547.12

THE STRUCTURE OF DIMETHYL
1,1'-DIMETHYLBICYCLOPROPYL-2,2'-DICARBOXYLATE

BY

C. JONGSMA * and H. VAN DER MEER **

Introduction

De Wolf and *Bickelhaupt* [1] synthesized a mixture of stereoisomers of dimethyl 1,1'-dimethylbicyclopropyl-2,2'-dicarboxylates ($C_{12}H_{18}O_4$) from which they obtained one of the six [2] possible stereoisomers in crystalline form (see Fig. 1).
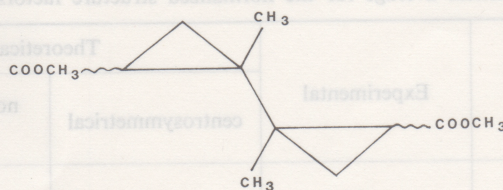

Fig. 1.   Structureformula.

To establish the stereochemistry of this compound and to aid in the interpretation of the NMR spectra of this and the other stereoisomers, an X-ray determination of the crystal structure was undertaken.

Crystal data

Recrystallization from methanol provided suitable crystals. The crystals are monoclinic with the following cell constants, found from Weissenberg films calibrated with Al-powder lines:

$$a = 12.460 \pm 0.001 \text{ Å}$$
$$b = 9.019 \pm 0.001 \text{ Å}$$
$$c = 11.806 \pm 0.001 \text{ Å}$$
$$\beta = 109.28° \pm 0.01°$$

* Laboratory of Organic Chemistry, Vrije Universiteit, Amsterdam, The Netherlands.
** Laboratory of Crystallography, Amsterdam, The Netherlands.
[1] *W. H. de Wolf* and *F. Bickelhaupt*, Rec. Trav. Chim. **89**, 0000 (1970).
[2] *G. Schrumpf* und *W. Lüttke*, L. Ann. Chem. **730**, 100-110 (1969).

The density determined by flotation in a solution of NaCl was 1.15 g/cm³. This leads to a unit cell contents of 4 molecules. The systematic absences indicate either the space group Cc or C2/c.

With an automatic Nonius diffractometer 739 independent non-zero observed intensities were collected; CuKα radiation was used. Since the crystal deteriorated fairly rapidly during the measurements, a correction for the decay was applied. The intensities were corrected further for Lorentz and polarization factors, absorption being neglected.

Determination

The structure was solved by the symbolic addition procedure. The statistical data obtained with the Wilson scaling of the intensities clearly indicated the existence of a centre of symmetry (see Table I). The space group therefore is C2/c.

Table I

Statistical average for the normalized structure factors

	Experimental	Theoretical	
		centrosymmetrical	non-centrosym-metrical
$< \mid E \mid >$	.776	.798	.886
$< \mid E^2-1 \mid >$	1.029	.968	.736
$< \mid E^2 \mid >$	.953	1.000	1.000

Procentual distribution of the normalized structure magnitudes $\mid E \mid$

$\mid E \mid >$	Experimental	Theoretical	
		centrosymmetrical	non-centrosym-metrical
3.0	.25	.27	.01
2.5	1.13	1.24	.19
2.0	4.41	4.55	1.83
1.8	7.18	7.19	3.92
1.6	11.34	10.96	7.73
1.4	17.13	16.15	14.09
1.2	23.43	23.01	23.69
1.0	32.12	31.73	36.79

Using the semi-automatic set of programs developed by *Schenk* [3] two acceptable solutions were found, which did not differ appreciably according to the criteria described by *Schenk*. A physically plausible structure could be found in one of the two E-maps. This model refined smoothly, the hydrogen atoms could be located in a difference Fourier-synthesis and the refinement was terminated at $R = 0.062$.

