The Crystal Structure of 2-*p*-Chlorophenyl-3,3-dimethyl-1-methoxycyclopropene

Inger Søtofte[a] and Ingolf Crossland[b]

[a]Structural Chemistry Group, Chemistry Department B, DTH 301 and [b]Department of Organic Chemistry, DTH 201, The Technical University of Denmark, DK-2800 Lyngby, Denmark

Søtofte, I. and Crossland, I., 1989. The Crystal Structure of 2-*p*-Chlorophenyl-3,3-dimethyl-1-methoxycyclopropene. – Acta Chem. Scand. 43: 168–171.

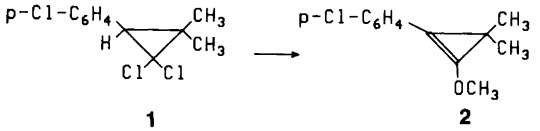
The title compound has been prepared and its structure investigated by X-ray diffraction techniques. The crystals are monoclinic, space group *Ic*, with a = 9.939 (5), b = 19.099(4), c = 5.828(4)Å and β = 91.60(5)°. The final R was 0.027. The angle between the cyclopropene ring and the phenyl ring is 12.6°. The methoxy group is nearly coplanar with the cyclopropene ring, the angle being 1.3°. The cyclopropene ring shows substantial bond asymmetry, the difference between the lengths of the two C_{sp^2}–C_{sp^3} bonds being 0.067Å.

The paucity of structural data on cyclopropenes,[1,2] and the special reactivity of 1-alkoxy-2-phenylcyclopropenes,[3] motivated the search for a crystalline derivative of one of the latter compounds. It turned out that the title compound was reasonably stable and could be induced to give crystals suitable for structural investigation (see Experimental).

Experimental

NMR spectra were recorded on Bruker WH-90 and HXE-90 instruments, using $CDCl_3$ as solvent.

Preparation of the title compound. Sulfuric acid-catalyzed elimination of water from the adduct of acetone and p-chlorobenzylmagnesium chloride gave a mixture of alkenes, which on dichlorocyclopropanation[4] gave crude cyclopropane **1**. Crystallization from MeOH (−20 °C) and recrystallization from hexane (0 °C) gave colourless crystals of **1** (Scheme 1), m.p. 61–63 °C. ^{1}H NMR: δ (ppm) 1.16 (s, 3H), 1.54 (s, 3H), 2.42 (s, 1H), 7.10–7.36 (m, 4H). A suspension of sodium methoxide (0.2 mol) and **1** (above, 12.5 g) in DMF (40 ml) was kept for one hour at −10 °C under N_2. The reaction mixture was rapidly quenched with hexane and water, and the aqueous phase extracted with hexane. The combined organic phases were washed with cold water and concentrated *in vacuo*. Crystallization was induced in cold MeOH (20 ml); yield 8.0 g (76 %) of **2**, m.p. 30–35 °C. After two recrystallizations from MeOH the product had m.p. 35–37 °C. ^{1}H NMR: δ (ppm) 1.38 (6H, s), 3.98 (3H, s) 7.20 (4H, m). ^{13}C NMR: δ (ppm) 24.7 (CH_3), 30.1 (C3), 60.6 (CH_3O), 90.0 (C2), 127.8, 128.2, 128.6, 131.2 (phenyl), 143.8 (C1). IR (KBr): 1845 cm^{-1} (vs). Crystals suitable for X-ray crystallographic work were kept at about 20 °C in an evacuated (0.1 mmHg) ampoule, and proved stable for several weeks; some sublimation took place. The product decomposes in the presence of atmospheric oxygen.



1 **2**

Scheme 1.

