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The Structure of Cyclopropane-1,1-dicarboxamide

BY R. USHA AND K. VENKATESAN*

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

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Abstract. $C_5H_8N_2O_2$, $M_r = 128$, monoclinic, *Cc* or *C*2/*c*, $a = 10{\cdot}236\ (2)$, $b = 6{\cdot}432\ (2)$, $c = 9{\cdot}444\ (2)$ Å, $\beta = 104{\cdot}62\ (2)°$, $V = 601{\cdot}6$ Å^3, $Z = 4$, $D_m = 1{\cdot}42$, $D_x = 1{\cdot}413$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å) = 0·12 mm^{-1}, $F(000) = 272$. The structure, which was solved by direct methods in the space group *C*2/*c*, has been refined to an *R* value of 5·2% using 464 intensity measurements. The C=O and C–N bonds of the amide groups show unusual bond lengths. A rotational-disorder mechanism which would account for both the bond-length anomaly and the space-group ambiguity, has been proposed.

Introduction. In an effort to assess the effect of substituents on cyclopropane geometry, we began a study of substituted cyclopropanes with cyclopropane-1,1-dicarboxamide. Such a study was motivated by recent observations (Lauher & Ibers, 1975; Jason & Ibers, 1977) which indicate that more work, both structural and theoretical, is needed to resolve the questions still surrounding the substituent–cyclopropane interaction.

A sample of cyclopropane-1,1-dicarboxamide, kindly supplied by Dr P. Balaram, was recrystallized from ethanol by slow evaporation at room temperature (~298 K). Preliminary Weissenberg photographs indicated the monoclinic space group *Cc* or *C*2/*c*. Since the number of molecules in the unit cell was found to be four, either *Cc* or *C*2/*c* could be chosen with the molecules in general positions in the former, and with the molecular twofold axis coinciding with the crystallographic twofold axis in the latter. Intensity data were collected with a crystal 0·2 × 0·5 × 0·3 mm on a CAD-4 diffractometer using monochromated Mo $K\alpha$ radiation by the $\omega/2\theta$ scan technique to a limit of $\theta = 25°$ using a scan speed of 1° min^{-1}. Two reflections, 150 and 404, were checked after every fifty reflections and they showed only statistical variations. A total of 560 reflections were measured, of which 464 were significant [$|F_o| > 2\sigma(|F_o|)$]. Corrections were then made for Lorentz and polarization factors but not for absorption.

The structure was solved by direct methods using the program *MULTAN* (Germain, Main & Woolfson, 1971) in the space group *C*2/*c*. This space group was chosen as the distribution of normalized structure factors was clearly centrosymmetric.

A difference Fourier map calculated after a few cycles of block-diagonal least-squares refinement with isotropic temperature factors for the non-hydrogen atoms (which converged at a rather high *R* value of 22·6%) showed electron densities on either side of each atom. Further refinement with anisotropic temperature factors brought the *R* factor down to 9·4%. At this stage the C=O and C–N bonds of the amide groups showed lengths of 1·280 and 1·283 Å respectively in contrast to 1·260 and 1·328 Å for the corresponding bonds in cyclopropanecarboxamide (Long, Maddox & Trueblood, 1969). Refinement in *Cc* did not solve the problem either. Like biuret in its metal complexes (Saito, Machida & Uno, 1970), there are three possible conformations for the title compound (Fig. 1). The *cis–cis* and *trans–trans* forms possess a twofold axis of symmetry, whereas the *trans–cis* form does not. Therefore in *C*2/*c* the structure could only be the *cis–cis* or the *trans–trans* form. The *cis–cis* form could be ruled out because of the proximity of the hydrogens. The *trans–trans* form too has the drawback of having short N···N intermolecular contacts. The *trans–cis* form in *Cc* also is not free from short intermolecular contacts. A disorder mechanism which involves the rotation of the *trans–cis* form through 180° along the dotted line shown in Fig. 1, following the application of any of the symmetry elements of space group *Cc* and also translations along the *x*, *y* or *z* directions, converts all the hitherto N···N short contacts into N–H···O=C hydrogen bonds. Presumably, in any micro-region, neighbouring molecules have identical *trans–cis* forms in order to facilitate the formation of hydrogen-bonded chains. But, overall, the averaged aspect of the molecule is twofold. Thus the distribution of normalized structure factors is centrosymmetric and the C=O and C–N distances are nearly the same with disorder appearing as a pseudo-vibration of the O/N and N/O atoms and a pair of half-hydrogen atoms on each. Peaks corresponding to these four hydrogens appeared in a difference map at strengths ranging from 0·25 to 0·6 e Å^{-3}. Block-diagonal least-squares refinement with atoms corresponding to the mean of N and O instead of oxygen and nitrogen atoms and with four half-weight hydrogens in place of two full N–H hydrogens resulted

* To whom correspondence should be addressed.

