

The Structures of Ethyl 1,2,2-Tricyano-3,3-dimethylcyclopropane-1-carboxylate and Ethyl 2',3',3'-Tricyanocyclohexanespirocyclopropane-2'-carboxylate

BY N. RAMASUBBU, J. RAJARAM AND K. VENKATESAN*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

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Abstract

The crystal and molecular structures of $C_{11}H_{11}N_3O_2$ (I) and $C_{14}H_{15}N_3O_2$ (II) have been determined by direct methods using three-dimensional X-ray diffractometer data. Crystals of (I) are orthorhombic, space group $Pna2_1$, with $a = 14.662$ (6), $b = 10.492$ (5), $c = 7.375$ (3) Å, $Z = 4$, $V = 1134.5$ Å³, $D_o = 1.25$ (by flotation), $D_c = 1.269$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.085$ mm⁻¹. Crystals of (II) are monoclinic, space group $P2_1/a$, with $a = 7.886$ (5), $b = 22.011$ (8), $c = 8.100$ (3) Å, $\beta = 103.12$ (5)°, $Z = 4$, $V = 1369.2$ Å³, $D_o = 1.23$ (by flotation), $D_c = 1.255$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.080$ mm⁻¹. Least-squares full-matrix refinement based on 782 (I) and 1400 independent reflections (II) converged at $R = 0.040$ (I) and 0.042 (II). The effect of electron-withdrawing substituents on the geometry of the cyclopropane ring is discussed.

Introduction

The crystal and molecular structures of the title compounds have been investigated as part of a programme of studies on substituted cyclopropanes. The cyclopropane ring has continued to be of interest both to synthetic and theoretical chemists. Of particular interest is the nature of chemical bonds in cyclopropane and its response to neighbouring π centres. It is a well established fact that the cyclopropane ring undergoes significant geometrical changes under the influence of electron-withdrawing substituents (Lemley, Skarstad & Hughes, 1976; Allen, 1980; Usha & Venkatesan, 1980). The Walsh model (Walsh, 1947, 1949) of bonding in cyclopropane has provided a useful model for the interpretation of the effect of substituents on ring geometry (Hoffmann, 1970, 1971).

Experimental

The compounds (I) and (II) were prepared by synthetic routes for substituted cyclopropanes reported in the

literature (Popp, 1960; Hesse, 1896; Kim & Hart, 1969). The compounds (I) and (II) were first characterized by IR and NMR spectroscopic techniques. Good, colourless single crystals were obtained by repeated recrystallization from a 1:1 ethanol–acetone mixture.

The lattice parameters were determined from a least-squares analysis of setting angles of 15 (I) and 25 reflections (II), which were centred on a CAD-4 automatic four-circle diffractometer using Mo $K\alpha$ radiation. Three-dimensional intensity data were collected on a CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation by the $\omega/2\theta$ scan in the range $0^\circ \leq 2\theta \leq 45^\circ$, using a scan speed of 1° min^{-1} .

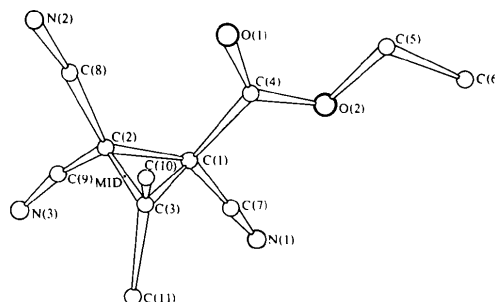


Fig. 1. Projection of the asymmetric unit of (I) down the c axis together with the numbering scheme.

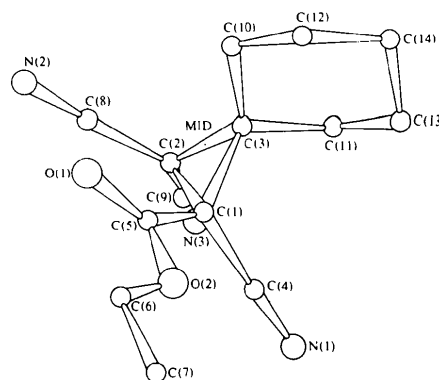


Fig. 2. Projection of the molecule (II) down the c axis together with the numbering scheme.

* To whom correspondence should be addressed.

