1)	1.46(2)	1.42(2)
C(2)–C(3)	1.32(1)	1.330(9)	1.383(9)	1.38(1)	1.57(2)	1.43(2)
C(2)–C(12)	—	—	—	—	1.59(4)	1.54(1)
C(3)–C(4)	1.48(1)	1.450(9)	—	1.41(2)	1.49(2)	1.38(2)
C(3)–C(15)	—	—	—	—	1.56(2)	1.53(2)
C(4)–O(2)	1.198(7)	1.209(7)	—	1.38(1)	1.21(2)	1.37(1)
C(4)–C(5)	1.515(9)	1.519(8)	1.37(1)	1.46(2)	1.39(2)	
C(5)–C(6)	1.554(8)	1.551(8)	1.41(1)	1.40(1)	1.36(3)	1.40(2)
C(5)–C(10)	1.568(8)	1.563(7)	—	1.52(2)	1.53(3)	1.56(2)
C(6)–C(7)	1.559(8)	1.559(8)	1.534(8)	1.53(1)	1.53(3)	1.56(2)
C(7)–C(8)	1.517(8)	1.528(7)	1.539(9)	1.56(3)	1.57(2)	1.57(2)
C(7)–C(11)	1.544(7)	1.532(7)	1.548(8)	1.57(3)	1.55(3)	1.60(2)
C(8)–C(9)	1.331(8)	1.307(8)	1.34(1)	1.30(1)	1.30(2)	1.29(2)
C(9)–C(10)	1.518(8)	1.523(8)	—	1.53(1)	1.54(3)	1.50(2)
C(10)–C(11)	1.533(8)	1.557(8)	—	1.58(1)	1.58(3)	1.57(2)
C(7)–Cl(1)	1.755(6)	1.748(6)	1.730(6)	1.75(1)	1.73(2)	1.72(1)
C(8)–Cl(2)	1.687(6)	1.683(6)	1.675(6)	1.70(1)	1.70(1)	1.71(1)
C(9)–Cl(3)	1.661(9)	1.697(6)	—	1.70(1)	1.69(2)	1.69(1)
C(10)–Cl(4)	1.741(5)	1.746(6)	—	1.74(1)	1.76(1)	1.76(1)
C(11)–Cl(5)	1.769(6)	1.749(6)	1.76(1)	1.75(2)	1.76(3)	1.76(1)
C(11)–Cl(6)	1.763(6)	1.778(6)	1.78(1)	1.76(1)	1.75(1)	1.75(1)
C(12)–C(13)	—	—	—	—	1.53(1)	1.52(2)
C(12)–C(16)	—	—	—	—	1.55(2)	1.63(2)
C(13)–C(14)	—	—	—	—	1.31(3)	1.30(2)
C(14)–C(15)	—	—	—	—	1.52(2)	1.50(2)
C(15)–C(16)	—	—	—	—	1.54(3)	1.62(2)
C(12)–Cl(17)	—	—	—	—	1.74(1)	1.76(1)
C(13)–Cl(8)	—	—	—	—	1.69(1)	1.72(1)
C(14)–Cl(9)	—	—	—	—	1.71(1)	1.71(2)
C(15)–Cl(10)	—	—	—	—	1.76(2)	1.74(1)
C(16)–O(3)	—	—	—	—	1.37(3)	1.29(2)
C(16)–O(4)	—	—	—	—	1.39(3)	1.37(1)

[a] Values for **6** and **8** have been averaged.

Table 10. Interatomic distances for compounds **11** and **12**

	11	12
C(1)–O(1)	1.194(4)	1.20(2)
C(1)–C(2)	1.489(5)	1.50(2)
C(1)–C(6)	1.553(5)	1.54(2)
C(2)–C(3)	1.415(5)	1.38(2)
C(2)–C(12)	1.391(5)	1.41(4)
C(3)–C(4)	1.480(6)	1.50(2)
C(3)–C(15)	1.402(5)	1.40(2)
C(4)–O(2)	1.200(4)	1.16(2)
C(4)–C(5)	1.509(6)	1.56(2)
C(5)–C(6)	1.563(5)	1.60(2)
C(5)–C(10)	1.549(6)	1.55(2)
C(5)–C(17)	—	1.58(2)
C(6)–C(7)	1.571(6)	1.53(2)
C(6)–O(5)	1.401(4)	—
O(5)–C(22)	1.425(5)	—
C(6)–C(20)	—	1.59(2)
C(7)–C(8)	1.512(5)	1.52(2)
C(7)–C(11)	1.552(6)	1.60(2)
C(8)–C(9)	1.322(6)	1.28(3)
C(9)–C(10)	1.527(5)	1.58(2)
C(10)–C(11)	1.546(6)	1.56(2)
C(7)–Cl(1)	1.746(6)	1.75(2)
C(8)–Cl(2)	1.690(4)	1.69(2)
C(9)–Cl(3)	1.695(4)	1.73(1)
C(10)–Cl(4)	1.756(4)	1.74(1)
C(11)–Cl(5)	1.781(4)	1.79(2)
C(11)–Cl(6)	1.765(4)	1.78(1)
C(12)–C(13)	1.387(6)	1.32(2)
C(13)–C(14)	1.399(6)	1.48(3)
C(14)–C(15)	1.368(6)	1.41(2)
C(15)–C(16)	1.485(7)	1.49(2)
C(17)–C(18)	—	1.53(2)
C(18)–C(19)	—	1.30(2)
C(19)–C(20)	—	1.48(2)
C(12)–Cl(7)	1.718(4)	1.75(1)
C(13)–Cl(8)	1.714(4)	1.72(1)
C(14)–Cl(9)	1.720(4)	1.63(2)
C(16)–O(3)	1.247(9)	1.19(2)
C(16)–O(4)	1.21(1)	1.35(2)

