The Crystal Structures of 2-Phenyl-3,3-dimethyl-1,1-dichlorocyclopropane (I), 2-p-Chlorophenyl-3,3-dimethyl-1,1-dichlorocyclopropane (II) and 2-p-Chlorophenyl-3,3-dimethyl-1,1-dimethoxycyclopropane (III)

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Søtofte, I. and Crossland, I., 1992. The Crystal Structures of 2-Phenyl-3,3-dimethyl-1,1-dichlorocyclopropane (I), 2-p-Chlorophenyl-3,3-dimethyl-1,1-dichloro-cyclopropane (II) and 2-p-Chlorophenyl-3,3-dimethyl-1,1-dimethoxycyclopropane (III). – Acta Chem. Scand. 46: 131–137.

The title compounds, $C_{11}H_{12}Cl_2$, $C_{11}H_{11}Cl_3$ and $C_{13}H_{17}ClO_2$, have been prepared and their structures investigated by X-ray diffraction techniques at $T \approx 120$ K. The crystals of I are triclinic, space group $I\bar{1}$, with $a = 12.268(5)$, $b = 6.774(2)$, $c = 12.408(6)$ Å, $\alpha = 90.70(3)$, $\beta = 97.31(4)$, $\gamma = 89.66(2)$ °, and four molecules in the unit cell. Crystals of II are monoclinic, space group $P2_1/n$, with four molecules in the unit cell of dimension $a = 6.466(2)$, $b = 14.172(2)$, $c = 12.210(6)$ Å, and $\beta = 94.04(3)$ °. The crystals of III are triclinic, space group $P\bar{1}$ with $a = 7.396(2)$, $b = 10.796(4)$, $c = 17.560(12)$ Å, $\alpha = 106.73(4)$, $\beta = 95.84(4)$, $\gamma = 104.00(3)$ ° and four molecules in the unit cell. The structures were solved by direct methods and refined by least-squares using 2471, 2831 and 3460 intensity measurements respectively, to R values of 0.043, 0.024 and 0.035. In all three structures the phenyl ring adopts the perpendicular conformation with respect to the cyclopropane ring. The substituent-induced bond length asymmetries observed in these cyclopropane derivatives are consistent with interactions involving asymmetry parameters such as $\delta(Cl_2) = 0.019$, $\delta[(OCH_3)_2] = 0.036$ and $\delta(phenyl) = 0$ Å.

The investigation of 2-p-chlorophenyl-3,3-dimethyl-1-methoxycyclopropene[1] showed that the methoxy group had a large effect on the geometry of the cyclopropene ring. No structural data on methoxy-substituted cyclopropenes or cyclopropanes had at that time been published; therefore, the present structure investigations were carried out in order to determine an asymmetry parameter for the methoxy group.

Experimental

Preparation of the title compounds. Compounds I[2] and II[1] were prepared according to known procedures. Compound III was prepared by treating II with sodium methoxide (4 mol) in dimethyl formamide (0.5 M) at 20–25 °C for 40 min. Pentane–water extractions and crystallizations from pentane and from methanol gave colourless crystals, m.p. 21–23 °C. ^{1}H NMR: δ(ppm) 0.96 (3H,s), 1.32 (3H,s), 1.83 (1H,s), 3.22 (3H,s), 3.43 (3H,s), 7.19 (4H,s).

The crystals were allowed to grow in glass ampules at ca. 0.3 mmHg. The growth was slow owing to low temperatures, in particular for compound III.

X-Ray techniques. Crystal and experimental data for the three compounds are listed in Table 1. By means of a conventional cryogenic device,[3] utilizing a flow of cold nitrogen gas, the single crystals were cooled to about 120 K. The space group symmetries were determined from systematic absences and by the unit cell parameters found by the least-squares method from 16 (for I) or 25 (for II and III) reflections. Four standards were measured for intensity and orientation control after every 200 reflections; no fading was observed. The intensities were corrected for Lorentz, polarization and absorption (Gaussian integration) effects. The structures were solved by direct methods and refined by a full-matrix least-squares technique using SHELX76,[4] with atomic scattering factors from Ref. 5. There are two independent molecules in the asymmetric unit in III. The hydrogen atoms were all located from electron density difference maps. Anisotropic thermal parameters were introduced for all non-hydrogen atoms, whereas all hydrogen atoms were refined with isotropic temperature factors. The space groups $I\bar{1}$ (I) and $P\bar{1}$ (III) were assumed in all calculations. The refinement confirms that these choices are correct. The space group $I\bar{1}$ was chosen in order to obtain angles as close to 90° as possible. The PLUTO program[6] was used for the illustrations.

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Table 1. Crystal and experimental data for the three compounds.

