

The Crystal Structure of 3,3-Dimethoxycarbonyl-1-methyl-2-phenylcyclopropene

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The crystal structure of the title compound has been determined by X-ray methods using 2210 observed reflections obtained by counter diffractometry. The crystals are monoclinic, space group $P2_1/c$, with four molecules per unit cell. The unit cell dimensions are: $a = 7.878(1) \text{ \AA}$; $b = 13.782(2) \text{ \AA}$; $c = 12.190(1) \text{ \AA}$; $\beta = 106.41(1)^\circ$. The structure was solved by direct methods and refined by full-matrix least-squares methods to a conventional R -factor of 0.041. Estimated standard deviations are 0.002 \AA in distances and $0.1\text{--}0.2^\circ$ in angles not involving hydrogen atoms.

The dimensions of the cyclopropene ring was found close to those reported for the free molecule. The phenyl ring is nearly coplanar with the cyclopropene moiety. The two methoxycarbonyl groups are planar and the planes form an angle of 47° with each other.

Treatment of dimethyl 2-bromo-1-phenylpropylenemalonate with a solution of sodium methoxide in methanol at room temperature for 25 h gave among other products a 19% yield of a compound assumed to be 3,3-dimethoxycarbonyl-1-methyl-2-phenylcyclopropene.¹ All spectroscopic data agreed with the cyclopropene structure. However, the band at 1900 cm^{-1} in the IR spectrum, probably owing to the skeletal vibration of the cyclopropene ring,² was weak and the two identical ester groups gave rise to strong absorptions at 1710 and 1740 cm^{-1} . Though β -diesters such as diethyl malonate (which does not enolise) also show two carbonyl bands,³ the isolation of a cyclopropene under these conditions was somewhat unexpected and the structure was further investigated by X-ray crystallographic methods.

EXPERIMENTAL

A crystal grown from a mixture of ether and pentane ground to approximate spheric form, diameter 0.35 mm , was used for the X-ray experiments. Unit cell dimensions were calculated from diffractometer measurements of 15 general reflections using $\text{MoK}\alpha$ -radiation ($\lambda = 0.71069 \text{ \AA}$). Intensity data were recorded at 18°C using a SYNTEX P1 diffractometer with graphite crystal monochromated $\text{MoK}\alpha$ radiation. All independent reflections with $\sin \theta/\lambda < 0.54 \text{ \AA}^{-1}$ were measured using the $\theta/2\theta$ scan technique, so were reflections with $\sin \theta/\lambda$ between 0.54 and 0.75 \AA^{-1} if a quick scan showed the intensity to be larger than a preset value. The scan speed was $2\text{--}4^\circ \text{ min}^{-1}$ depending on the intensity and the scan range from 0.7° below $2\theta(\alpha_1)$ to 0.9° above $2\theta(\alpha_2)$, background counts were taken for 0.35 times the scan time at each of the scan range limits. Three standard reflections were measured after every 100 reflections; they showed no systematic variation during the experiment. 2210 reflections were recorded as observed, the intensities being larger than 2.5 times their standard deviations. The intensity data were corrected for Lorentz and polarization effects; no absorption or extinction corrections were applied.

Atomic form factors used were those of Doyle and Turner⁴ for oxygen and carbon, and of Stewart, Davidson and Simpson⁵ for hydrogen. A description of the computer programs employed is given in Ref. 6.

CRYSTAL DATA

3,3-Dimethoxycarbonyl-1-methyl-2-phenylcyclopropene, $\text{C}_{14}\text{H}_{14}\text{O}_4$, monoclinic, $a = 7.878(1) \text{ \AA}$; $b = 13.782(2) \text{ \AA}$; $c = 12.190(1) \text{ \AA}$; $\beta = 106.41(1)^\circ$, ($t = 18^\circ \text{C}$). $V = 1269.6 \text{ \AA}^3$; $F(000) = 529$; $Z = 4$; $M =$

246.26; $D_x = 1.289 \text{ g cm}^{-1}$. $\mu(\text{MoK}\alpha) = 1.02 \text{ cm}^{-1}$. Absent reflections: $(0k0)$ for k odd, $(h0l)$ for l odd. Space group $P2_1/c$ (No. 14).

STRUCTURE DETERMINATION

The structure was solved by the use of the program assembly MULTAN;⁷ hydrogen atom positions were calculated from stereochemical considerations. Refinements were performed by full-matrix least-squares calculations minimizing the function $\sum w(\Delta F)^2$, where the weights were taken as the inverse of the variance in the structure factors. Positional parameters were refined for all atoms; for the oxygen and carbon atoms anisotropic thermal parameters were refined. The hydrogen atoms of the methyl groups were refined with a common isotropic thermal parameter, as were the phenyl hydrogen atoms. The refinements terminated with a conventional R -factor of 0.041, $R_w = 0.046$

and $S = [\sum w(\Delta F)^2 / (n - m)]^{1/2}$ of 1.84. The corresponding atomic parameters are listed in Table 1.