addition from the side opposite the hindering dichloromethano bridge. The resulting cyclohexene ring is in a boat conformation with the C(18)–C(19) double bond now opposite the C(2)–C(3) π-system.

In general, the cyclohexenedione and quinone (cyclohexadienedione) rings prefer to be planar; however, a slight folding along the C(1)··C(4) axis is not energetically unfavorable due to a broad potential energy minimum. If intramolecular steric interactions are relieved by this small change in conformation, the molecule readily folds.

Table 11. Selected valence angles for compounds **4**, **5**, **6**, **8**, and **9**[a]

	4a	4b	5	6	8	9
C(2)C(1)C(6)	119.7(6)	118.7(6)	—	117.5(9)	117(1)	114(1)
C(2)C(1)O(1)	121.4(6)	120.1(7)	—	120.2(9)	121(1)	125(1)
C(6)C(1)O(1)	119.0(6)	121.6(6)	—	122.2(9)	122(1)	121(1)
C(1)C(2)C(3)	123.2(7)	123.6(7)	—	121(2)	117(1)	124(1)
C(2)C(3)C(4)	123.0(7)	123.2(7)	120.8(4)	122(2)	117(1)	120(1)
C(3)C(4)C(5)	118.9(6)	118.8(6)	119.0(5)	117.0(9)	117(1)	117(1)
C(3)C(4)O(2)	119.2(7)	121.9(7)	119.3(6)	121(2)	121(1)	123(1)
C(5)C(4)O(2)	121.8(7)	119.3(6)	121.5(6)	122(2)	122(1)	120(1)
C(4)C(5)C(6)	115.7(5)	117.3(5)	120.0(3)	121(1)	124(2)	123(1)
C(1)C(6)C(5)	117.4(5)	116.9(5)	—	121(1)	122(2)	122(1)
C(4)C(5)C(10)	109.6(5)	111.2(5)	133.7(5)	132.4(9)	130(3)	132(1)
C(6)C(5)C(10)	102.2(4)	102.5(5)	106.3(3)	106(1)	106(3)	106(1)
C(1)C(6)C(7)	109.4(5)	111.9(5)	—	132.7(9)	130(2)	131(1)
C(5)C(6)C(7)	102.8(4)	102.8(5)	—	106.1(9)	108(2)	107(1)
C(6)C(7)C(8)	108.3(5)	106.4(5)	—	106(1)	105(3)	107(1)
C(6)C(7)C(11)	100.9(8)	102.8(5)	—	100.0(7)	100(1)	97(1)
C(6)C(7)Cl(1)	115.4(4)	155.3(4)	—	119.0(7)	119(1)	119(1)
C(8)C(7)C(11)	98.6(5)	99.2(4)	—	97.4(8)	98(1)	97(1)
C(7)C(8)C(9)	108.1(5)	106.9(5)	—	107(1)	107(1)	109(1)
C(7)C(8)Cl(2)	123.3(5)	123.3(5)	—	122.9(8)	123(1)	121(1)
C(8)C(9)C(10)	106.3(5)	108.5(5)	107.6(3)	108(1)	108(2)	109(1)
C(8)C(9)Cl(3)	128.2(5)	127.9(5)	128.5(2)	127.1(9)	129(3)	129(1)
C(5)C(10)C(9)	107.3(5)	106.4(5)	105.5(5)	106.6(8)	107(1)	109(1)
C(5)C(10)C(11)	101.7(5)	102.3(4)	99.2(5)	100(1)	100(1)	98(1)
C(5)C(10)Cl(4)	115.8(4)	116.0(4)	119.1(4)	118.3(9)	118(3)	117(1)
C(9)C(10)C(11)	100.2(4)	98.0(5)	97.9(5)	98.0(7)	98(3)	99(1)
C(7)C(11)C(10)	92.9(4)	92.6(4)	94.6(6)	92(1)	92(3)	92(1)
C(7)C(11)Cl(5)	114.4(4)	115.7(4)	114.4(5)	114(1)	116(1)	113(1)
C(7)C(11)Cl(6)	114.0(4)	113.7(4)	112.7(5)	113.1(7)	114(2)	113(1)
C(1)C(2)C(12)					112(1)	131(1)
C(3)C(2)C(12)					102(1)	105(1)
C(4)C(3)C(15)					113(2)	133(1)
C(2)C(3)C(15)					102(1)	106(1)
C(2)C(12)C(13)					105(2)	107(1)
C(2)C(12)C(16)					101(2)	98(1)
C(2)C(12)Cl(7)					114(3)	117(1)
C(13)C(12)C(16)					100(1)	100(1)
C(12)C(13)C(14)					107(1)	109(1)
C(12)C(13)Cl(8)					124(2)	121(1)
C(13)C(14)C(15)					108(1)	108(1)
C(13)C(14)Cl(9)					128(1)	126(1)
C(3)C(15)C(14)					106(1)	108(1)
C(3)C(15)C(16)					103(1)	99(1)
C(3)C(15)Cl(10)					114(2)	116(1)
C(14)C(15)C(16)					100(1)	101(1)
C(12)C(16)C(15)					93(1)	88(1)
C(12)C(16)O(3)					108(1)	120(1)
C(12)C(16)O(4)					115(1)	104(1)
O(3)C(16)O(4)					113(2)	118(1)

