$C_{14}H_{10}N_4O_2S$

Table 3. *Relevant parameters of the* O=S⟨N,O *and* O=S⟨N,N *and* O=S⟨O,O *groups* O=S⟨O,O *groups assumes an axial or a*

	S=O	S–N	OSN	NSN	OSNC
Title compound	1·452 Å	1·705 Å	104·5°	102·1°	80·5°
		1·669	107·0		−76·7
BOTSTZ*	1·430	1·717	107·0	90·6	75·6
		1·705	107·8		−80·1
CATZQO†	1·439	1·741	111·9	82·9	91·8
		1·716	108·5		−96·5
PHTDZO‡	1·478	1·692	110·5	97·2	128·2
		1·692	110·5		−128·2
	S–O	OSO	OSO	OSOC	
o-Phenylene	1·427	1·670	107·7	93·0	−90·3
sulphite§		1·670	107·7		90·3

* L'Abbé, van Asch, Declercq, Germain & Van Meerssche (1978).

† Reimlinger, Vandewalle, King, Lingier & Merényi (1970).

‡ Arora (1974).

§ Schultz, Serke & Kapovits (1979).

exhibits a similarly short S=O distance [1·433 (5) Å] accompanied by two S–O single bonds [1·669 (4) Å]. Accordingly, as claimed by Bennett, Cotton, Weaver, Williams & Watson (1967), it must be assumed that S is using at least one d orbital from back-accepting π electrons from O. However, the bond order 2·5 for the S=O distance of 1·476 Å calculated by Bennett and co-workers has to be taken with care. It seems to be overestimated. At any rate these S=O distances approach those of the sulphone groups [cf., for example, 1·431–1·439 (1) Å of Kálmán et al. (1981)]. As shown by the corresponding torsional angles in Table 3, except in PHTDZO, the exo O atom of both

pseudoaxial orientation. The thiatriazine ring possesses an envelope conformation [$Q = 0·36$ Å, $\varphi = 245·4°$, $\theta = 113·8°$ (Cremer & Pople, 1975)], to which a coplanar benzimidazole ring system is fused. The 4-phenoxy group is bound equatorially. The C(8)–O(7)–C(6)–N(1) torsion angle is 11·3° (synperiplanar). The dihedral angle between the best planes of the phenyl rings is 85·2°. Dimeric associates related by a centre of symmetry are formed via hydrogen-bond pairs: N(14)–H···N(3): 2·864 (1), 2·02 (3) Å, 153 (2)°.

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Structure of Ethyl 1,2,2-Tricyano-3-(4-nitrophenyl)cyclopropane-1-carboxylate

By N. Ramasubbu and K. Venkatesan

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

Abstract. $C_{15}H_{10}N_4O_4$, monoclinic, $P2_1/c$, $a = 10·694$ (8), $b = 11·743$ (8), $c = 12·658$ (8) Å, $\beta = 113·10$ (7)°, $V = 1462·1$ Å³, $Z = 4$, $D_m = 1·38$, $D_c = 1·408$ g cm⁻³, μ(Mo $K\alpha$, $\lambda = 0·7107$ Å) = 0·99 cm⁻¹, $F(000) = 640$. The structure was solved by direct methods and refined to an R value of 0·054 using 1398 intensity measurements. The relative magnitudes of interaction of the substituents and the extent to which a ring can accommodate interactions with substituents are discussed.

Table 1. *Fractional coordinates* $(\times 10^4$, *for* H $\times 10^3)$ *and isotropic temperature factors*

For non-hydrogen atoms $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$. E.s.d.'s are in parentheses.