The dimensions of the crystals used were $0.2 \times 0.3 \times 0.5$ (I) and $0.8 \times 0.25 \times 0.07$ mm (II). During data collection, the intensities of two reflections were monitored and showed only statistical variations. A total of 1126 (I) and 2067 reflections (II) were collected. Reflections with $|F_o| < 2\sigma(|F_o|)$ were rejected as insignificant. A total of 782 (I) and 1400 reflections (II) were used in all subsequent calculations. No absorption correction was applied.

Structure determination and refinement

The structures of (I) and (II) were solved by the direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971). Figs. 1 and 2 show views of the molecules (I) and (II) respectively down the *c* axes. Since the intensity distribution of normalized structure factors was clearly non-centric for (I), the space group *Pna2*₁ was chosen and successful X-ray analysis of the structure in this space group confirms the choice. The *E* maps with the highest combined figure of merit (CFOM) calculated from 160 reflections (I) with $E > 1.28$ and 180 reflections (II) with $E > 1.66$ revealed the positions of all non-H atoms of (I) and (II). In the initial stages a large-block least-squares method (program by Shiono, 1968), modified by B. S. Reddy to suit an IBM 360/44 computer, was used with isotropic temperature factors for all atoms. The *R* factor converged at 0.121 (I) and 0.144 (II). The H atoms were stereochemically fixed and then located in a difference Fourier synthesis. Refining the non-H atoms anisotropically and the H atoms isotropically gave an *R* index of 0.048 for both (I) and (II). Full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1961) led to a final *R* value of 0.040 (I) and 0.042 (II). H atoms were not refined in the final two cycles of full-matrix refinement. The function mini-

Table 1. Final fractional positional parameters for non-H atoms ($\times 10^5$) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

	$B_{eq.} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
O(1)	49002 (19)	57903 (26)	13156	5.34 (8)
O(2)	41099 (17)	73579 (23)	395 (68)	4.86 (8)
N(1)	25187 (28)	62785 (33)	-28087 (83)	5.13 (10)
N(2)	50761 (28)	27877 (36)	8936 (90)	6.80 (13)
N(3)	28738 (26)	26007 (33)	-27872 (78)	5.26 (10)
C(1)	34758 (21)	53541 (30)	-1705 (78)	3.04 (8)
C(2)	35927 (21)	38931 (31)	-1602 (71)	3.15 (9)
C(3)	29529 (23)	45266 (31)	11865 (77)	3.28 (9)
C(4)	42596 (24)	61782 (33)	4862 (73)	3.58 (9)
C(5)	47950 (30)	83036 (40)	6501 (121)	7.31 (18)
C(6)	44320 (36)	95479 (41)	3999 (112)	7.50 (20)
C(7)	29536 (25)	58762 (32)	-16668 (75)	3.37 (9)
C(8)	44425 (27)	33187 (36)	4490 (80)	4.26 (10)
C(9)	31916 (25)	31805 (32)	-16662 (78)	3.58 (10)
C(10)	32310 (31)	45536 (39)	31732 (73)	4.58 (12)
C(11)	19383 (23)	43685 (33)	8756 (81)	4.00 (10)

mized was $\sum w(|F_o| - |F_c|)^2$ where *w* is of the form $(12 + |F_o| + 0.03 |F_o|^2)^{-1}$ for (I) and $(25 + |F_o| + 0.025 |F_o|^2)^{-1}$ for (II). The final atomic positional parameters for all the atoms in (I) and (II) are listed in Tables 1 and 2.* The bond lengths and bond angles involving all the non-H atoms are listed in Tables 3-6.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36172 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final fractional positional parameters for non-H atoms ($\times 10^5$) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

	$B_{eq.} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
O(1)	48248 (26)	28016 (9)	93094 (25)	4.98 (6)
O(2)	70610 (21)	34427 (8)	100439 (22)	3.80 (5)
N(1)	74787 (31)	43090 (12)	67581 (33)	5.25 (8)
N(2)	23060 (33)	23236 (12)	60213 (34)	5.64 (9)
N(3)	42277 (34)	35821 (13)	29934 (31)	5.41 (9)
C(1)	50567 (29)	36425 (11)	75070 (31)	2.96 (7)
C(2)	37340 (30)	33757 (11)	59738 (31)	3.20 (7)
C(3)	32049 (30)	39007 (10)	69851 (31)	3.18 (7)
C(4)	64379 (33)	40069 (12)	70933 (32)	3.37 (7)
C(5)	56232 (31)	32391 (11)	90525 (31)	3.34 (7)
C(6)	77482 (35)	30716 (13)	115509 (33)	4.22 (8)
C(7)	94246 (47)	33455 (17)	124315 (47)	7.13 (13)
C(8)	29927 (33)	27777 (13)	60953 (34)	3.72 (8)
C(9)	40387 (31)	34925 (12)	43150 (33)	3.55 (7)
C(10)	19041 (34)	37840 (13)	80682 (37)	4.10 (9)
C(11)	29793 (34)	45204 (12)	61362 (35)	3.73 (8)
C(12)	20288 (42)	42928 (15)	93714 (39)	5.21 (11)
C(13)	31483 (40)	50121 (13)	74908 (40)	4.64 (10)
C(14)	18147 (43)	49197 (14)	85528 (42)	5.14 (11)