[a] Averaged values for **6** and **8** are reported.

Table 12. Selected valence angles for compound **11** and **12**

	11	**12**
C(2)C(1)C(6)	119.4(3)	116(1)
C(2)C(1)O(1)	123.2(4)	120(1)
C(6)C(1)O(1)	117.4(3)	123(2)
C(1)C(2)C(3)	118.1(3)	119(1)
C(2)C(3)C(4)	119.8(3)	122(2)
C(3)C(4)C(5)	117.9(3)	116(1)
C(3)C(4)O(2)	121.7(4)	120(2)
C(5)C(4)O(2)	120.3(4)	124(1)
C(4)C(5)C(6)	114.9(3)	116(1)
C(1)C(6)C(5)	114.4(3)	113(1)
C(4)C(5)C(10)	113.7(3)	114(1)
C(6)C(5)C(10)	103.0(3)	105(1)
C(1)C(6)C(7)	108.8(3)	115(1)
C(5)C(6)C(7)	101.8(3)	103(1)
C(6)C(7)C(8)	108.0(3)	107(1)
C(6)C(7)C(11)	103.0(3)	101(1)
C(6)C(7)Cl(1)	114.6(3)	119(1)
C(8)C(7)C(11)	97.7(3)	97(1)
C(7)C(8)C(9)	107.6(3)	109(2)
C(7)C(8)Cl(2)	125.3(3)	124(1)
C(8)C(9)C(10)	107.4(3)	111(1)
C(8)C(9)Cl(3)	129.7(3)	130(1)
C(5)C(10)C(9)	109.7(3)	105(1)
C(5)C(10)C(11)	101.9(3)	100(1)
C(5)C(10)Cl(4)	114.1(3)	123(1)
C(9)C(10)C(11)	97.5(3)	94(2)
C(7)C(11)C(10)	92.4(3)	96(1)
C(7)C(11)Cl(5)	113.5(3)	111(1)
C(7)C(11)Cl(6)	116.0(3)	114(1)
C(1)C(2)C(12)	122.3(3)	123(1)
C(3)C(2)C(12)	119.4(4)	118(2)
C(2)C(3)C(15)	119.9(4)	122(1)
C(4)C(3)C(15)	120.1(4)	116(2)
C(2)C(12)C(13)	120.1(4)	122(1)
C(2)C(12)Cl(7)	121.6(3)	120(1)
C(12)C(13)C(14)	119.8(4)	122(1)
C(12)C(13)Cl(8)	120.4(4)	122(1)
C(13)C(14)C(15)	121.2(4)	115(2)
C(13)C(14)Cl(9)	118.7(3)	122(1)
C(3)C(15)C(14)	119.4(4)	121(2)
C(3)C(15)C(16)	122.1(4)	122(1)
C(1)C(6)O(5)	109.7(3)	
C(5)C(6)O(5)	113.0(3)	
C(1)C(6)C(20)		102(1)
C(5)C(6)C(20)		111(1)
C(4)C(5)C(17)		101(1)
C(6)C(5)C(17)		111(1)
C(17)C(18)C(19)		119(2)
C(17)C(18)C(23)		113(2)
C(18)C(19)C(20)		118(1)
C(18)C(19)C(22)		125(2)
C(6)C(20)C(19)		113(1)