The structure factor list may be obtained from the authors. Structural data are given in Table 2; estimated standard deviations are calculated from the correlation matrix. The numbering of the atoms may be seen from Fig. 1.

DISCUSSION

The assumption of the molecular constitution based on spectroscopic evidence was confirmed by the X-ray analysis.

The cyclopropene ring dimensions differ slightly from those found for the cyclopropene ring in the gas phase investigated by microwave spectroscopy⁸ and by electron diffraction.⁹ The double bond, 1.283(2) Å, may be shorter than that measured in the gas phase, 1.300(1) Å (MW) and 1.304(3) Å (ED), the difference being 7–9 times the combined

Table 1. Fractional atomic parameters and thermal parameters with estimated standard deviations. The temperature factor is given as $\exp[-2\pi^2(U_{11}a^2h^2 + \dots + 2U_{23}b^*c^*kl)]$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	.2429(1)	.1497(1)	.3604(1)	.0410(6)	.0411(6)	.0636(7)	-.0026(5)	.0224(5)	-.0036(5)
O2	.6743(2)	-.0155(1)	.2374(1)	.0554(7)	.0474(7)	.0720(8)	.0111(6)	.0335(6)	.0035(6)
O3	.2196(2)	-.0097(1)	.3281(1)	.0486(7)	.0425(7)	.0805(9)	-.0098(5)	.0289(6)	-.0036(6)
O4	.5855(2)	-.0753(1)	.3819(1)	.0628(8)	.0475(7)	.0635(8)	.0143(6)	.0202(6)	.0148(6)
C1	.4680(2)	.1497(1)	.2047(1)	.0354(7)	.0392(8)	.0475(9)	.0012(6)	.0153(7)	.0071(7)
C2	.5571(2)	.1742(1)	.3062(1)	.0343(7)	.0323(7)	.0472(9)	.0019(6)	.0153(7)	.0048(6)
C3	.4670(2)	.0762(1)	.2982(1)	.0340(7)	.0331(7)	.0418(8)	-.0008(6)	.0118(6)	.0015(6)
C4	.6696(2)	.2362(1)	.3926(1)	.0299(7)	.0337(7)	.0454(9)	.0031(6)	.0145(6)	.0019(6)
C5	.7210(2)	.3272(1)	.3630(2)	.0402(8)	.0364(8)	.0511(10)	.0019(6)	.0141(7)	.0057(7)
C6	.8261(2)	.3861(1)	.4461(2)	.0536(10)	.0386(9)	.0699(13)	-.0085(8)	.0183(9)	-.0004(9)
C7	.8819(3)	.3556(2)	.5582(2)	.0506(10)	.0595(12)	.0605(12)	-.0104(9)	.0120(9)	-.0138(10)
C8	.8341(2)	.2651(2)	.5876(2)	.0490(10)	.0655(12)	.0438(10)	.0015(9)	.0114(8)	.0018(9)
C9	.7273(2)	.2054(1)	.5054(1)	.0427(8)	.0434(9)	.0485(10)	.0015(7)	.0180(7)	.0061(7)
C10	.3916(3)	.1623(2)	.0810(2)	.0509(11)	.0709(14)	.0469(10)	-.0077(10)	.0090(8)	.0131(10)
C11	.2996(2)	.0650(1)	.3316(1)	.0350(7)	.0373(8)	.0352(8)	.0004(6)	.0077(6)	.0020(6)
C12	.0811(3)	.1463(2)	.3937(2)	.0411(9)	.0643(13)	.0639(12)	.0076(9)	.0220(9)	-.0029(10)
C13	.5785(2)	-.0137(1)	.3122(1)	.0337(7)	.0342(8)	.0443(8)	-.0029(6)	.0072(6)	-.0032(7)
C14	.7908(3)	-.0977(2)	.2456(3)	.0564(12)	.0553(12)	.0944(17)	.0136(10)	.0321(12)	-.0073(12)

Atom	x	y	z	B	Atom	x	y	z	B
H5	.685(3)	.346(2)	.283(2)	4.8(2)	H6	.863(3)	.449(2)	.422(2)	4.8
H7	.956(3)	.400(2)	.615(2)	4.8	H8	.872(3)	.243(2)	.662(2)	4.8
H9	.690(3)	.143(2)	.526(2)	4.8	H121	.057(4)	.210(2)	.410(2)	7.0(2)
H122	.096(4)	.106(2)	.457(3)	7.0	H123	-.018(4)	.121(2)	.332(2)	7.0
H141	.856(4)	-.084(2)	.190(2)	7.0	H142	.728(4)	-.156(2)	.231(2)	7.0
H143	.880(4)	-.097(2)	.315(3)	7.0	H101	.413(3)	.224(2)	.057(2)	7.0
H102	.270(4)	.148(2)	.058(2)	7.0	H103	.444(4)	.113(2)	.041(2)	7.0

Table 2. Structural data.