Compound	2-Phenyl-3,3-dimethyl-1,1-dichlorocyclopropane (I)	2-p-Chlorophenyl-3,3-dimethyl-1,1-dichlorocyclopropane (II)	2-p-Chlorophenyl-3,3-dimethyl-1,1-dimethoxycyclopropane (III)
Formula	$C_{11}H_{12}Cl_2$	$C_{11}H_{11}Cl_3$	$C_{13}H_{17}ClO_2$
Formula weight	215.1	249.6	240.7
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$I\bar{1}$	$P2_1/n$	$P\bar{1}$
Unit-cell dimensions /Å	$a = 12.268(5)$	$a = 6.466(2)$	$a = 7.396(2)$
	$b = 6.774(2)$	$b = 14.172(2)$	$b = 10.796(4)$
	$c = 12.408(6)$	$c = 12.210(6)$	$c = 17.560(12)$
	$\alpha = 90.70(3)°$		$\alpha = 106.73(4)°$
	$\beta = 97.31(4)°$	$\beta = 94.04(3)°$	$\beta = 95.84(4)°$
	$\gamma = 89.66(2)°$		$\gamma = 104.00(3)°$
Unit-cell volume, $V/Å^3$	1022.7	1116.1	1280.5
Formula units per unit cell, Z	4	4	4
$F(000)$	448	512	512
Calculated density, $D_x/g\ cm^{-3}$	1.40	1.48	1.25
Radiation	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
Wavelength, $\lambda/Å$	0.71069	0.71069	0.71069
Linear absorption coefficient/cm^{-1}	5.86	7.81	2.80
Temperature, T/K	123	120	124
Crystal description	Colourless	Colourless	Colourless
Crystal size/mm	0.18×0.14×0.26	0.40×0.14×0.24	0.26×0.18×0.34
Diffractometer	Enraf–Nonius CAD-4 F	As I	As I
Unit-cell determination			
No. of reflections used	16	25	25
θ-range/°	9.2–12.6	11.3–16.4	8.3–11.4
Intensity data collection			
Maximum $(\sin \theta/\lambda)/Å^{-1}$	0.7035	0.7034	0.7035
Range of h	−17–17	0–9	−10–10
Range of k	−9–9	0–19	−15–15
Range of l	0–17	−17–17	−24–24
ω-scan, $\Delta\omega = a + 0.35 \tan \theta$	$a = 1.00$	$a = 0.90$	$a = 1.00$
Total no. of reflections	3238	3487	7372
No. of independent reflections, $[I > 2\sigma(I)]$	2471	2831	3460
Corrections	Lorenz-polarization and absorption	As I	As I
Transmission factors	0.8042–0.9642	0.7808–0.8997	0.9405–0.9592
Structure refinement:			
Minimization of	$\Sigma w(|F_o|-|F_c|)^2$	As I	As I
Anisotropic thermal parameters	All non-hydrogen atoms	As I	As I
Isotropic thermal parameters	Hydrogen atoms	As I	As I
No. of refined parameters	166	171	213
Weighting scheme	$[\sigma^2(F_o) + 0.005|F_o|^2]^{-1}$	$[\sigma^2(F_o) + 0.0002|F_o|^2]^{-1}$	$[\sigma^2(F_o) + 0.0002|F_o|^2]^{-1}$
$R = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$	0.043	0.024	0.035
$R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$	0.055	0.034	0.036
Final $(\Delta/\sigma)_{max}$	0.11	0.16	0.09
Final $\Delta\varrho_{min}$ and $\Delta\varrho_{max}/e\ Å^{-3}$	−1.25 and 0.57	−0.26 and 0.39	−0.24 and 0.26

The final positional parameters with estimated standard deviations are listed in Tables 2 and 3, and the labelling of the atoms is shown in Fig. 1.

Description and discussion of the structures

Bond lengths, bond angles and torsion angles[7] with their estimated standard deviations are listed in Tables 4 and 5. The molecular structures of the three cyclopropane derivatives are very similar.

The phenyl rings are nearly planar, the deviations of the atoms from the least-squares planes through them being less than 0.003(2) Å for I, 0.010(7) Å for II, 0.012(9) Å for III-1 and 0.004(8) Å for III-2. The chlorine atom is 0.055(7) and 0.071(10) Å out of the plane for II and III-1, respectively, and in the plane for III-2. The six bond lengths average 1.394(1), 1.389(2) and 1.386(3) Å for I, II and III, respectively, a result which compares quite well with the average of 1.387(4) Å reported in the survey of Allen.[8] The deformations of the endocyclic angles in the phenyl rings are almost symmetric around the C6–C9 line, with an angle at C6 of 118.8(1), 118.6(1), 118.4(2) and 117.8(2)° for I, II, III-1 and III-2, respectively. Furthermore, the C6–C7 and C6–C11 bonds in all three com-

Table 2. Final fractional coordinates and equivalent temperature factors with estimated standard deviations for atoms in 2-phenyl-3,3-dimethyl-1,1-dichlorocyclopropane (I) and 2-*p*-chlorophenyl-3,3-dimethyl-1,1-dichlorocyclopropane (II).