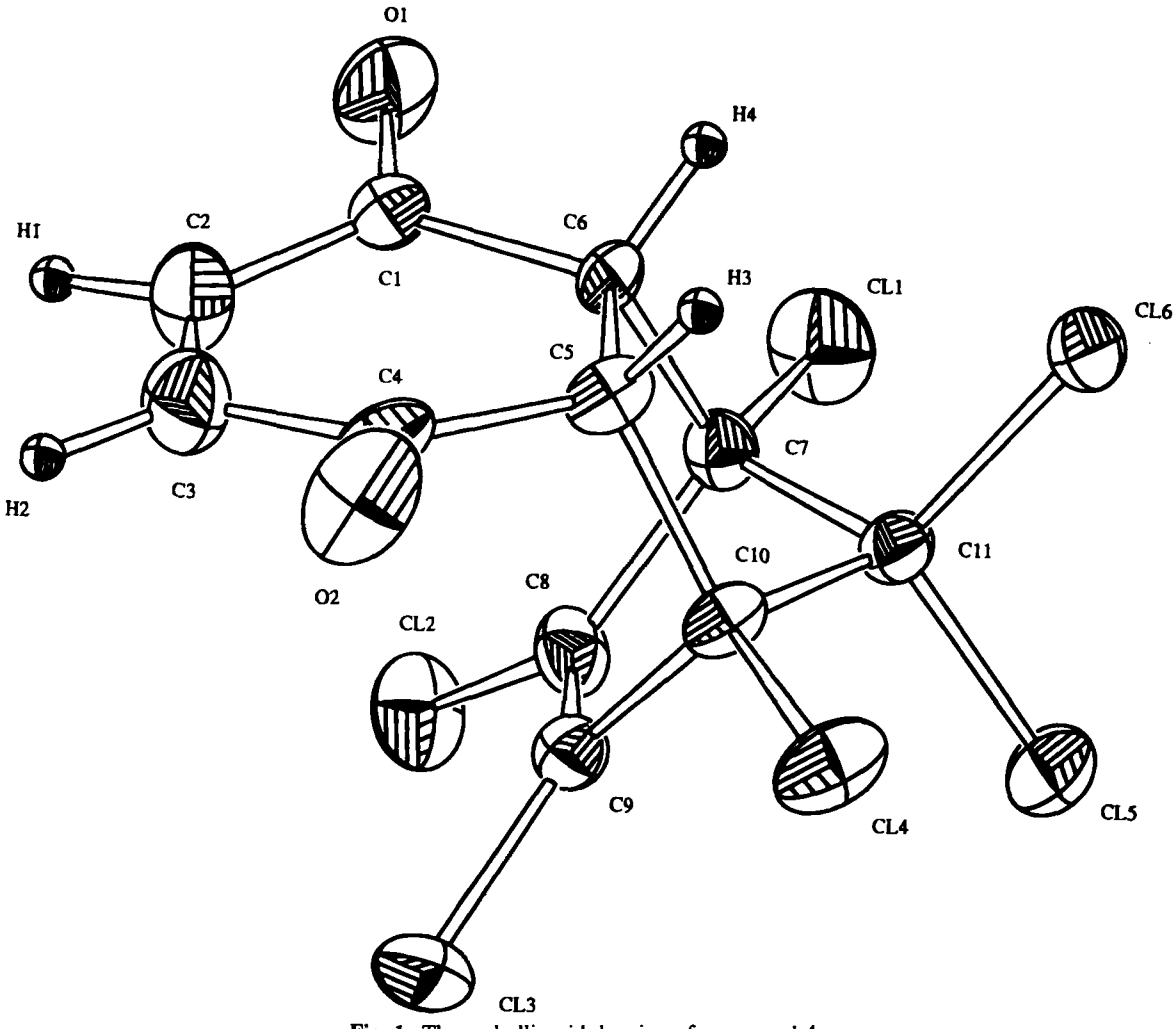


Fig. 1. Thermal ellipsoid drawing of compound **4**.