X-Ray technique. The possible space groups were established from Weissenberg photographs using Cu radiation. Unit cell dimensions and their standard deviations were determined by least-squares refinement based on reflections measured on a four-circle diffractometer (CAD-4F). By means of a conventional cryogenic device[5] utilizing a flow of cold nitrogen gas, the single crystal was cooled to 120 K. For data collection a crystal of dimensions 0.48×0.18×0.28 mm was used. Three-dimensional data with $\theta \leq 30°$ were measured on the four-circle diffractometer using monochromated Mo$K\alpha$ radiation and the ω-scan technique. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods[6] and Patterson techniques.[7] The calculations included full-matrix least-squares refinements of positional parameters and of anisotropic and isotropic thermal parameters, respectively, for non-hydrogen and hydrogen atoms.[8] The atomic scattering factors used for Cl, O and C were those given by Cromer and Mann,[9] and for H those given by Stewart *et al.*[10] The anomalous dispersion corrections were those given by Cromer and Lieberman.[11] There is a significant difference between the R values for the two possible enantiomorphic structures. A significance test made on the ratio of these R-values[12] shows that at a 0.005 level, the hypothesis that the enantiomorphic structure shown in Fig. 2 is incorrect can be rejected. The weights were of the form $w^{-1} = a + b\sigma^2(F_o) + c|F_o| + d|F_o|^2$ with the coefficients adjusted to

Table 1. Crystal data.

Formula	$C_{12}H_{13}ClO$
M_r	208.7
μ(Mo$K\alpha$)/cm^{-1}	3.08
Crystal system	Monoclinic
V/Å^3	1105.9
a/Å	9.939(5)
b/Å	19.099(4)
c/Å	5.828(4)
β/°	91.60(5)
Space group	$I\,c$ (No. 9)
D_c/g cm^{-3}	1.25
Z	4
Total number of refl.	1844
Number of independent refl. with $I \geq 2\sigma$ (I)	1520
Number of variables	177
$R = \Sigma(\|F_o\|-\|F_c\|)/\Sigma\|F_o\|$	0.027
$R_w = [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.032
$S = [\Sigma w(\|F_o\|-\|F_c\|)^2/(N_{obs}-N_{var})]^{\frac{1}{2}}$	1.15

Equiv. positions (0,0,0; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$): x,y,z; $x,\bar{y}$, $\frac{1}{2}+z$

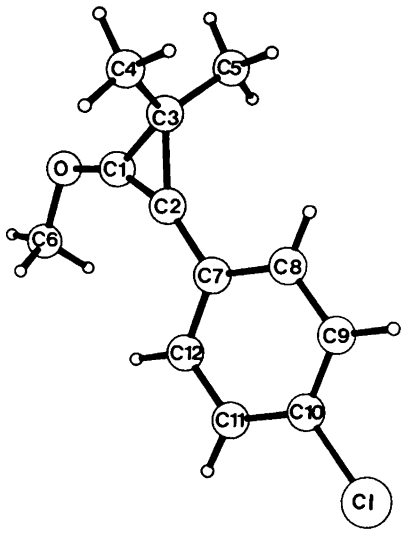


Fig. 1. The structure viewed along the *b*-axis.

give as uniform a distribution of $w|\Delta F|^2$ as possible.[13] For the illustrations the PLUTO programme[14] was used.

Crystal data and R-values are listed in Table 1. The final positional parameters with estimated standard deviations are listed in Table 2, and the labelling of the atoms is shown in Fig. 1. Lists of thermal parameters, and observed and calculated structure factors may be obtained from the authors on request.

Table 2. Atomic coordinates × 10^4. The estimated standard deviations × 10^4 are given in parentheses. The values of the hydrogen atoms are multiplied by 10^3. The isotropic temperature factors for the non-hydrogen atoms are estimated from the anisotropic values (Ref. 22).