Table 3. Bond lengths involving non-H atoms (Å) with e.s.d.'s in parentheses (I)

C(1)-C(2)	1.542 (5)	C(1)-C(3)	1.531 (6)
C(1)-C(4)	1.518 (5)	C(1)-C(7)	1.452 (7)
C(2)-C(3)	1.520 (6)	C(2)-C(8)	1.455 (5)
C(2)-C(9)	1.462 (7)	C(3)-C(10)	1.521 (8)
C(3)-C(11)	1.514 (5)	C(4)-O(1)	1.192 (5)
C(4)-O(2)	1.300 (5)	C(5)-O(2)	1.482 (6)
C(5)-C(6)	1.422 (7)	C(7)-N(1)	1.138 (7)
C(8)-N(2)	1.132 (6)	C(9)-N(3)	1.127 (7)

Table 4. Bond lengths involving non-H atoms (Å) with e.s.d.'s in parentheses (II)

C(1)-C(2)	1.545 (3)	C(1)-C(3)	1.534 (3)
C(1)-C(4)	1.452 (4)	C(1)-C(5)	1.517 (3)
C(2)-C(3)	1.528 (3)	C(2)-C(8)	1.453 (4)
C(2)-C(9)	1.441 (4)	C(3)-C(10)	1.515 (4)
C(3)-C(11)	1.520 (4)	C(4)-N(1)	1.136 (4)
C(5)-O(1)	1.194 (3)	C(5)-O(2)	1.311 (3)
C(6)-O(2)	1.466 (3)	C(6)-C(7)	1.481 (5)
C(8)-N(2)	1.132 (4)	C(9)-N(3)	1.131 (4)
C(10)-C(12)	1.527 (4)	C(11)-C(13)	1.525 (4)
C(12)-C(14)	1.524 (5)	C(13)-C(14)	1.516 (5)

Table 5. Bond angles ($^\circ$) involving non-H atoms with *e.s.d.*'s in parentheses (I)

C(2)—C(1)—C(3)	59.3 (3)	C(1)—C(3)—C(10)	119.0 (4)
C(2)—C(1)—C(4)	118.7 (4)	C(1)—C(3)—C(11)	117.1 (4)
C(2)—C(1)—C(7)	116.0 (4)	C(2)—C(3)—C(10)	118.2 (4)
C(3)—C(1)—C(4)	119.6 (4)	C(2)—C(3)—C(11)	117.4 (4)
C(3)—C(1)—C(7)	116.6 (4)	C(10)—C(3)—C(11)	114.3 (4)
C(4)—C(1)—C(7)	115.3 (4)	O(1)—C(4)—O(2)	126.0 (4)
C(1)—C(2)—C(3)	60.0 (3)	O(1)—C(4)—C(1)	124.5 (4)
C(1)—C(2)—C(8)	120.6 (4)	O(2)—C(4)—C(1)	109.5 (4)
C(1)—C(2)—C(9)	117.4 (4)	O(2)—C(5)—C(6)	108.8 (5)
C(3)—C(2)—C(8)	120.5 (4)	N(1)—C(7)—C(1)	177.8 (5)
C(3)—C(2)—C(9)	118.2 (4)	N(2)—C(8)—C(2)	175.0 (5)
C(8)—C(2)—C(9)	111.5 (4)	N(3)—C(9)—C(2)	177.7 (5)
C(1)—C(3)—C(2)	60.8 (3)	C(4)—O(2)—C(5)	116.5 (4)

Table 6. Bond angles ($^\circ$) involving non-H atoms with *e.s.d.*'s in parentheses (II)