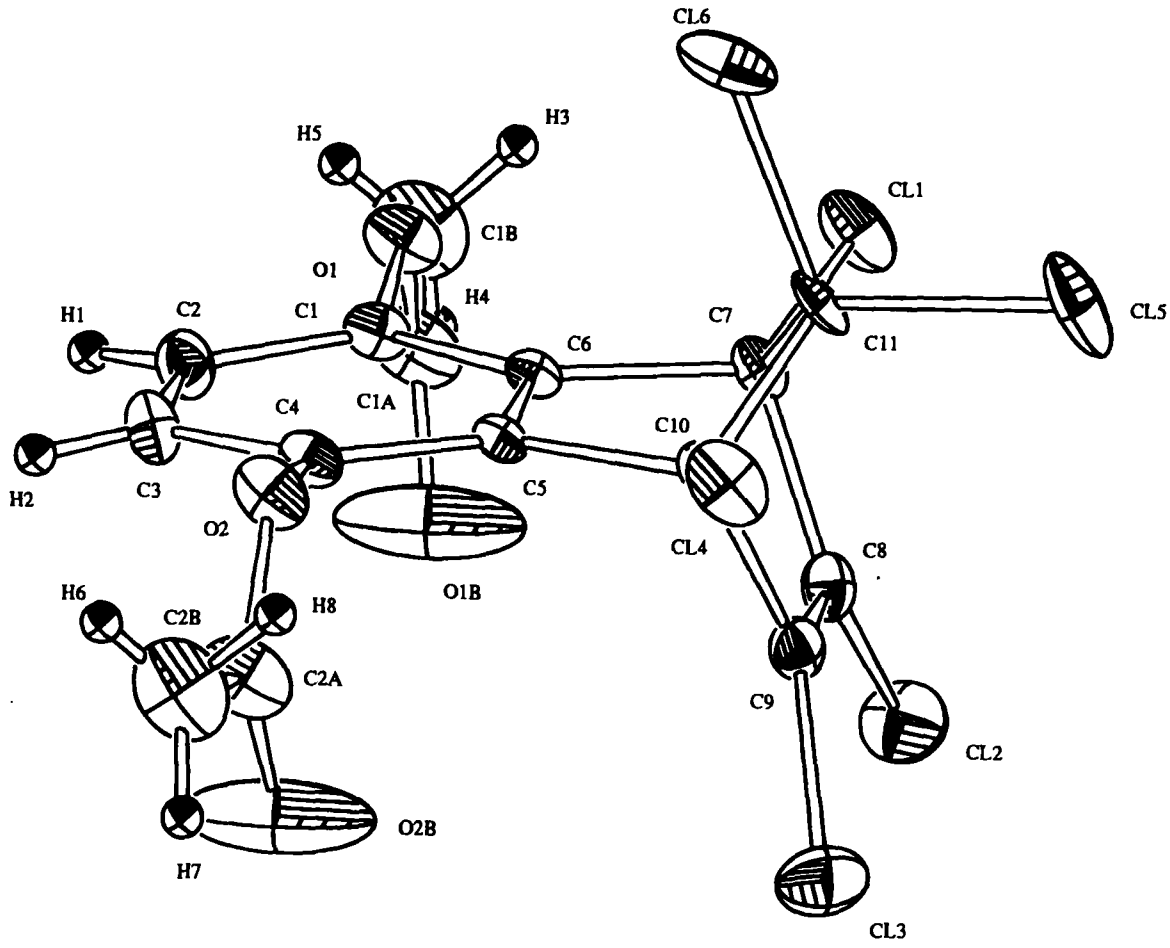


Fig. 2. Thermal ellipsoid drawing of compound 5.