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in an R index of 5·2% in $C2/c$. However, refinement of these disordered H atoms resulted in very high standard deviations in their positional and thermal parameters. Therefore the stereochemically fixed H atoms were used for the calculations of the hydrogen-bond parameters (Table 3). Consequently, the standard deviations in the H···A lengths and D–H···A angles are not recorded. The N/O–H distances are also omitted from the table. The quantity minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$. The program used was that of Shiono (1968) modified by B. S. Reddy for use on an IBM 360/44 computer. The occurrence of unexplained residual electron densities (up to 0·25 e Å^{-3}) in the final difference synthesis lends further support to the disorder. This is reminiscent of the situation encountered in the study of a crystalline enamine (Brown, Damm, Dunitz, Eschenmoser, Hobi & Kratky, 1978) which has space-group ambiguity between $P1$ and $P\bar{1}$.

Positional parameters of the non-hydrogen atoms are given in Table 1,* bond distances and angles in Table 2 and details of the hydrogen bonding in Table 3.

* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34584 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

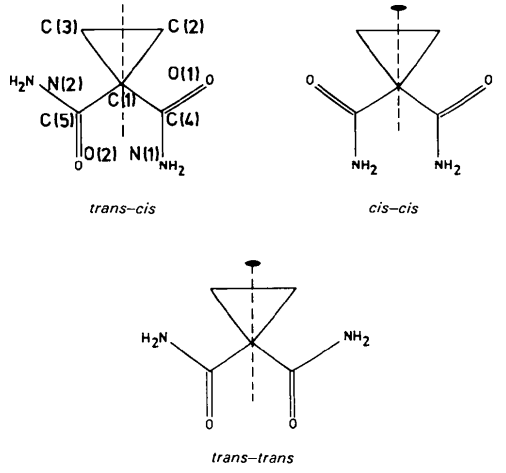

Fig. 1. The three possible conformations of cyclopropane-1,1-dicarboxamide.

Table 1. *Fractional coordinates* (×10^4) *of the non-hydrogen atoms with e.s.d.'s in parentheses*

	x	y	z
C(1)	5000 (0)	521 (8)	2500 (0)
C(2)	5420 (5)	2608 (6)	1982 (6)
C(4)	6094 (4)	−630 (7)	3570 (5)
O/N(1)	6977 (4)	369 (5)	4514 (5)
O/N(2)	6126 (3)	−2623 (5)	3519 (4)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·527 (7)	C(2)–C(1)–C(3)	57·3 (3)
C(1)–C(3)	1·527 (7)	C(1)–C(2)–C(3)	61·4 (3)
C(1)–C(4)	1·500 (6)	C(1)–C(3)–C(2)	61·4 (3)
C(2)–C(3)	1·456 (7)	C(2)–C(1)–C(4)	115·3 (3)
C(4)–O/N(1)	1·272 (6)	C(1)–C(4)–O/N(1)	120·0 (4)
C(4)–O/N(2)	1·283 (5)	C(1)–C(4)–O/N(2)	119·3 (4)
C(2)–H(1)	0·97 (3)	O/N(1)–C(4)–O/N(2)	120·7 (4)
C(2)–H(2)	1·02 (4)		

Table 3. *Details of the hydrogen bonds,* D–H···A

D	H	A	D···A	H···A	D–H···A
O/N(2)^{i}	H(3)^{i}	···O/N(2)^{ii}	2·603 (5) Å	2·00 Å	143°
O/N(2)^{i}	H(4)^{i}	···O/N(1)^{iii}	2·919 (5)	2·25	172
O/N(1)^{iv}	H(5)^{iv}	···O/N(1)^{i}	3·001 (5)	2·38	151

Symmetry code

(i)	x,y,z	(ii)	$1-x, y, \frac{1}{2}-z$
(iii)	$1{\cdot}5-x, -\frac{1}{2}-y, 1-z$	(iv)	$1{\cdot}5-x, \frac{1}{2}-y, 1-z$