Atom	I				II			
	x	*y*	*z*	$B_{eq}{}^a$	*x*	*y*	*z*	$B_{eq}{}^a$
C1	0.4346(1)	0.0724(2)	0.2253(1)	0.89(2)	0.3689(2)	0.3278(1)	0.5432(1)	1.18(2)
C2	0.3541(1)	−0.0948(2)	0.2023(1)	0.85(2)	0.3814(2)	0.3704(1)	0.6564(1)	1.14(2)
C3	0.4700(1)	−0.1334(2)	0.2605(1)	0.88(2)	0.4442(2)	0.2672(1)	0.6398(1)	1.18(2)
C4	0.4809(1)	−0.1842(2)	0.3813(1)	1.08(3)	0.6731(2)	0.2442(1)	0.6552(1)	1.54(3)
C5	0.5554(1)	−0.2377(2)	0.1997(1)	1.04(3)	0.3027(2)	0.1885(1)	0.6739(1)	1.54(3)
C6	0.3128(1)	−0.1673(2)	0.0904(1)	0.81(2)	0.1949(2)	0.3996(1)	0.7135(1)	1.13(2)
C7	0.2564(1)	−0.0402(2)	0.0146(1)	1.07(3)	0.0547(2)	0.4653(1)	0.6670(1)	1.22(2)
C8	0.2102(1)	−0.1113(2)	−0.0867(1)	1.28(3)	−0.1147(2)	0.4947(1)	0.7220(1)	1.29(2)
C9	0.2204(1)	−0.3101(2)	−0.1136(2)	1.32(3)	−0.1424(2)	0.4577(1)	0.8252(1)	1.28(2)
C10	0.2766(1)	−0.4374(2)	−0.0390(1)	1.15(3)	−0.0033(2)	0.3940(1)	0.8744(1)	1.56(3)
C11	0.3225(1)	−0.3664(2)	0.0625(1)	1.00(2)	0.1648(2)	0.3652(1)	0.8185(1)	1.45(3)
Cl1	0.4074(0.3)	0.2524(0.5)	0.3227(0.3)	1.35(1)	0.5444(0.5)	0.3678(0.2)	0.4491(0.2)	1.62(1)
Cl2	0.4935(0.2)	0.1821(0.5)	0.1195(0.3)	1.19(1)	0.1248(0.5)	0.3042(0.2)	0.4752(0.2)	1.52(1)
Cl					−0.3578(0.5)	0.4918(0.2)	0.8935(0.3)	1.84(1)
H1	0.302(2)	−0.097(3)	0.24902)	1.0(3)	0.498(3)	0.413(1)	0.666(1)	1.4(3)
H2	0.474(2)	−0.312(4)	0.386(2)	2.9(5)	0.705(3)	0.193(1)	0.615(2)	3.1(4)
H3	0.540(2)	−0.156(4)	0.409(2)	3.0(5)	0.708(3)	0.227(1)	0.735(1)	2.1(3)
H4	0.417(2)	−0.131(4)	0.413(2)	2.4(5)	0.762(3)	0.296(1)	0.636(1)	2.0(3)
H5	0.550(2)	−0.373(4)	0.206(2)	2.6(5)	0.309(3)	0.135(1)	0.627(1)	2.3(4)
H6	0.618(2)	−0.205(4)	0.224(2)	2.5(5)	0.334(3)	0.170(1)	0.750(1)	2.4(4)
H7	0.549(2)	−0.197(3)	0.125(2)	2.3(4)	0.161(3)	0.208(1)	0.669(1)	1.6(3)
H8	0.241(2)	0.093(4)	0.032(2)	2.7(5)	0.075(3)	0.493(1)	0.597(2)	2.3(4)
H9	0.170(2)	−0.020(4)	−0.141(2)	2.2(4)	−0.205(3)	0.537(1)	0.691(1)	2.3(4)
H10	0.188(2)	−0.346(3)	−0.180(2)	2.2(4)				
H11	0.284(2)	−0.570(3)	−0.057(2)	2.2(4)	−0.015(3)	0.369(1)	0.948(1)	2.5(4)
H12	0.352(2)	−0.457(3)	0.117(2)	1.9(4)	0.260(3)	0.324(1)	0.853(1)	2.1(3)

$${}^a B_{eq} = \frac{4}{3} \sum_i \sum_j b_{ij}(a_i \cdot a_j).$$

pounds are larger than the average bond length. This might indicate that the substituted cyclopropane has a small effect on the geometry of the phenyl ring. The angles at C9 of 119.7(1), 121.3(1), 121.8(2) and 121.4(2)° for I, II, III-1 and III-2, respectively, indicate a highly electronegative substituent bonded to C9 in compounds II and III. The C9–Cl bond lengths of 1.741–1.747 Å are similar to those found for other analogous compounds. The angle between the cyclopropane ring and the phenyl ring is 45.7(1), 48.6(1), 52.2(2) and 46.9(2)° for I, II, III-1 and III-2, respectively.

The C1–Cl bond lengths of 1.752–1.767 Å are in agreement with those found in other *gem*-dichloro-substituted cyclopropanes.[8]

The C1–O mean bond length of 1.390(2) Å in III is somewhat longer than the value of 1.371(3) Å reported for *cis*-1,2-dicyano-1,2-dimethoxycyclopropane.[9] The latter value is close to that found in methoxy groups substituted in benzene.

The cyclopropane ring in all three structures has unequal C–C bond lengths, with the C2–C3 bond being the longest in each case. Substituent-induced bond-length asymmetry in cyclopropane has been surveyed by Allen.[8] Using his formalism to express the bond-length variations, the

asymmetry parameter δ is defined as a lengthening (positive δ) and shortening (negative δ) of the distal bond relative to the mean C–C (ring) bond length. The vicinal bonds are each modified by $-\frac{1}{2}\delta$. On the assumption that bond-length asymmetry in multiply substituted cyclopropanes is the sum of the asymmetries induced by each individual substituent, the asymmetry parameters for *gem*-dichloro-,
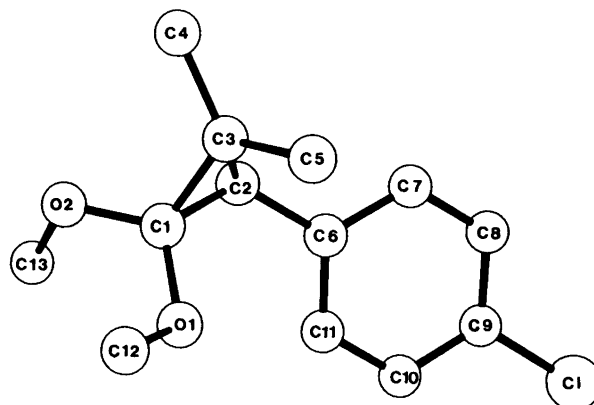

Fig. 1. The molecule of 2-*p*-chlorophenyl-3,3-dimethyl-1,1-dimethoxycyclopropane (III). In the molecules of I and II the methoxy groups are replaced by chlorine atoms.