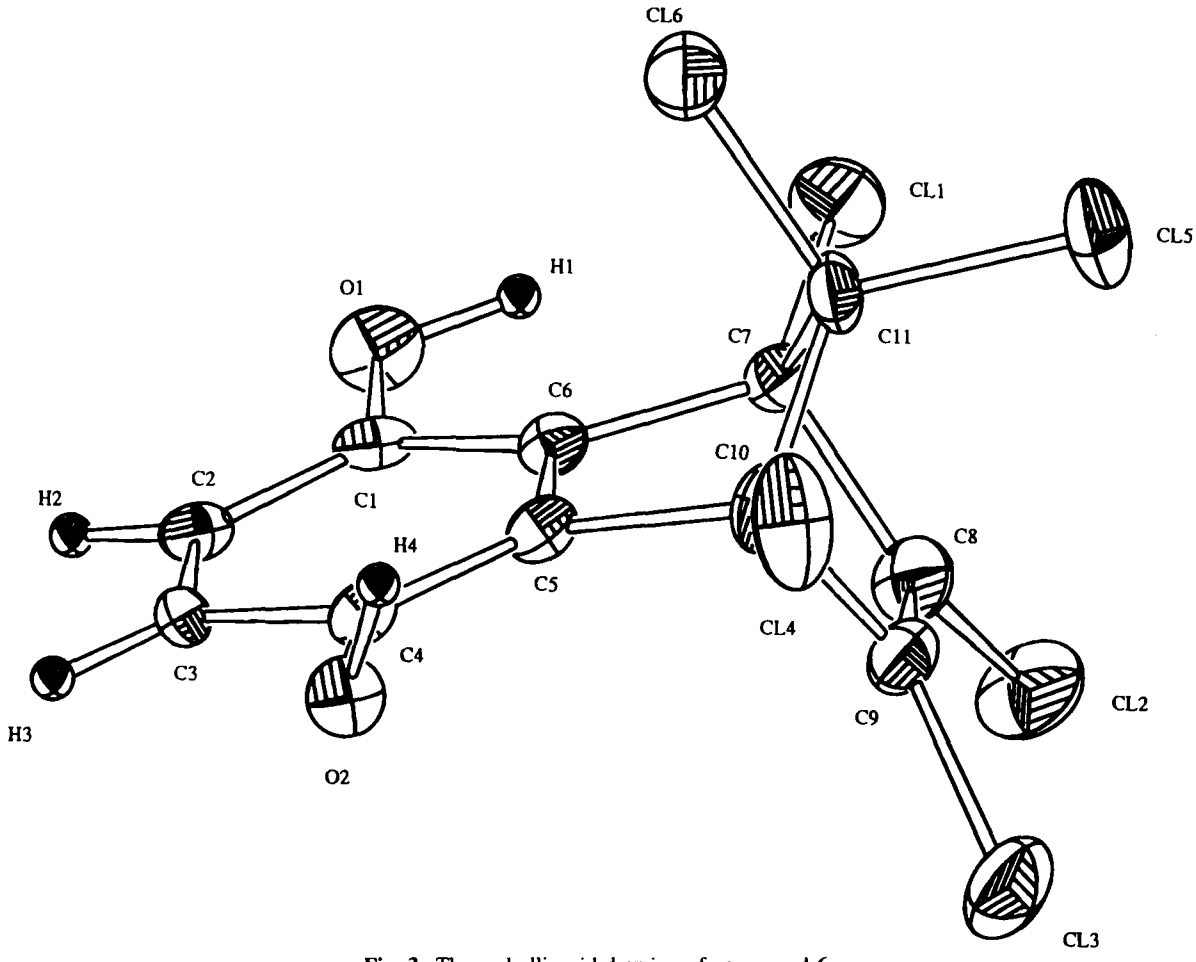


Fig. 3. Thermal ellipsoid drawing of compound **6**.

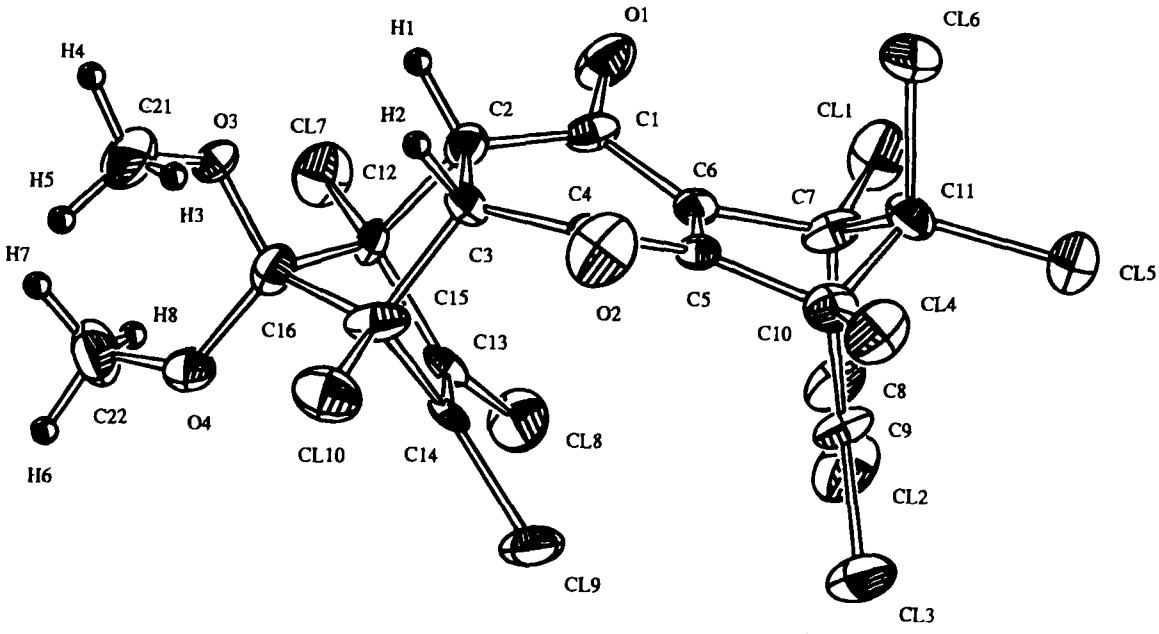


Fig. 4. Thermal ellipsoid drawing of compound **8**.