Atom	x	y	z	B_{eq}[a]
C1	6513(2)	8166(1)	−4865(3)	2.0
C2	5857(2)	8540(1)	−3422(3)	1.8
C3	7403(2)	8610(1)	−3412(3)	2.0
C4	8020(3)	9260(1)	−4423(5)	3.0
C5	8232(2)	8278(1)	−1473(4)	2.7
C6	5275(3)	7428(1)	−7252(4)	2.8
C7	4690(2)	8769(1)	−2229(3)	1.7
C8	4850(2)	9142(1)	−172(3)	1.8
C9	3746(2)	9348(1)	1056(3)	2.0
C10	2474(2)	9181(1)	201(3)	2.0
C11	2278(2)	8823(1)	−1848(4)	2.1
C12	3382(2)	8616(1)	−3059(3)	2.0
O	6564(2)	7685(1)	−6526(3)	2.5
Cl	1082	9435(1)	1725	2.7
H1	823(3)	960(2)	−323(6)	3.9
H2	739(4)	950(2)	−550(6)	4.8
H3	893(3)	915(2)	−510(5)	3.4
H4	912(4)	813(2)	−204(6)	4.2
H5	841(3)	863(2)	−35(5)	3.4
H6	777(3)	786(2)	−83(6)	4.0
H7	474(3)	780(2)	−790(5)	3.4
H8	540(4)	707(2)	−835(7)	6.0
H9	479(3)	722(2)	−598(6)	4.2
H10	572(3)	922(1)	44(4)	2.1
H11	387(3)	963(1)	251(5)	2.7
H12	140(3)	872(1)	−253(4)	2.4
H13	325(3)	836(1)	−448(5)	2.3

[a] $B_{eq} = \frac{4}{3}\sum_i \sum_j b_{ij}\,(\mathbf{a}_i \cdot \mathbf{a}_j)$.

Description and discussion of the structure

Bond lengths, bond angles and torsion angles with their estimated standard deviations are listed in Tables 3 and 4. The cyclopropene ring shows substantial bond asymmetry, the difference between the lengths of the two C_{sp^2}–C_{sp^3} bonds being 0.067 Å. Compared to the bond length of 1.509 Å in unsubstituted cyclopropene, determined by microwave spectroscopy,[15] the C1–C3 bond is seen to be 0.034 Å shorter, whereas C2–C3 is 0.033 Å longer. The length of the C1–C2 double bond does not differ significantly from the value of 1.2956 Å found for cyclopropene. The deformation of the cyclopropene ring geometry is greater than reported for other cyclopropenes, and the ring bond pattern is quite the opposite of what is found for 3,3-dimethoxy-carbonyl-1-methyl-2-phenylcyclopropene[16] and 1-phenyl-2-methyl-cyclopropene-3-carboxylic acid,[17] where the longer of the two C_{sp^2}–C_{sp^3} bonds is opposite the phenyl substituent. Mainly due to the NO_2 substituent, a shortening of the two C_{sp^2}–C_{sp^3} bonds in 1,2-diphenyl-3-nitrocyclopropene is found,[18] whereas in 1,2,3-triphenyl-cyclopropene and in 3-isopropyl-1,2,3-triphenyl-cyclopropene[19] the geometry of the cyclopropene ring is in reasonably good agreement with that for cyclopropene itself.[15]

The phenyl substituent is expected to cause some bond-length deformations, although not as large as observed here, whereas the methyl groups appear to have no significant effect. It therefore appears that the methoxy group attached to a carbon atom involved in the cyclopropene C = C double bond has a great effect on the geometry of the ring.

To the best of the authors' knowledge, no structural data

Table 3. Bond distances (Å) and bond angles (°) with estimated standard deviations.

Atoms	Distance or angle
C1–C2	1.294(3)
C1–C3	1.475(3)
C1–O	1.336(2)
C2–C3	1.542(3)
C2–C7	1.437(3)
C3–C4	1.511(3)
C3–C5	1.518(3)
O–C6	1.425(3)
C7–C8	1.400(3)
C7–C12	1.405(3)
C8–C9	1.384(3)
C9–C10	1.383(3)
C10–C11	1.385(3)
C10–Cl	1.734(2)
C11–C12	1.379(3)
C2–C1–C3	67.3(1)
C2–C1–O	151.7(2)
C3–C1–O	140.9(2)
C1–C2–C3	61.9(1)
C1–C2–C7	155.6(2)
C3–C2–C7	142.2(2)
C1–C3–C2	50.7(1)
C1–C3–C4	119.4(2)
C1–C3–C5	119.4(2)
C2–C3–C4	118.9(2)
C2–C3–C5	119.1(2)
C4–C3–C5	114.6(2)
C1–O–C6	113.6(2)
C2–C7–C8	119.7(2)
C2–C7–C12	121.5(2)
C8–C7–C12	118.9(2)
C7–C8–C9	121.0(2)
C8–C9–C10	118.6(2)
C9–C10–C11	122.0(2)
C9–C10–Cl	119.0(2)
C11–C10–Cl	119.0(1)
C10–C11–C12	119.2(2)
C11–C12–C7	120.4(2)