Table 3. Final fractional coordinates and equivalent temperature factors with estimated standard deviations for atoms in the two independent molecules in 2-*p*-chlorophenyl-3,3-dimethyl-1,1-dimethoxycyclopropane (III).

Atom	III-1				III-2			
	x	*y*	*z*	B_{eq}	*x*	*y*	*z*	B_{eq}
C1	0.4110(3)	0.7294(2)	0.9360(1)	1.26(6)	0.9772(3)	0.7910(2)	0.6048(1)	1.40(6)
C2	0.3328(3)	0.6192(2)	0.8567(1)	1.21(6)	0.9320(3)	0.7302(2)	0.6694(1)	1.28(6)
C3	0.5489(3)	0.6740(2)	0.8893(1)	1.27(6)	1.1370(3)	0.7674(2)	0.6531(1)	1.50(6)
C4	0.6654(3)	0.7578(2)	0.8464(2)	1.83(7)	1.2797(4)	0.8860(2)	0.7167(2)	2.09(7)
C5	0.6449(3)	0.5841(2)	0.9187(2)	1.71(7)	1.2154(4)	0.6537(2)	0.6128(2)	2.17(8)
C6	0.2193(3)	0.4793(2)	0.8478(1)	1.15(5)	0.8179(3)	0.5884(2)	0.6552(1)	1.23(6)
C7	0.0869(3)	0.4566(2)	0.8965(1)	1.23(6)	0.6476(3)	0.5287(2)	0.6001(1)	1.56(6)
C8	−0.0216(3)	0.3273(2)	0.8874(1)	1.34(6)	0.5355(3)	0.4007(2)	0.5924(1)	1.64(6)
C9	0.0041(3)	0.2199(2)	0.8284(1)	1.35(6)	0.5964(3)	0.3315(2)	0.6399(1)	1.50(6)
C10	0.1302(3)	0.2383(2)	0.7774(1)	1.44(6)	0.7642(3)	0.3869(2)	0.6949(1)	1.76(7)
C11	0.2386(3)	0.3688(2)	0.7879(1)	1.33(6)	0.8738(3)	0.5150(2)	0.7021(1)	1.69(6)
C12	0.2245(3)	0.8771(3)	0.9448(2)	2.12(8)	0.7931(3)	0.9402(2)	0.6051(2)	2.01(7)
C13	0.5144(4)	0.7848(3)	1.0759(2)	2.11(7)	1.0123(4)	0.7512(3)	0.4693(2)	2.56(8)
O1	0.4073(2)	0.8589(1)	0.9394(1)	1.60(4)	0.9790(2)	0.9255(1)	0.6189(1)	1.56(4)
O2	0.3759(2)	0.6979(1)	1.0053(1)	1.40(4)	0.9040(2)	0.7087(1)	0.5254(1)	1.67(4)
Cl	−0.1279(0.9)	0.0574(0.5)	0.8199(0.4)	2.32(2)	0.4568(0.8)	0.1703(0.5)	0.6305(0.4)	2.04(2)
H1	0.290(3)	0.652(2)	0.814(1)	1.5(5)	0.913(3)	0.799(2)	0.719(1)	1.4(5)
H2	0.602(3)	0.818(2)	0.829(1)	2.1(5)	1.220(3)	0.952(2)	0.739(1)	1.0(4)
H3	0.781(4)	0.821(3)	0.885(2)	3.3(6)	1.389(4)	0.927(2)	0.693(1)	2.7(6)
H4	0.704(4)	0.699(3)	0.803(2)	3.2(6)	1.334(4)	0.854(3)	0.761(2)	2.9(6)
H5	0.572(3)	0.535(2)	0.950(1)	1.9(5)	1.320(4)	0.684(2)	0.590(1)	2.3(5)
H6	0.668(3)	0.514(3)	0.872(2)	2.8(6)	1.122(4)	0.584(3)	0.570(2)	2.4(5)
H7	0.764(4)	0.637(3)	0.953(2)	2.8(6)	1.259(4)	0.610(3)	0.651(2)	3.5(6)
H8	0.065(3)	0.532(2)	0.936(1)	1.0(4)	0.612(3)	0.573(2)	0.569(1)	0.9(4)
H9	−0.108(3)	0.315(2)	0.919(1)	2.0(5)	0.421(3)	0.361(2)	0.556(1)	1.4(4)
H10	0.143(3)	0.166(2)	0.738(1)	1.8(5)	0.804(3)	0.339(2)	0.727(1)	2.3(5)
H11	0.323(3)	0.380(2)	0.752(1)	1.2(4)	0.981(4)	0.552(3)	0.740(2)	3.1(6)
H12	0.139(4)	0.817(3)	0.897(2)	3.4(6)	0.804(3)	1.036(3)	0.624(1)	2.5(5)
H13	0.179(4)	0.861(2)	0.992(2)	2.6(6)	0.743(3)	0.909(2)	0.549(2)	2.2(5)
H14	0.219(4)	0.962(3)	0.944(2)	3.6(6)	0.710(3)	0.891(2)	0.633(1)	1.8(5)
H15	0.638(4)	0.781(2)	1.067(2)	2.7(6)	0.962(4)	0.689(3)	0.419(2)	2.9(6)
H16	0.506(3)	0.880(2)	1.090(1)	2.2(5)	1.002(4)	0.841(3)	0.469(2)	2.9(6)
H17	0.481(4)	0.753(3)	1.121(2)	3.3(6)	1.152(4)	0.761(3)	0.486(2)	4.1(7)