	x	y	z	B_{eq}/B (Å²)
O(1)	7668 (3)	5018 (3)	3386 (2)	5·14 (8)
O(2)	7419 (3)	4288 (3)	4946 (2)	4·89 (8)
O(3)	−1034 (3)	4019 (3)	−1493 (3)	6·88 (12)
O(4)	−1079 (3)	2528 (4)	−545 (3)	7·28 (12)
N(1)	5216 (4)	2184 (4)	4359 (3)	5·63 (10)
N(2)	5407 (4)	868 (3)	1719 (3)	5·06 (9)
N(3)	8464 (4)	3289 (4)	1749 (3)	5·78 (11)
N(4)	−486 (4)	3339 (4)	−736 (3)	4·84 (11)
C(1)	6089 (4)	3524 (3)	3157 (3)	2·88 (8)
C(2)	6294 (3)	2926 (3)	2138 (3)	2·90 (8)
C(3)	5226 (3)	3852 (3)	1938 (3)	2·89 (8)
C(4)	5578 (4)	2790 (4)	3831 (3)	3·47 (9)
C(5)	7163 (4)	4380 (4)	3841 (3)	3·86 (10)
C(6)	8526 (5)	5018 (5)	5748 (4)	6·63 (15)
C(7)	7902 (6)	5906 (5)	6198 (5)	8·23 (20)
C(8)	5807 (4)	1769 (4)	1896 (3)	3·45 (8)
C(9)	7516 (4)	3148 (3)	1932 (3)	3·71 (9)
C(10)	3713 (4)	3682 (3)	1290 (3)	3·25 (7)
C(11)	3083 (4)	4383 (4)	360 (4)	4·43 (10)
C(12)	1695 (4)	4288 (4)	−307 (4)	4·59 (11)
C(13)	972 (4)	3457 (4)	−22 (3)	3·75 (9)
C(14)	1566 (4)	2766 (4)	899 (3)	4·46 (11)
C(15)	2955 (4)	2860 (4)	1558 (3)	4·02 (10)
C(6)H(1)	913 (7)	528 (6)	537 (5)	5·7 (1·8)
C(6)H(2)	915 (5)	456 (4)	641 (4)	2·7 (1·1)
C(7)H(1)	736 (5)	556 (4)	660 (4)	2·7 (1·1)
C(7)H(2)	886 (9)	621 (7)	693 (7)	10·5 (2·5)
C(7)H(3)	725 (7)	646 (6)	544 (6)	7·7 (2·0)
C(11)H	351 (4)	489 (4)	9 (3)	1·4 (0·8)
C(12)H	127 (6)	470 (4)	−97 (5)	2·2 (0·8)
C(14)H	104 (6)	227 (5)	112 (5)	4·0 (2·0)
C(15)H	336 (3)	238 (3)	217 (3)	2·0 (0·7)
C(10)H	557 (3)	460 (3)	175 (3)	2·0 (0·8)

Table 2. *Bond lengths* (Å) *involving non-hydrogen atoms*

O(1)—C(5)	1·195 (6)	C(1)—C(5)	1·517 (6)
O(2)—C(5)	1·319 (5)	C(2)—C(3)	1·525 (5)
O(2)—C(6)	1·491 (6)	C(2)—C(8)	1·444 (6)
O(3)—N(4)	1·208 (6)	C(2)—C(9)	1·453 (6)
O(4)—N(4)	1·220 (6)	C(3)—C(10)	1·513 (6)
N(1)—C(4)	1·142 (6)	C(6)—C(7)	1·467 (9)
N(2)—C(8)	1·130 (6)	C(10)—C(11)	1·376 (6)
N(3)—C(9)	1·137 (7)	C(10)—C(15)	1·385 (6)
N(4)—C(13)	1·470 (6)	C(11)—C(12)	1·395 (7)
C(1)—C(2)	1·557 (5)	C(12)—C(13)	1·378 (7)
C(1)—C(3)	1·504 (5)	C(13)—C(14)	1·356 (6)
C(1)—C(4)	1·461 (6)	C(14)—C(15)	1·394 (6)