Bond	(Å)	Bond	(Å)	Bond	(Å)
C1–C2	1.283(2)	C2–C3	1.517(2)	C1–C3	1.527(2)
C2–C4	1.448(2)	C4–C5	1.396(3)	C5–C6	1.377(3)
C6–C7	1.377(3)	C7–C8	1.380(3)	C8–C9	1.383(3)
C9–C4	1.388(2)	C1–C10	1.467(3)	C3–C11	1.495(2)
C11–O3	1.201(2)	C11–O1	1.332(2)	O1–C12	1.443(2)
C3–C13	1.499(2)	C13–O4	1.193(2)	C13–O2	1.338(2)
O2–C14	1.443(2)				
Angle	(°)	Angle	(°)	Angle	(°)
C3–C1–C2	64.7(1)	C1–C2–C3	65.5(1)		
C2–C3–C1	49.8(1)	C3–C2–C4	138.7(1)		
C1–C2–C4	155.8(1)	C2–C4–C5	120.3(1)		
C2–C4–C9	120.2(1)	C4–C5–C6	119.8(2)		
C5–C6–C7	120.5(2)	C6–C7–C8	119.9(2)		
C7–C8–C9	120.3(2)	C8–C9–C4	119.9(2)		
C9–C4–C5	119.5(2)	C2–C1–C10	156.0(2)		
C3–C1–C10	139.3(2)	C2–C3–C11	120.5(1)		
C2–C3–C13	118.7(1)	C1–C3–C11	117.6(1)		
C1–C3–C13	120.5(1)	C11–C3–C13	114.7(1)		
C3–C11–O3	124.9(1)	C3–C11–O1	111.6(1)		
O3–C11–O1	123.3(1)	C11–O1–C13	115.7(1)		
C3–C13–O4	125.3(1)	C3–C13–O2	111.3(1)		
O4–C13–O2	123.4(1)	C13–O2–C14	116.0(2)		
Torsion angle	(°)	Torsion angle	(°)		
C10–C1–C3–C11	–70.2(3)	C10–C1–C3–C13	78.4(3)		
C4–C2–C3–C11	78.6(2)	C2–C3–C11–O1	3.5(2)		
C2–C3–C13–O2	–56.0(2)	C1–C3–C11–O1	–54.1(2)		
C13–C3–C11–O1	155.6(1)	C11–C3–C13–O2	151.4(1)		
C2–C1–C10–H101	–4(2)	C11–O1–C12–H121	–179(2)		
C13–O2–C14–H141	–175(2)				

standard deviations. If the difference is real, it can be rationalized by a slightly smaller *p*-contribution to the hybridization of the C1 and C2 atoms in the present compound relative to that in cyclopropene.⁸ This is in accordance with an opening of the C2–C1–C10 and C1–C2–C4 angles [156.0(2)° and 155.8(2)°] as compared to the corresponding C=C–H angles observed in cyclo-

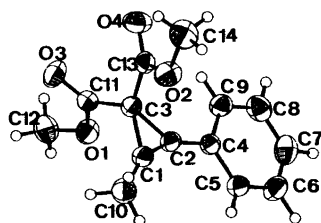


Fig. 1. ORTEP plot of the molecule.

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propene (149.9° (MW), 132.9(2.5)° (ED)). The C1–C10 and C2–C4 bond lengths observed correspond to a covalent single bond radius of 0.705 Å for C1 and C2, slightly closer to the C(*sp*) single bond radius than to that of C(*sp*²). The C1–C3 and C2–C3 bond lengths are as found for cyclopropene within the accuracy of the determinations. The C11–C3–C13 angle is the same (114.7(1)°) as the methylenic H–C–H bond angle (114.9(2)°, MW) in cyclopropene.

The methyl group (C10) has one of its hydrogen atoms *syn planar* to the C1–C2 bond with respect to the C1–C10 bond. The atoms of the phenyl ring are coplanar and exhibit normal bond lengths and angles. The phenyl ring plane forms an angle of 3° with the plane of the cyclopropene ring.

The geometries of the two ester groups are identical and correspond closely to that reported, *e.g.* in Ref. 10. C1 is situated in the plane formed by

C3–C13(O4)–O2–C14 and C2 is situated in the plane of the other ester group. The planes of the groups form an angle of 47° with each other.

No intermolecular distances are less than the sum of relevant van der Waals radii.

REFERENCES

1. Berg, A. S. *Acta Chem. Scand.* To be published.
2. Closs, G. L. In Hart, H. and Karabatsos, G. J., Eds., *Adv. Alicyclic Chem.* 1 (1966) 73.
3. Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*, Chapman and Hall, London 1975, p. 211.
4. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* 24 (1968) 390.
5. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
6. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
7. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
8. Kasai, P. H., Myers, R. J., Eggers, D. E. and Wiberg, K. B. *J. Chem. Phys.* 30 (1959) 512.
9. Chiang, J. F. *J. Chin. Chem. Soc. (Taipei)* 17 (1970) 65.
10. Carr, P., Finney, J. L., Lindley, P. F. and De Titta, G. T. *Acta Crystallogr. B* 33 (1977) 1022.

Received October 20, 1978.