*gem*-dimethoxy- and phenyl substituents could be calculated. The above considerations may be summarized in form of eqn. (1), where $n = 1,2,3$. The δ_{subst} are the

$$\delta_n = \Sigma\delta_{subst.distal} - \tfrac{1}{2}\Sigma_{subst.vicinal} \qquad (1)$$

asymmetry parameters for the substituents, and δ_n are the asymmetry parameters for the substituted cyclopropanes. Here δ_n are taken from Table 6.

The mean C–C (ring) bond lengths of 1.517, 1.518 and 1.514 Å for I, II and III, respectively, are longer than that of 1.4991(17) Å found for the unsubstituted cyclopropane determined by an accurate single-crystal X-ray measurement at $T \simeq 100$ K,[10] but in agreement with that reported for other substituted cyclopropanes. Assuming that the effect of the methyl groups is negligible, an asymmetry parameter for the *gem*-dichloro substituents, $\delta_{Cl_2} = 0.019$ Å, was found. This result is in agreement with the value of 0.025(7) Å reported by Allen. For the *gem*-dimethoxy substituents an asymmetry parameter $\delta_{(OMe)_2}$ of 0.036 Å was obtained. Since a value greater than δ_{Cl_2} was expected,

the result seems reasonable and is in agreement with the distal bond lengthening found in 2-*p*-chlorophenyl-3,3-dimethyl-1-methoxycyclopropene[1] and from MO calculations.[11] The negative value of δ_{OMe} (−0.016 Å) found in *cis*-1,2-dicyano-1,2-dimethoxycyclopropane[9] may be rationalized by assuming a π-interaction of the two (captodative) substituents via the C^1–C^2 bond of the cyclopropane [reaction (i)]. Thus, we suggest that electronegative sub-

$$N \equiv C\!-\!C^1\!-\!C^2\!-\!OMe \leftrightarrow \overset{\delta-}{N{\cdots}C}\!\cdots\!C^1\!\cdots\!\overset{\delta+}{C^2}\!\cdots\!OMe \qquad (i)$$
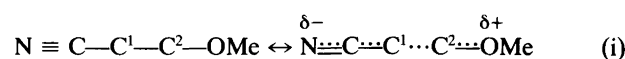
stituents (X = OR, F, Cl)[8] give distal bond lengthening (asymmetry parameters δ_X positive) if rehybridization effects dominate; any π-conjugation through the cyclopropane ring may give distal bond shortening (δ_X negative). More data are needed to allow evaluation of any trends in the values of δ_X for various substituents. A first guess may be that the asymmetry parameter is determined by the electronegativity of the substituent if no π-conjugation takes place.

Table 4. Bond distances (in Å) and bond angles (in °) with estimated standard deviations for 2-phenyl-3,3-dimethyl-1,1-dichlorocyclopropane (I), 2-p-chlorophenyl-3,3-dimethyl-1,1-dichlorocyclopropane (II) and the two molecules in 2-p-chlorophenyl-3,3-dimethyl-1,1-dimethylcyclopropane (III).