Table 3. *Bond angles* (°) *involving non-hydrogen atoms*

O(3)—N(4)—O(4)	123·0 (4)	N(1)—C(4)—C(1)	177·3 (5)
O(3)—N(4)—C(13)	119·6 (4)	O(1)—C(5)—O(2)	128·1 (4)
O(4)—N(4)—C(13)	117·4 (4)	O(1)—C(5)—C(1)	121·6 (4)
C(2)—C(1)—C(3)	59·7 (2)	O(2)—C(5)—C(1)	110·3 (4)
C(2)—C(1)—C(4)	115·1 (3)	O(2)—C(6)—C(7)	108·2 (5)
C(2)—C(1)—C(5)	116·8 (3)	N(2)—C(8)—C(2)	178·4 (4)
C(3)—C(1)—C(4)	122·0 (3)	N(3)—C(9)—C(2)	177·6 (5)
C(3)—C(1)—C(5)	116·0 (3)	C(3)—C(10)—C(11)	116·4 (3)
C(4)—C(1)—C(5)	115·5 (3)	C(3)—C(10)—C(15)	124·3 (3)
C(1)—C(2)—C(3)	58·4 (2)	C(11)—C(10)—C(15)	119·3 (4)
C(1)—C(2)—C(8)	116·4 (3)	C(10)—C(11)—C(12)	121·1 (4)
C(1)—C(2)—C(9)	119·7 (3)	C(11)—C(12)—C(13)	118·1 (4)
C(3)—C(2)—C(8)	116·9 (3)	N(4)—C(13)—C(12)	118·3 (4)
C(3)—C(2)—C(9)	120·6 (3)	N(4)—C(13)—C(14)	120·0 (4)
C(8)—C(2)—C(9)	113·9 (3)	C(12)—C(13)—C(14)	121·8 (4)
C(1)—C(3)—C(2)	61·9 (2)	C(13)—C(14)—C(15)	119·7 (4)
C(1)—C(3)—C(10)	128·2 (3)	C(10)—C(15)—C(14)	119·8 (4)
C(2)—C(3)—C(10)	124·6 (3)		
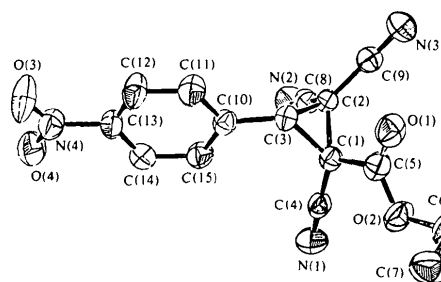
Introduction. The cyclopropane ring undergoes drastic geometrical changes under the influence of electron-withdrawing and -donating substituents; these changes were discussed earlier (Usha & Venkatesan, 1980). Continuing our studies on substituent effects on ring geometry, we report here the structure of a cyclopropane derivative in which all the substituents are electron withdrawing in nature.

The compound was prepared by procedures reported in the literature (Hesse, 1896; Popp, 1960; Kim & Hart, 1969). Suitable crystals were grown from an ethanol : acetone mixture. Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer using a crystal of dimensions 0·5 ×0·4 × 0·2 mm (λ = 0·7107 Å, $\omega/2\theta$ scan) in the range $0° \le 2\theta < 45°$. The stability and quality of the crystal were monitored by repeatedly measuring the intensities of two reflections every 2000 s. The analysis was based on 1398 reflections with $|F_o| > 2\sigma(|F_o|)$, out of a total of 2268.

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). The

Fig. 1. A perspective view of the molecule down the *b* axis.

block-diagonal least-squares refinement with anisotropic thermal parameters for C, N and O atoms converged at R = 0·08. A difference synthesis computed at this stage revealed the H atoms at stereochemically meaningful positions. The final cycles of full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1961), with H atoms given isotropic thermal parameters and other atoms anisotropic, converged at an R value of 0·054. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where w is of the form $(25 + |F_o| + 0·025|F_o|^2)^{-1}$ (Cruickshank, 1961).

$C_{15}H_{10}N_4O_4$

Atomic coordinates are given in Table 1.* Geometric details of the structure are in Tables 2 and 3. A perspective view of the molecule down the *b* axis is shown in Fig. 1.