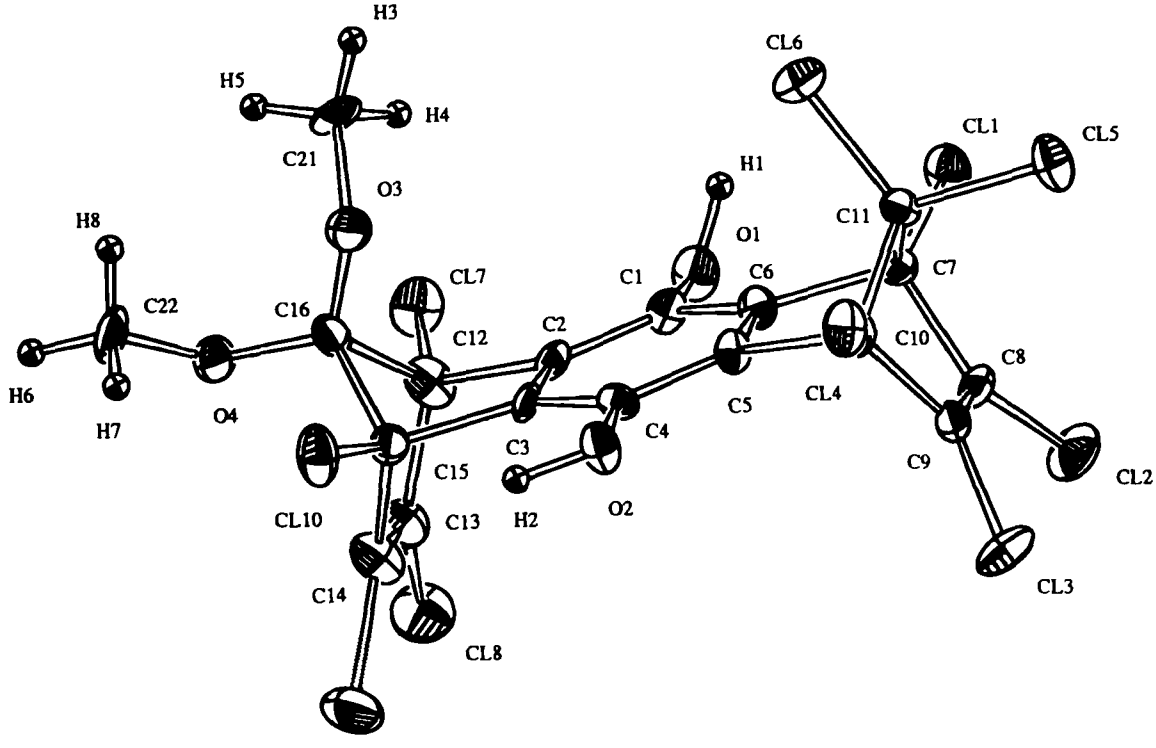


Fig. 5. Thermal ellipsoid drawing of compound **9**.