Table 4. Selected torsion angles (°) with estimated standard deviations.

Atoms	Angle
C2–C1–C3–C4	−104.8(2)
C2–C1–C3–C5	105.1(2)
C7–C2–C3–C4	−79.1(3)
C7–C2–C3–C5	69.3(3)
C7–C2–C1–O	4.9(8)
C12–C7–C2–C1	−17.8(5)
C12–C7–C2–C3	172.9(2)
O–C1–C3–C4	77.0(3)
O–C1–C3–C5	−73.0(3)
C2–C1–O–C6	2.8(5)

on methoxy-substituted cyclopropanes or cyclopropenes have been published. If the effect of fluorine on the bond lengths of cyclopropane[2] may be used as a model for the similar effect of a methoxy substituent in cyclopropene, a lengthening of the distal bond should be expected. This is in agreement with the result given above. Further structural data are clearly required to rationalize the observed bond lengths.

The structural data give no clues as to the origin of the special reactivity of 1-alkoxy-2-phenylcyclopropene towards alkanols to give atropaldehyde acetals:[3,4] rupture takes place at C1–C3, i.e. it is the shortest of the two C_{sp^2}–C_{sp^3} bonds which is opened, and it is the longest (C2–C3) bond that gives rise to the double bond.

The variation of the ring geometry with substituents is dependent on each individual substituent, on the substitution site and on the conformation adopted by the π-acceptor or π-donor with respect to the ring.[1] Since the substitution patterns of the five structures[16–19] differ from that of the structure described here, a close comparison is not possible. However, it could be of interest to follow up this investigation by a systematic change of the substituents at sites 1 and 2.

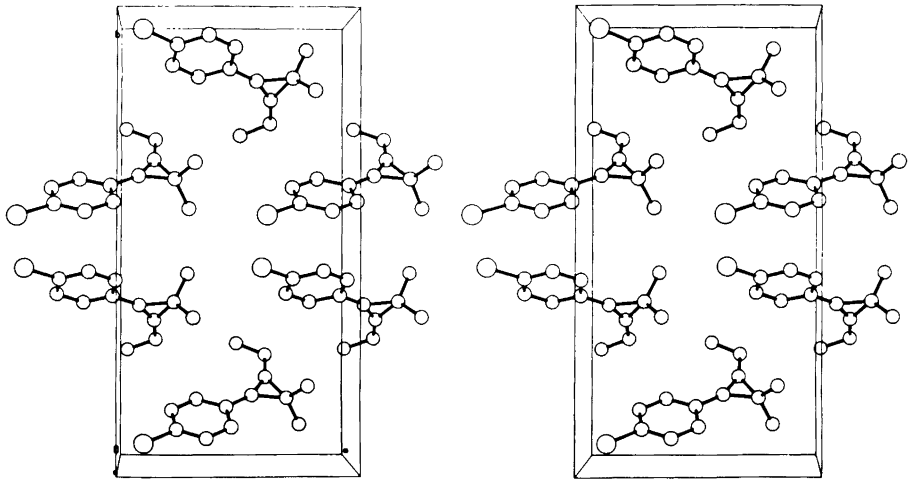


Fig. 2. Stereoscopic view along the c^*-axis of the structure.