In Table II the coordinates and temperature factors are listed together with their estimated standard deviations. The resulting bond lengths, bond angles and some non-bonded distances are presented in Fig. 2.
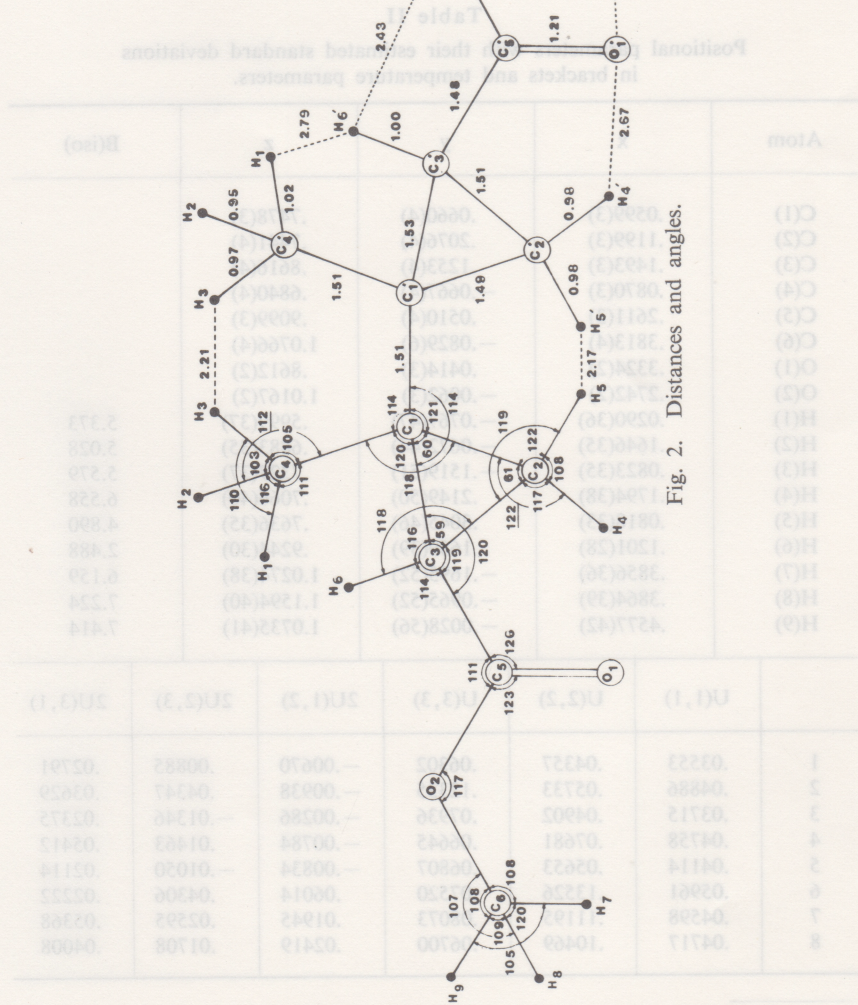
Table II

Positional parameters with their estimated standard deviations in brackets and temperature parameters.

Atom	x	y	z	B(iso)
C(1)	.0599(3)	.0660(4)	.7478(3)	
C(2)	.1199(3)	.2076(4)	.7441(4)	
C(3)	.1493(3)	.1253(4)	.8616(4)	
C(4)	.0870(3)	−.0667(4)	.6840(4)	
C(5)	.2611(3)	.0510(4)	.9099(3)	
C(6)	.3813(4)	−.0829(6)	1.0766(4)	
O(1)	.3324(2)	.0414(3)	.8612(2)	
O(2)	.2742(2)	−.0062(3)	1.0167(2)	
H(1)	.0290(36)	−.0767(47)	.5999(37)	5.373
H(2)	.1646(35)	−.0672(44)	.6883(35)	5.028
H(3)	.0823(35)	−.1519(51)	.7327(37)	5.579
H(4)	.1794(38)	.2149(50)	.7066(40)	6.558
H(5)	.0818(33)	.3045(46)	.7636(35)	4.890
H(6)	.1201(28)	.1659(39)	.9244(30)	2.488
H(7)	.3856(36)	−.1695(52)	1.0274(38)	6.159
H(8)	.3864(39)	−.0965(52)	1.1594(40)	7.224
H(9)	.4577(42)	−.0028(56)	1.0735(41)	7.414

	U(1,1)	U(2,2)	U(3,3)	2U(1,2)	2U(2,3)	2U(3,1)
1	.03553	.04357	.06302	−.00670	.00885	.02791
2	.04886	.05733	.12335	−.00938	.04347	.03629
3	.03715	.04902	.07936	−.00286	−.01346	.02375
4	.04758	.07681	.06645	−.00784	.01463	.05412
5	.04114	.05653	.06807	−.00834	−.01050	.02114
6	.05961	.13526	.07520	.06014	.04306	.02222
7	.04598	.11195	.08073	.01945	.02595	.05368
8	.04717	.10469	.06700	.02419	.01708	.04008

[3] *H. Schenk*, Automation of the Symbolic Addition Method, diss. Amsterdam.