C(2)—C(1)—C(3)	59.5 (2)	C(2)—C(3)—C(11)	117.0 (2)
C(2)—C(1)—C(4)	115.4 (2)	C(10)—C(3)—C(11)	112.9 (2)
C(2)—C(1)—C(5)	117.4 (2)	N(1)—C(4)—C(1)	177.6 (3)
C(3)—C(1)—C(4)	116.7 (2)	O(1)—C(5)—O(2)	125.9 (2)
C(3)—C(1)—C(5)	121.9 (2)	O(1)—C(5)—C(1)	123.2 (2)
C(4)—C(1)—C(5)	114.7 (2)	O(2)—C(5)—C(1)	110.9 (2)
C(1)—C(2)—C(3)	59.9 (2)	O(2)—C(6)—C(7)	107.2 (2)
C(1)—C(2)—C(8)	119.9 (2)	N(2)—C(8)—C(2)	172.6 (3)
C(1)—C(2)—C(9)	117.2 (2)	N(3)—C(9)—C(2)	178.0 (3)
C(3)—C(2)—C(8)	119.1 (2)	C(3)—C(10)—C(12)	109.3 (2)
C(3)—C(2)—C(9)	119.3 (2)	C(3)—C(11)—C(13)	109.2 (2)
C(8)—C(2)—C(9)	112.3 (2)	C(10)—C(12)—C(14)	112.3 (3)
C(1)—C(3)—C(2)	60.6 (2)	C(11)—C(13)—C(14)	110.8 (3)
C(1)—C(3)—C(10)	120.3 (2)	C(12)—C(14)—C(13)	110.2 (3)
C(1)—C(3)—C(11)	117.6 (2)	C(5)—O(2)—C(6)	115.1 (2)
C(2)—C(3)—C(10)	119.0 (2)		

Results and discussion

Cyclopropane geometry

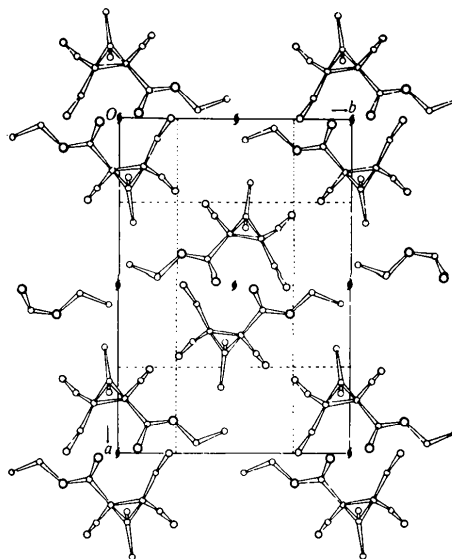
The focal point of this structural study is to see the effect of four strong electron-withdrawing substituents on the cyclopropane geometry.

The analysis by Hoffmann (1970, 1971) suggests that the bond C(1)—C(2) flanked by these four electron-withdrawing substituents should be significantly longer than the average bond length found in the unsubstituted cyclopropane molecule (Bastiansen, Fritsch & Hedberg, 1964). This prediction clearly agrees with our observation for (I) and (II) where the bond length C(1)—C(2) is 1.542 (5) *vs* 1.510 Å in (I) and 1.545 (3) *vs* 1.510 Å in (II). It is interesting to note that even though there are four strongly electron-withdrawing groups in these molecules, the observed bond length C(1)—C(2) in (I) and (II) is significantly shorter than that found in 1,1,2,2-tetracyanocyclopropane [Lemley *et al.*, 1976; 1.559 (2) Å], in 2,5-dimethyl-7,7-dicyanonorcaradiene [Fritchie, 1966; 1.557 (2) Å] and in 3-(2-methoxyphenyl)-1,1,2,2-cyclopropanetetracarbonitrile [Usha & Venkatesan, 1980; 1.557 (3) Å].

In the present cases the dihedral angles O(1)—C(4)—C(1)—MID for (I) and O(1)—C(5)—C(1)—MID for (II) are 20.1 (6) and 15.1 (4) $^\circ$ respectively and the molecules fall in the *cg* conformation (Allen, 1980). It appears that such a deviation from the bisected conformation may be responsible for the observed shorter bond length of C(1)—C(2) in (I) and (II). The observed bond lengths C(2)—C(3) and C(1)—C(3) for (II) are significantly longer than 1.510 Å [1.528 (3) and 1.534 (3) Å respectively]. The observed pattern in (I) also shows this trend even though the standard deviations are slightly large. These significant variations from the expected ring bond-length pattern as suggested by Hoffmann (1970, 1971) analysis may arise partially from the steric interactions between the all-*cis* substituents in these two molecules.