Discussion. There are five substituents of three kinds attached to the cyclopropane ring. In a situation like this one could expect to observe (i) a distribution due to cumulative interaction of all the substituents or (ii) selective interaction of substituents with the ring based on the electronegativity of the groups attached to the ring. In order to observe a situation as in (i), all the substituents must be in the required conformations and the ring must be capable of accommodating all the interactions. The ethoxycarbonyl and nitrophenyl groups are in a bisected conformation with the dihedral angles C(15)—C(10)—C(3)—*M*(1) −17·3 (6)° and O(1)—C(5)—C(1)—*M*(2) 5·9 (6)°. [*M*(1) and *M*(2) are the mid-points of C(1)—C(2) and C(2)—C(3) respectively.] The 4-nitrophenyl group can interact through the orbital $3E'(a)$ (Jorgensen & Salem, 1973). Consequently, one should expect a decrease in the bond length C(1)—C(2). The other four substituents interact through the $3E'(b)$ orbital and this interaction will increase the bond length C(1)—C(2). The observed bond length C(1)—C(2), 1·557 (5) Å, agrees well with bond lengths found in similar compounds: ethyl 1,2,2-tricyano-3,3-dimethylcyclopropane-1-carboxylate, 1·552 (3) Å (Ramasubbu, Rajaram & Venkatesan, 1982); ethylenetetracarbonitrile, 1·559 (2) Å (Lemley, Skarstad & Hughes, 1976); 3-(2-methoxyphenyl)cyclopropane-1,1,2,2-tetracarbonitrile, 1·557 (3) Å (Usha & Venkatesan, 1980). If the nitrophenyl group had also been interacting, then the bond length C(1)—C(2) would be significantly shorter than 1·557 (5) Å. The fact that it is not seems to suggest that there is a maximum limit beyond which further interactions do not produce changes in the geometry of the ring and that interactions are selective in nature based on electronegativity.

The other two ring bonds C(1)—C(3) and C(2)—C(3), 1·504 (5) and 1·525 (5) Å respectively, are not equal as would be anticipated from Hoffman (1970, 1971) analysis.

The ethoxycarbonyl group is in an extended conformation, the torsion angles C(1)—C(5)—O(2)—C(6) and C(5)—O(2)—C(6)—C(7) being 178·9 (4) and 108·9 (5)° respectively. In other instances where an ethoxycarbonyl group is attached to a cyclopropane ring (Ramasubbu *et al.*, 1982) the corresponding torsion angles are 177·5 (3) and 167·5 (5)°, and 178·2 (2)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36545 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Intermolecular contacts less than 3·4 Å involving* N *and* O *atoms*

N(2)^I···C(1)^{II}	3·219 (5) Å	O(4)^{IV}···C(1)^{III}	3·081 (5) Å
N(2)^I···C(3)^{II}	3·139 (5)	O(4)^{IV}···C(2)^{III}	3·211 (5)
N(2)^I···C(5)^{II}	3·095 (5)	O(4)^{IV}···C(4)^{III}	3·366 (5)
N(1)^I···C(2)^{III}	3·247 (5)	O(4)^{IV}···C(5)^{III}	2·830 (5)
N(1)^I···C(8)^{III}	3·261 (5)	O(4)^{IV}···C(9)^{III}	3·052 (5)
N(1)^I···C(9)^{III}	3·245 (5)	O(1)^I···O(4)^V	3·337 (5)
O(3)^{IV}···C(8)^{III}	3·321 (5)	O(2)^I···O(4)^V	2·881 (5)
O(3)^{IV}···C(9)^{III}	3·229 (5)		

Symmetry code: (I) $-x,y,z$; (II) $-1 - x$, $y - \frac{1}{2}, \frac{1}{2} - z$; (III) $-x$, $\frac{1}{2} - y, \frac{1}{2} + z$; (IV) $-1 + x, y$, $1 + z$; (V) $-1 + x, \frac{1}{2} - y, \frac{1}{2} + z$.
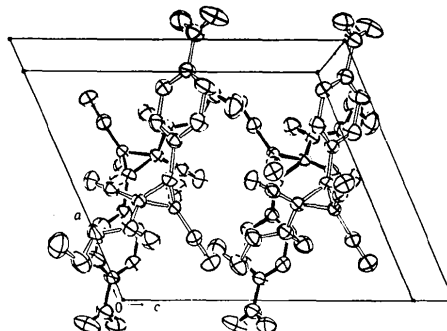

Fig. 2. Packing of the molecules viewed down the *b* axis.

and 175·8 (2)° for ethyl 1,2,2-tricyano-3,3-dimethylcyclopropane-1-carboxylate and ethyl 2′,3′,3′-tricyanocyclohexanespirocyclopropane-2′-carboxylate respectively. The bond lengths in the ethoxycarbonyl and CN groups are normal. We observe significant non-linearity in the cyano groups (Table 3).