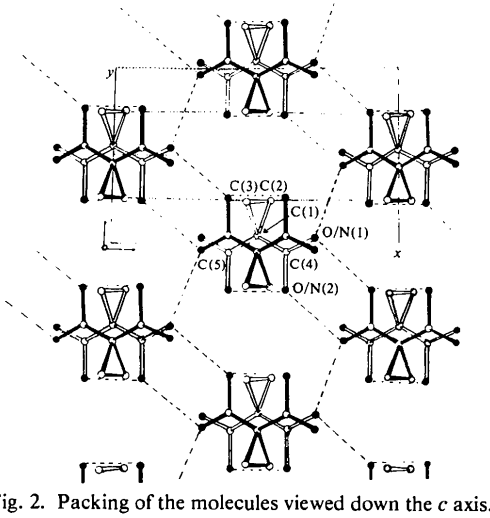

Fig. 2. Packing of the molecules viewed down the c axis.

Discussion. Fig. 2 shows the packing of the molecules viewed down the c axis. The disorder, mentioned earlier, results in intermolecular hydrogen bonding in addition to the intramolecular hydrogen bonds present in the *trans–cis* model.

The amide-group atoms do not deviate significantly from coplanarity. The plane through the amide group is orthogonal to the cyclopropane plane.

The abnormality of the C=O and C–N lengths has already been discussed. The average C–C distance in the cyclopropyl ring is 1·503 Å which is comparable to that in the monocarboxamide, 1·498 Å (Long, Maddox & Trueblood, 1969), and is not significantly shorter than the value found for gaseous cyclopropane, 1·510

Å (Bastiansen, Fritsch & Hedberg, 1964) and for the corresponding dicarboxylic acid, 1·510 Å (Meester, Schenk & MacGillavry, 1971). However, the individual lengths within the ring show remarkable differences. Those involving the C atom which connects the amide groups are 1·527 Å and the 'back' ring bond is 1·456 Å. Similarly, in cyclopropane-1,1-dicarboxylic acid (Meester, Schenk & MacGillavry, 1971), cyclopropanecarboxamide (Long, Maddox & Trueblood, 1969) and cyclopropanecarbohydrazide (Chesnut & Marsh, 1958), the bond between the unsubstituted C atoms is the smaller one (1·462, 1·481 and 1·478 Å respectively). In all these cases, the overlapping substituent has the 'bisecting' orientation and the appropriate π orbitals are parallel.

These structural results are easily explained by the Walsh (1949) model. As shown by Hoffmann (1970), transfer of π electron density out of the Walsh orbital to a substituent will weaken the adjacent bonds for which this orbital has bonding character. The orbital has antibonding character for the bond across the ring from the point of substitution and thus that bond is strengthened by a withdrawal of electron density from the orbital. The orbitals of the substituent can only overlap with the Walsh orbital if the molecule is in the 'bisecting' orientation.

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The Structure and Absolute Configuration of Ajugareptansin *p*-Bromobenzoate

BY X. SOLANS AND C. MIRAVITLLES

Departamento de Cristalografía y Mineralogía, Universidad de Barcelona, Sección de Cristalografía del Instituto 'Jaime Almera' del CSIC, Granvia 585, *Barcelona* 7, *Spain*

AND J. P. DECLERCQ* AND G. GERMAIN

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, 1 *place Louis Pasteur, B*-1348 *Louvain-la-Neuve, Belgium*

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Abstract. $C_{36}H_{47}BrO_{11}$, $M_r = 733{\cdot}7$, monoclinic, $P2_1$, $a = 14{\cdot}152\ (5)$, $b = 15{\cdot}662\ (4)$, $c = 8{\cdot}182\ (2)$ Å, $\beta = 93{\cdot}31\ (3)°$, $Z = 2$, $V = 1810\ (1)$ Å^3, $D_m = 1{\cdot}30$, $D_c = 1{\cdot}35$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 1·27 mm^{-1}. Crystals of this derivative of ajugareptansin were isolated from *Ajuga reptans*. The structure was refined to an R of 0·070 for 1591 observed reflexions. The absolute configuration was determined by the Bijvoet method. Rings A and B of the diterpene group are *trans*-fused, adopting skew-boat and chair conformations, respectively.

Introduction. Ajugareptansin is a compound isolated from *Ajuga reptans* (Camps, Coll, Cortel & Messeguer, 1979) with an antifeeding activity for insects. It is a diterpenoid with a clerodane skeleton.

A tentative structure was assigned by Camps, Coll, Cortel & Messeguer (1979) from spectral (IR, UV, mass and NMR) and chemical methods. In order to confirm this structure and to determine unambiguously its absolute configuration, we have undertaken an X-ray study of ajugareptansin *p*-bromobenzoate (I).

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