The C \equiv N bond lengths in (I) and (II) lie in the range 1.126 (7)—1.136 (4) Å and agree well with the values obtained for this group in other related studies (Usha & Venkatesan, 1980). We also observe significant non-linearity in the C—CN groups (Tables 5 and 6). This effect has been discussed in detail by Matthews, Swanson, Mueller & Stucky (1971).

The ethoxycarbonyl group in both these structures has an extended conformation with torsion angles C(1)—C(4)—O(2)—C(5) 177.5 (3) and C(4)—O(2)—C(5)—C(6) 167.5 (5) $^\circ$ in (I) and the corresponding angles C(1)—C(5)—O(2)—C(6) 178.11 (20) and C(5)—O(2)—C(6)—C(7) 175.82 (24) $^\circ$ in (II). The bond lengths for C(6)—C(7) and O(2)—C(6) found in (II) agree well with the corresponding values found in 5-ethoxycarbonyl-3,4'-diethyl-4,3',5'-trimethyl-2,2'-dipyrrolyl ketone (Sheldrick, Becker & Engel, 1978) [1.481 (5) *vs* 1.471 (8) Å

Fig. 3. Packing of the molecules of (I) viewed down the *c* axis.

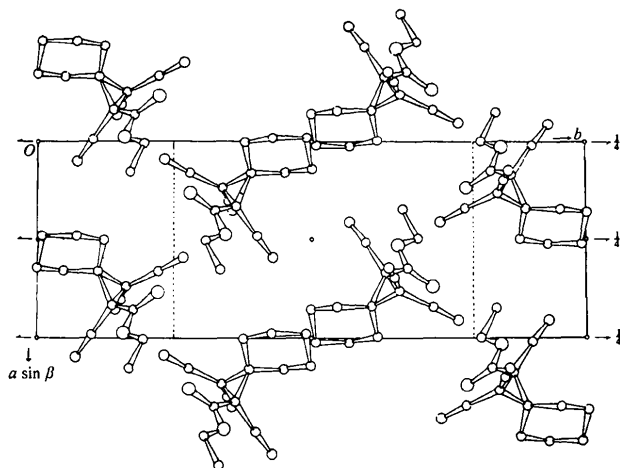
Fig. 4. Packing of the molecules of (II) viewed down the *c* axis.

Table 7. Some selected intermolecular contacts (<3.5 Å) in (I)

O(1 ^l)...C(8 ^{ll})	3.326 (6)	O(1 ^l)...C(9 ^{ll})	3.346 (6)
O(1 ^l)...C(2 ^{ll})	3.427 (6)	O(2 ^{ll})...N(2 ^l)	3.282 (6)

Symmetry code: (i) x, y, z ; (ii) $-x, -y, \frac{1}{2} + z$.

Table 8. Some selected intermolecular contacts (<3.5 Å) in (II)

N(2 ^l)...C(1 ^{ll})	3.173 (4)	N(2 ^l)...C(4 ^{ll})	3.166 (4)
N(2 ^l)...C(5 ^{ll})	3.283 (4)	N(2 ^l)...C(2 ^{ll})	3.198 (4)
N(2 ^l)...C(9 ^{ll})	3.184 (4)		

Symmetry code: (i) x, y, z ; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

and 1.466 (3) vs 1.459 (5) Å respectively]. The values for C(5)–C(6) 1.422 (7) and O(2)–C(5) 1.482 (6) Å in (I) deviate from the values in (II). However, this disagreement appears to be due to the large thermal motion of the terminal atoms of the end ethyl group in (I).

The cyclohexyl group in (II) exists in a chair form. The geometry of the cyclohexyl group agrees well with values reported by Dunitz & Strickler (1966). The packing of the molecules (I) and (II) viewed down the *c* axes is presented in Figs. 3 and 4 respectively. In (I),

O(1) makes close approaches to C(8), C(9) and C(2), all electron deficient, indicating the possibility of a weak acid–base interaction (Table 7). In (II), one of the N atoms, N(2), makes close approaches to electron-deficient atoms C(1), C(2), C(9) and C(4) (Table 8). If we accept 3.4 Å as the van der Waals distance for a C...N contact with no acid–base character (Witt, Britton & Mahon, 1972), then the observed C...N contacts indicate a weak acid–base interaction. Such an interaction has also been found in 3-(2-methoxyphenyl)-1,1,2,2-cyclopropanetetracarbonitrile (Usha & Venkatesan, 1980).

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