The packing of the molecules viewed down the *b* axis is shown in Fig. 2. Looking at the molecular-packing arrangement, with the idea that N···C and O···C distances less than 3·4 Å (Witt, Britton & Mahon, 1972; Klug, 1965) are suggestive of acid–base interactions, we find several situations where there is a reasonably strong acid–base interaction (Table 4). Particularly noteworthy is the distance O(4)···C(5) which is as short as 2·83 Å. Such interactions have also been found in the crystal structures of BrC(CN)₃, ClC(CN)₃, CH₃C(CN)₃ (Witt *et al.*, 1972), tetrahydroxy-*p*-benzoquinone (Klug, 1965), and ethyl 1,2,2-tricyano-3,3-dimethylcyclopropane-1-carboxylate (Ramasubbu *et al.*, 1982).

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trans-2-Pivaloylcyclopropanecarboxylic acid

BY R. ROQUES AND F. CRASNIER

Laboratoire Structure et Vie, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse CEDEX, France

J. P. DECLERCQ AND G. GERMAIN

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, 1348 Louvain-la-Neuve, Belgium

AND H. COUSSE AND G. MOUZIN

Centre de Recherches Pierre Fabre, 17 avenue Jean Moulin, 81106 Castres, France

Abstract. $C_9H_{14}O_3$, monoclinic, $P2_1/n$ ($Z = 4$), $a = 5.888$ (2), $b = 16.237$ (10), $c = 10.252$ (6) Å, $\beta = 96.56$ (4)°, $V = 973.7$ (9) Å^3, $M_r = 170.2$. The structure was solved by direct methods and refined by full-matrix least-squares calculations to $R = 0.047$ for 865 observed reflections. These results were compared with those previously obtained by the use of a conformational theoretical study (CNDO/2 method). The conformational similarity found between the solid state (X-ray diffraction) and the gaseous state (quantum calculation) makes it likely that 2-pivaloylcyclopropanecarboxylic acid keeps the same conformation in solution.

Introduction. In the field of therapeutic chemistry, a renewal of interest in small cyclic compounds has been stimulated by methods of synthesis developed for pyrethrin-type insecticides. In a general study, Cussac, Pierre, Boucherle & Favier (1975) tried to find out how the cyclopropane ring contributes to pharmacological activity, with the aid of many examples; the often favorable contribution of this structural element suggests that it merits the name 'pharmacophore'.

Bifunctional cyclopropane derivatives have been prepared (Mouzin, Cousse & Bonnaud, 1978); in pharmacology they act particularly on the central nervous system [as anticonvulsants or muscle relaxants (Lattes, Mouzin, Bonnaud & Cousse, 1977)]. However, the compound that has proved most interesting (Lauressergues, Stenger & Charveron, 1978) is 2-pivaloylcyclopropanecarboxylic acid (Fig. 1), which shows anorexiant action without noteworthy effects on the central nervous system.

In the case of the anorexiant amphetamines, this action is accompanied by a stereoselective central one (Goldstein & Anagnoste, 1965). To study further the structure–activity relationships among the cyclopropane derivatives, we have undertaken a crystallographic study to determine their molecular geometry.

We have previously studied their conformations theoretically, using the CNDO/2 methods of quantum chemistry (Crasnier, Labarre, Cousse, Dussourd &
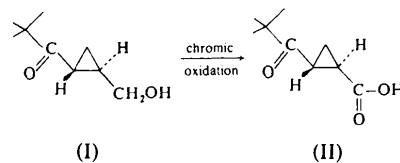

Fig. 1. Synthesis scheme for *trans*-2-pivaloylcyclopropane-carboxylic acid.