Both the carbon and the oxygen atoms of the methoxy group are nearly coplanar with the cyclopropene ring, the angle between the two planes being 1.3°. The C–O bond length of 1.336 Å is, as expected as a result of the attachment to a double bond, somewhat shorter than found in methoxy groups substituted in benzene. The angle between the two methyl groups is the same [114.6(2)°] as the angle found between the two H atoms in cyclopropene. The C2–C7 bond length of 1.437(3)Å is in agreement with those of the bonds of attachment reported in Refs. 16–19.

The phenyl ring is nearly planar, the deviations of the atoms from the least-squares planes through them being less than 0.007 Å. The six distances average 1.389 Å, which compares quite well with the average of 1.387 Å reported in the survey by Allen.[2] The phenyl ring plane forms an angle of 12.6° with the plane of the cyclopropene ring, and the angle between the normal to the cyclopropene ring and the C2–C7–C10 line is 85.6°. The Cl atom is in the plane. The deformations of the endocyclic angles in the phenyl ring are almost symmetric around the C7–C10 line, with an angle of 122.0° at C10. This indicates a highly electronegative substituent bonded to C10.[20] The methoxy-substituted cyclopropene may have a small effect on the phenyl ring geometry, the C12–C7–C8 angle being somewhat smaller, and the C7–C8 and C7–C12 bond lengths being somewhat larger than expected to be caused by the chlorine atom.[20,21] The C–Cl bond length of 1.734 Å is similar to those found for other analogous compounds.

The packing of the structure is shown in Fig. 2. No intermolecular distances are less than the sum of relevant van der Waals radii, the shortest distance being the C5–C6 ($\frac{1}{2}+x$, $1\frac{1}{2}-y$, $1+z$) distance of 3.423 Å.

References

1. Allen, F. H. *Tetrahedron 38* (1982) 645 and references therein.
2. Allen, F. H. *Acta Crystallogr., Sect. B 36* (1980) 81 and references therein.
3. Crossland, I. *Acta Chem. Scand., Ser. B 41* (1987) 310.
4. Crossland, I. *Org. Synth. 60* (1981) 6.
5. van Bolhuis, F. *J. Appl. Crystallogr. 4* (1971) 263.
6. Main, P., Woolfson, M. M. and Germain, G. *MULTAN: A Computer Program for the Automatic Solution of Crystal Structures,* Department of Physics, University of York, York 1980.
7. Sheldrick, G. M. *SHELX-76: Program for Crystal Structure Determination,* University of Cambridge, U.K. 1976.
8. Stewart, J. M., Kundell, F. A. and Baldwin, J. C. *The X-Ray System, Version of 1972,* University of Maryland, College Park, MD 1972.
9. Cromer, D. T. and Mann, J. B. *Acta Crystallogr., Sect. A 24* (1980) 321.
10. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1980) 321.
11. Cromer, D. T. and Lieberman, D. J. *J. Chem. Phys. 53* (1970) 1891.
12. Hamilton, W. C. *Acta Crystallogr. 18* (1965) 502.
13. Nielsen, K. *Acta Crystallogr., Sect. A 33* (1977) 1009.
14. Motherwell, W. D. S. *PLUTO*: University of Cambridge, Cambridge 1976.
15. Stigliani, W. M., Laurie, V. W. and Li, J. C. *J. Chem. Phys. 62* (1975) 1890.
16. Rømming, C. and Berg, A. S. *Acta Chem. Scand., Ser. A 33* (1979) 271.
17. Korp, J. D., Bernal, I. and Fuchs, R. *Can. J. Chem. 61* (1983) 50.
18. Cheer, C. J., Bernstein, D., Greenberg, A. and Lyu, P.-C. *J. Am. Chem. Soc. 110* (1988) 226.
19. Domnin, I. N., Kopf, J., Keyaniyan, S. and De Meijere, A. *Tetrahedron 41* (1985) 5377.
20. Norrestam, R. and Schepper, L. *Acta Chem. Scand., Ser. A 35* (1981) 91.
21. Domenicano, A. and Murray-Rust, P. *Tetrahedron Lett. 24* (1979) 2283.
22. Hamilton, W. C. *Acta Crystallogr. 12* (1959) 609.

Received June 13, 1988.