The numbering of the atoms C(2) and C(3) in this article is interchanged with respect to the IUPAC conventions, which lists them as C(3) and C(2), respectively; in the title the IUPAC numbering is given.

Description of the structure

Following the nomenclature of *Schrumpf* and *Lüttke* [2] this compound is the syn-*trans,trans*-dimethyl 1,1'-dimethyl bicyclopropyl-2,2'-dicarboxylate. The molecule lies on a twofold rotation axis, passing through the midpoint of the bond joining the two cyclopropane rings. We find no short central C—C bond as reported by *Eraker* and *Rømming* [4] for bicyclopropyl.
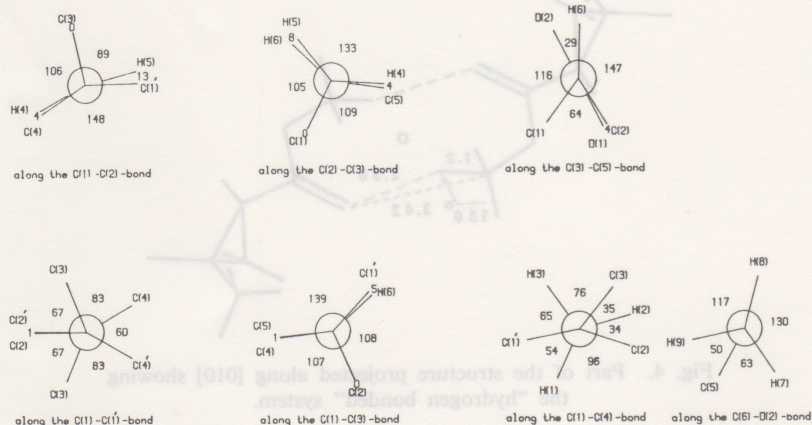

Fig. 3. Newman projections.

The relative orientation of the cyclopropane rings shows the following features. The planes of the rings make an angle of 60° with each other. In the Newman projection along the C(1)—C(1') bond (see Fig. 3) it can be seen, that the bonds C(1)—C(1'), C(1)—C(2), C(1')—C(2') lie in one plane. It seems probable that the interaction between H(5) and H(5') effects a small distortion at C(2): the plane H(4)C(2)H(5) makes an angle of 83° with the plane of the ring, while H(6)C(3)C(5) is nearly perpendicular to it (89°) and the H(4)C(2)H(5)-angle is 108° in contrast with the 114° of H(6)C(3)C(5) and C(1')C(1)C(4). A comparable interaction occurs between the hydrogen atoms H(3) and H(3'). The Newman projection along the C(1)—C(4) bond shows a completely staggered conformation, with H(2) favourable situated with respect to the ring. Where rotation of

[4] *J. Eraker* and *C. Rømming*, Acta Chem. Scand. **21**, 2721-2726 (1967).

the methyl group would bring H(2) in a less favourable situation, the strain seems to be released mostly by deformation of the C(4)—H(3) bond, as can be seen by considering the small angle H(3)C(4)H(2) of 103°. The intermolecular H—H distances range from 2.3 to 2.9 Å. A peculiar fact is the configuration of the carboxyl oxygen O(1) and one of the hydrogen atoms of the ester methyl group H(8), which simulates a hydrogen-bonded system around the centre of inversion (see Fig. 4). A similar situation is reported by *Dougill* and *Jeffrey* [5] in dimethyl oxalate and by *Gaultier* [6] in 1,4-naphthoquinone.
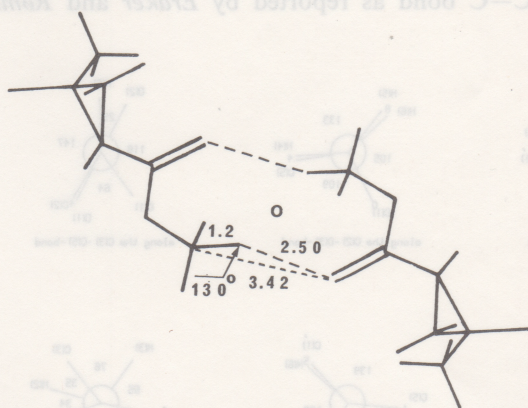

Fig. 4.   Part of the structure projected along [010] showing the "hydrogen bonded" system.

Acknowledgement

[5] *M. W. Dougill* and *G. A. Jeffrey*, Acta Cryst. **6**, 831-837 (1953).
[6] *J. Gaultier*. Thèses fac. des Siences, Bordeaux 1966, 38.