Atoms	Distance or angle			
	I	II	III-1	III-2
C1–C2	1.508(2)	1.505(2)	1.495(3)	1.494(4)
C1–C3	1.511(2)	1.513(2)	1.501(3)	1.500(3)
C1–Cl1	1.766(2)	1.764(1)		
C1–Cl2	1.752(2)	1.763(1)		
C1–O1			1.389(3)	1.397(3)
C1–O2			1.387(3)	1.388(3)
C2–C3	1.533(2)	1.536(2)	1.547(3)	1.550(3)
C2–C6	1.494(2)	1.493(3)	1.494(3)	1.494(3)
C3–C4	1.532(2)	1.514(2)	1.507(4)	1.510(3)
C3–C5	1.531(2)	1.519(2)	1.504(4)	1.507(3)
C6–C7	1.398(2)	1.393(2)	1.388(3)	1.392(3)
C6–C11	1.397(2)	1.398(2)	1.393(3)	1.394(4)
C7–C8	1.393(2)	1.389(2)	1.386(3)	1.389(3)
C8–C9	1.392(2)	1.388(2)	1.382(3)	1.380(4)
C9–C10	1.388(2)	1.382(2)	1.376(3)	1.376(3)
C9–Cl		1.741(1)	1.745(2)	1.747(2)
C10–C11	1.394(2)	1.385(2)	1.391(3)	1.385(3)
C12–O1			1.421(3)	1.427(3)
C13–O2			1.440(3)	1.438(4)
C2–C1–C3	61.0(1)	61.2(1)	62.2(1)	62.4(2)
C2–C1–Cl1	117.8(1)	118.3(1)		
C2–C1–Cl2	120.6(1)	119.8(1)		
C2–C1–O1			117.7(2)	117.9(2)
C2–C1–O2			117.1(2)	116.8(2)
C3–C1–Cl1	120.3(1)	120.3(1)		
C3–C1–Cl2	119.2(1)	119.2(1)		
C3–C1–O1			116.5(2)	116.2(1)
C3–C1–O2			119.7(2)	120.2(2)
Cl1–C1–Cl2	110.3(1)	110.4(1)		
O1–C1–O2			114.1(2)	114.0(2)
C1–C2–C3	59.6(1)	59.6(1)	59.1(1)	59.0(2)
C1–C2–C6	123.5(1)	123.1(1)	124.4(2)	125.3(2)
C3–C2–C6	124.6(1)	123.7(1)	123.4(2)	123.1(2)
C1–C3–C2	59.4(1)	59.2(1)	58.7(1)	58.6(2)
C1–C3–C4	119.2(1)	118.5(1)	118.8(2)	119.4(2)
C1–C3–C5	117.7(1)	117.6(1)	118.9(2)	118.2(2)
C2–C3–C4	117.5(1)	117.0(1)	117.1(2)	116.9(2)
C2–C3–C5	119.8(1)	119.6(1)	117.5(2)	117.8(2)
C4–C3–C5	113.3(1)	114.2(1)	114.6(2)	114.7(2)
C2–C6–C7	120.5(1)	121.2(1)	121.0(2)	122.1(2)
C2–C6–C11	120.5(1)	120.0(1)	120.6(2)	119.9(2)
C7–C6–C11	118.8(1)	118.6(1)	118.4(2)	117.8(2)
C6–C7–C8	120.5(1)	121.1(1)	121.3(2)	121.4(2)
C7–C8–C9	120.2(1)	118.9(1)	118.7(2)	118.9(2)
C8–C9–C10	119.7(1)	121.3(1)	121.8(2)	121.4(2)
C8–C9–Cl		119.2(1)	118.2(2)	119.3(1)
C10–C9–Cl		119.4(1)	120.0(2)	119.3(2)
C9–C10–C11	120.1(1)	119.2(1)	118.5(2)	118.9(2)
C10–C11–C6	120.7(1)	120.9(1)	121.2(2)	121.5(2)

Table 5. Selected torsion angles (in °) with estimated standard deviations for the molecules.

Atoms	I	II	III-1	III-2
C6–C2–C3–C4	−138.8(1)	−139.6(1)	138.0(2)	−136.0(2)
C6–C2–C3–C5	5.5(2)	5.4(2)	−4.5(3)	6.7(3)
C6–C2–C1–Cl1	135.3(1)	136.3(1)		
C6–C2–C1–Cl2	−4.9(2)	−3.6(2)		
C6–C2–C1–O1			−141.3(2)	142.5(2)
C6–C2–C1–O2			0.5(3)	1.0(3)
C7–C6–C2–C1	−59.4(2)	−57.7(2)	38.7(3)	−45.6(3)
C7–C6–C2–C3	−133.1(1)	−130.9(1)	111.6(3)	−118.7(3)
C11–C6–C2–C1	125.5(1)	126.1(1)	−143.9(2)	139.2(2)
C11–C6–C2–C3	51.7(2)	52.9(2)	−71.0(3)	66.1(3)
Cl1–C1–C3–C4	0.6(2)	1.7(1)		
Cl1–C1–C3–C5	−142.9(1)	−142.6(1)		
Cl2–C1–C3–C4	142.6(1)	143.9(1)		
Cl2–C1–C3–C5	−1.0(1)	−0.4(1)		
O1–C1–C3–C4			−3.0(3)	4.1(3)
O1–C1–C3–C5			144.7(2)	−143.7(2)
O2–C1–C3–C4			−147.2(2)	148.2(2)
O2–C1–C3–C5			0.5(2)	0.6(3)
M–C1–O1–C12[a]			114.1(2)	−115.8(2)
M–C1–O2–C13[a]			120.2(2)	−120.4(3)

[a]M is the midpoint of the distal bond C2–C3.

There are two ways in which a phenyl ring can interact with the molecular orbitals of cyclopropane.[12] The first is donation of electron density from one of the occupied 3e' orbitals of the cyclopropane to an unoccupied orbital in the phenyl ring. Such a donation requires bisected conforma-