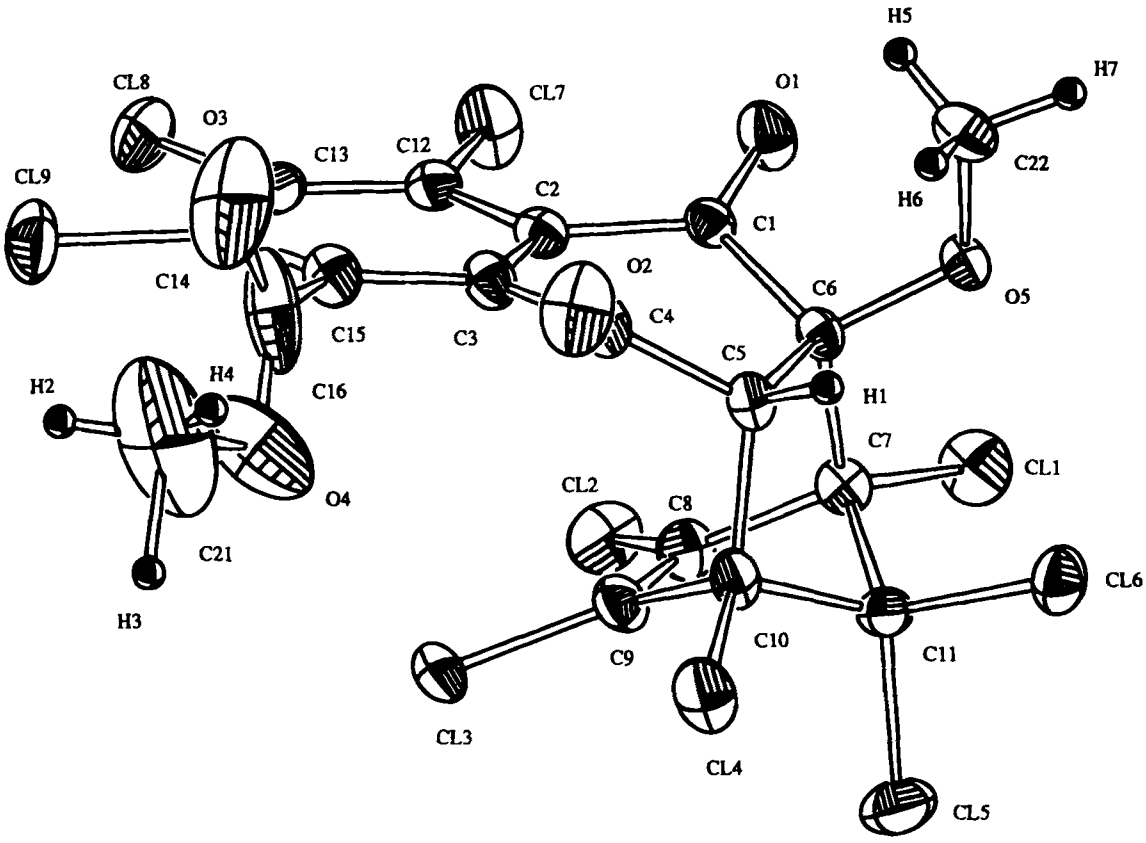


Fig. 6. Thermal ellipsoid drawing of compound **11**.

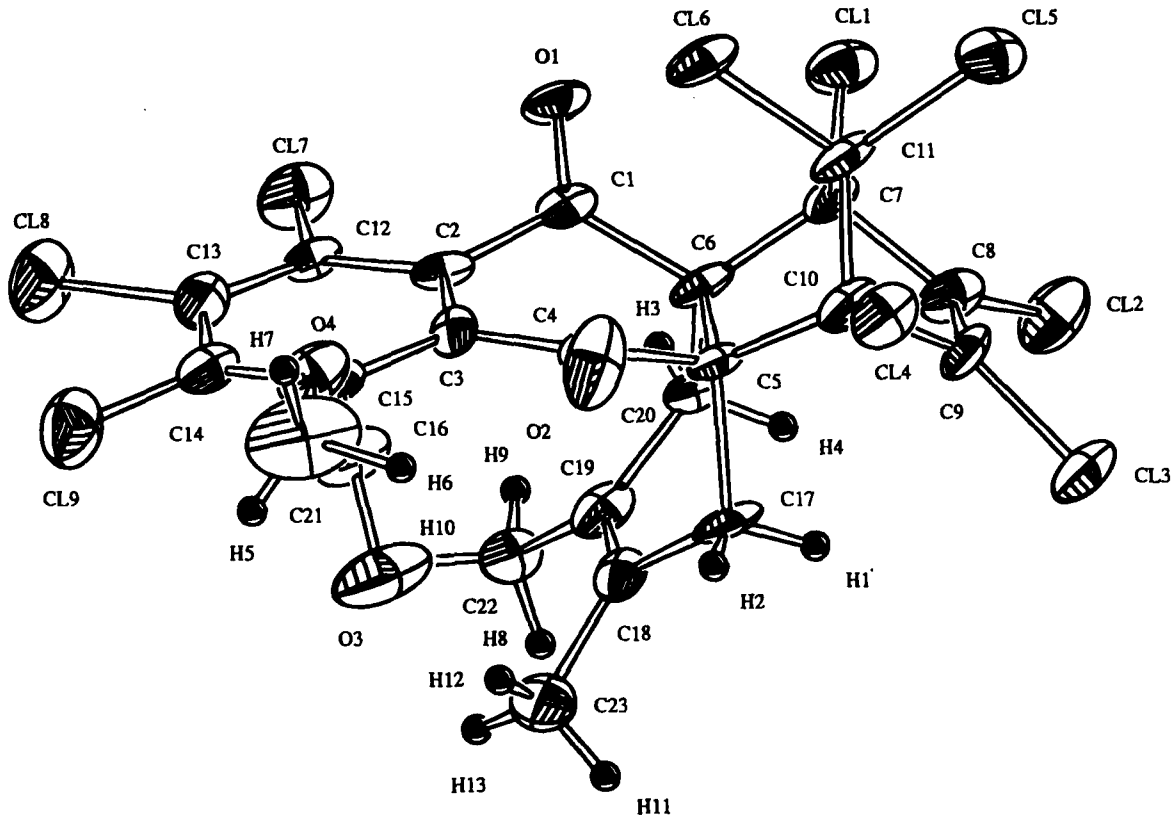


Fig. 7. Thermal ellipsoid drawing of compound **12**.

Acknowledgments

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Supplementary material. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5071 (for **4**), CCDC-1003/5072 (for **5**), CCDC-1003/5073 (for **6**), CCDC-1003/5074 (for **8**), CCDC-1003/5075 (for **9**), CCDC-1003/5076 (for **11**), CCDC-1003/5077 (for **12**). Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: teched@chemcrys.cam.ac.uk).

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