tion (b, $\tau = 0°$) for maximum overlap. The second is donation from the phenyl ring to one of the unoccupied 4e' or $1a_2'$ orbitals of cyclopropane. The $1a_2'$ orbitals require bisected conformation, while both the unfilled 4e' orbitals require the perpendicular conformation (p, $\tau = ±90°$). In the three structures reported here the phenyl ring is close to the perpendicular conformation, the torsion angle τ being 86.1(2), 87.3(2), 74.8(3) and −81.1(3)° for I, II, III-1 and III-2, respectively. The angle τ is derived from the mean value of τ(M–C2–C6–C7) and τ(M–C2–C6–C11) normalized to the range $−90 ≤ \tau ≤ 90°$, M being the midpoint of the distal C1–C3 bond. A comparison of the asymmetry of the cyclopropane ring in I and II indicates that the cyclopropane ring is unaffected by the presence of the chlorosubstituent in the phenyl ring (Table 6). An asymmetry parameter for phenyl $\delta_{ph} = 0.004$ Å was found, in agreement with the result that $\delta_{ph} = 0$ for $\tau = ±90°$ reported by Tinant et al.[13] The small value of δ_{ph} indicates that there is hardly any electron density donation from the phenyl ring to the 4e' orbitals of cyclopropane in the three compounds I, II and III. This is in disagreement with the result found in 3-(2-methoxyphenyl)-1,1,2,2-cyclopropanetetracarbonitrile.[14] Here the methoxyphenyl ring also adopts the perpendicular conformation, but a comparison of the structure with 1,1,2,2-cyclopropanetetracarbonitrile reveals that the distal bond in the former structure is shorter and the vicinal bonds longer than the corresponding bonds in the latter structure. The fact that the methoxy group is substituted vicinally to the cyclopropane ring may affect the electron donation from the phenyl group to the cyclopropane ring. In (−)-2,2-dichloro-1-(4-ethoxyphenyl)-1-cyclopropanecarboxylic acid[15] the phenyl group is close to a perpendic-

Table 6. The asymmetry parameters (δ) in some substituted cyclopropanes.[a]

No.	R	C1		C2		C3		D_1	D_2	D_3	Δ	$δ_1$	$δ_2$	$δ_3$
		R_1	R_2	R_3	R_4	R_5	R_6							
(I)	4.3	Cl	Cl	Ph	H	Me	Me	1.533(2)	1.511(2)	1.508(2)	1.517	16	−6	−9
(II)	2.4	Cl	Cl	ClPh	H	Me	Me	1.536(2)	1.513(2)	1.505(2)	1.518	18	−5	−13
(III)	3.5	OMe	OMe	ClPh	H	Me	Me	1.548(2)	1.500(1)	1.494(1)	1.514	34	−14	−20
Ref. 9	4.4	CN	OMe	CN	OMe	H	H	1.493(4)	1.483(4)	1.538(4)	1.505	−12	−22	33
Ref. 14	3.5	CN	CN	H	MeOPh	CN	CN	1.528(3)	1.552(3)	1.527(3)	1.536	−8	16	−9
Ref. 15	3.9	Cl	Cl	COOH	EtOPh	H	H	1.519(2)	1.486(2)	1.518(1)	1.508	11	−22	10
Ref. 17	3.9	H	H	H	Ph	H	H	1.512(4)	1.494(5)	1.514(5)	1.507	5	−13	7

[a] R, crystallographic R factor (%); R_n, substituents; D_n, bond lengths $D_1–D_3$ in the cyclopropane ring (in Å) (D_1 = C2–C3; D_2 = C1–C3; D_3 = C1–C2); Δ, mean C–C (cyclopropane) length (in Å); $δ_n$, D_n–Δ for the C–C (cyclopropane) bonds.

ular conformation (τ = 107.6°) and the carbonyl group (τ = 49.1°) is not far from the *cg 2* conformation (τ = +30°). In addition to the influence of the *gem*-dichloro group, the asymmetry in the cyclopropane ring may be ascribed to the carbonyl group or to some interaction of both substituents and not as suggested only by the effect of the phenyl group, the two substituents being attached to the same carbon atom (Table 6).

The C2–C6 bond lengths of 1.494(2), 1.493(2) and 1.494(3) Å for **I**, **II** and **III**, respectively, are similar to the bond of attachment of 1.492(3) Å found in 3-(2-methoxyphenyl)-1,1,2,2-cyclopropanetetracarbonitrile,[14] but are somewhat shorter than that of 1.500(1) Å reported for (−)-2,2-dichloro-1-(4-ethoxyphenyl)-1-cyclopropanecarboxylic acid.[15] The values are in agreement with those reported for other phenyl-substituted cyclopropanes, independent of the conformation of the phenyl rings.[8,13,16] Thus, since there is no significant trend in the variation of these
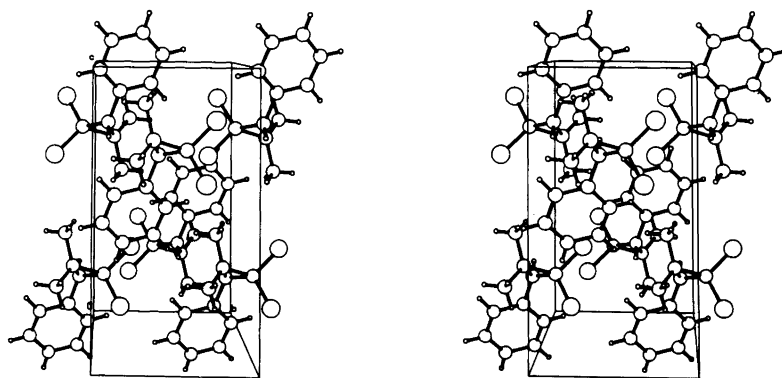

Fig. 2. Stereo view along the *a**-axis of 2-phenyl-3,3-dimethyl-1,1-dichlorocyclopropane (**I**).
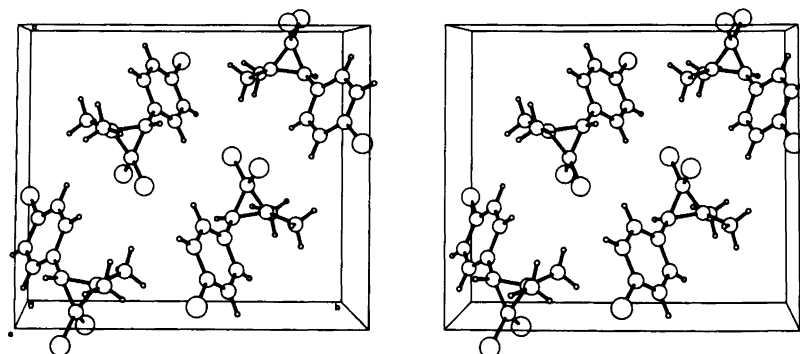

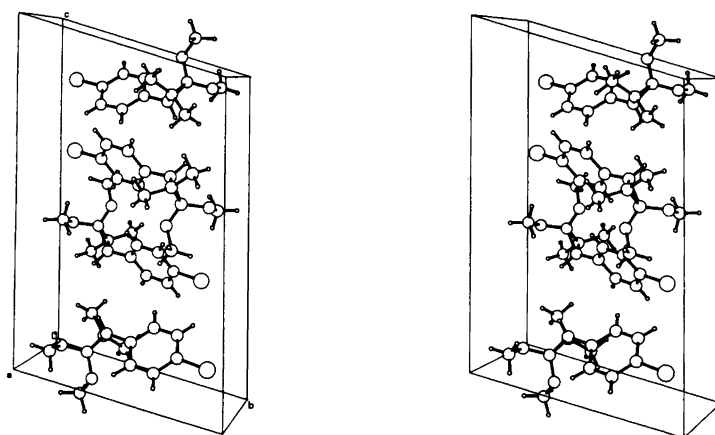*Fig. 3.* Stereo view along the *a**-axis of 2-*p*-chlorophenyl-3,3-dimethyl-1,1-dichlorocyclopropane (**II**).

Fig. 4. Stereo view along the a*-axis of 2-p-chlorophenyl-3,3-dimethyl-1,1-dimethoxycyclopropane (III).

bonds, the bond of attachment is not suggestive as to what extent the phenyl group is involved in the conjugation between the cyclopropane ring and the phenyl group. However, in phenylcyclopropane (at 173 K)[17] the short ring-connecting bond of 1.471(7) Å may be due to a considerable conjugation between the two rings, the phenyl group being in the bisected conformation.

The packings of the structures are shown in Fig. 2–4. In I no intermolecular distances are less than the sum of the corresponding van der Waals radii, the shortest distances being the Cl2–C10$(1-x, \bar{y}, \bar{z})$ distance of 3.572(2) Å and the Cl1–C7$(\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z)$ distance of 3.579(2) Å. In II the Cl–Cl$(-1-x, 1-y, 2-z)$ distance of 3.297(2) Å is shorter than the sum of the corrersponding van der Waals radii. The shortest distances in III are Cl(III-1)–C4(III-1)$(x-1, y-1, z)$ of 3.412(3) Å and Cl(III-1)–C12(III-2)$(x-1, y-1, z)$ of 3.551(4) Å, but both are longer than the sum of the corresponding van der Waal radii.

References

1. Søtofte, I. and Crossland, I. Acta Chem. Scand. 43 (1989) 168.
2. Henseling, K.-O. and Weyerstahl, P. Chem. Ber. 108 (1975) 2803.
3. Van Bolhuis, F. J. Appl. Crystallogr. 4 (1971) 263.
4. Sheldrick, G. M. SHELX 76: Program for Crystal Structure Determination, University of Cambridge, Cambridge, UK 1976.
5. International Tables for X-Ray Crystallography. Kynoch Press, Birmingham 1974, Vol. IV. (Present distributor: Kluwer Academic Publishers, Dordrecht).
6. Motherwell, W. D. S. PLUTO, University of Cambridge, Cambridge, UK 1976.
7. Stewart, J. M., Kundell, F. A. and Baldwin, J. C. The X-Ray System, Version of 1972, University of Maryland, College Park, MD 1972.
8. Allen, F. H. Acta Crystallogr., Sect. B36 (1980) 81 and references therein.
9. Tinant, B., Wu, S., Declercq, J. P., Van Meerssche, M., Masamba, W., De Mesmaeker, A. and Viehe, H. G. J. Chem. Soc., Perkin Trans. 2 (1988) 1045.
10. Nijveldt, D. and Vos, A. Acta Crystallogr., Sect. B44 (1988) 289.
11. Deakyne, C. A., Allen, L. C. and Laurie, V. W. J. Am. Chem. Soc. 99 (1977) 1343.
12. Jason, M. E. and Ibers, J. A. J. Am. Chem. Soc. 99 (1977) 6012.
13. Tinant, B., De Block, I., Declercq, J. P., Germain, G., Van Meerssche, M., Leroy, G. and Weiler, J. Bull. Soc. Chim. Belg. 91 (1982) 629.
14. Usha, R. and Venkatesan, K. Acta Crystallogr., Sect. B36 (1980) 335.
15. Poppleton, B. J. Acta Crystallogr. Sect. C42 (1986) 879.
16. Cameron, T. S., Linden, A. and Jochem, K. Acta Crystallogr., Sect. C46 (1990) 2110.
17. De Boer, J. S. A. M., Loopstra, B. O. and Stam, C. H. Recl. Trav. Chim. Pays-Bas 106 (1987) 537.