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Structure of 2,2,2-Trichloroethyl 2-(2-Benzyl-4-methoxycarbonyl-1-imidazolyl)-3-methylisocrotonate

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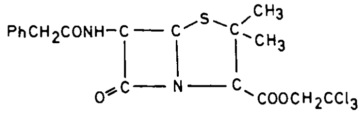
(*Received* 26 *April* 1980; *accepted* 5 *August* 1980)

Abstract

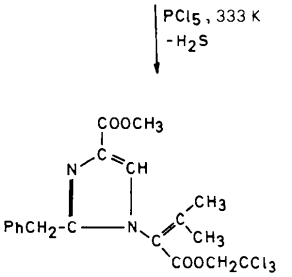
$C_{19}H_{19}Cl_3N_2O_4$ crystallizes in space group $P2_1/c$ with $a = 9{\cdot}542$ (6), $b = 21{\cdot}331$ (10), $c = 11{\cdot}728$ (7) Å, $\beta = 117{\cdot}94$ (3)°, $Z = 4$. The structure was refined to $R = 0{\cdot}064$ for 2735 observed reflexions [$I > 2\sigma(I)$]. The interatomic distances and angles are in agreement with the given atom type and hybridization with the exception of N(1)–C(2) [1·377 (7) Å] in the imidazole moiety. The relative orientation of the imidazole ring to the benzyl group is defined by a torsion angle of −68·4 (6)°. The trichloroethyl acetate group is in a *trans* orientation to the benzyl group [−78·5 (5)°] whereas the α-isopropylidene group is *cis*. Molecular packing is realized through close contacts involving two Cl atoms and C atoms belonging to the methyl groups of the 4-methoxycarbonyl [C···Cl 3·476 (9) Å] and α-isopropylidene substituent [C···Cl 3·597 (6) Å]. The shortest intermolecular contact is 3·191 (8) Å between the methyl group (in the α-isopropylidene) and a carbonyl O atom.

Introduction

During the study of the reaction of PCl_5 with a trichloroester of benzylpenicillin (I) at 333 K in non-aqueous medium, a corresponding benzylpenillate was formed; elimination of H_2S resulted in a final product identified by ^1H NMR, ^{13}C and IR methods (Kovačević, Herak & Gašpert, private communication). On the basis of chemical reaction and spectroscopic data two different structural formulae (II, III) were proposed. An X-ray structure determination establishes (II) as the correct one.



(I)



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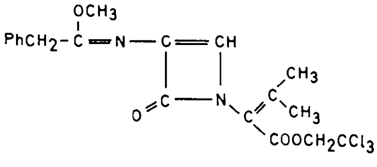

(III)

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Table 1. *Crystallographic and physical data*

Numbers in parentheses here and throughout this paper are the e.s.d.'s in the least significant digits.

$C_{19}H_{19}Cl_3N_2O_4$

$M_r = 445{\cdot}73$	$U = 2108{\cdot}88$ Å
Space group: $P2_1/c$	$Z = 4$
$a = 9{\cdot}542\ (6)$ Å	$D_c = 1{\cdot}403$ Mg m^{-3}
$b = 21{\cdot}331\ (10)$	μ(Mo $K\alpha$) = 0·296 mm^{-1}
$c = 11{\cdot}728\ (7)$	Crystal dimensions: 0·34 × 0·38 × 0·56 mm
$\beta = 117{\cdot}94\ (3)°$	Crystal shape: prismatic

Experimental

The space group was determined from Weissenberg photographs recorded with Cu $K\alpha$ radiation. The diffraction symmetry and extinctions determined $P2_1/c$ uniquely. Table 1 lists crystallographic and physical data.

The intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer in the $\theta/2\theta$ scan mode (scan width = 1·6° θ, scan speed = 0·08° θ s^{-1}) with graphite-monochromated Mo $K\alpha$ radiation. 3011 independent reflexions in the range $2 < \theta < 30°$ were recorded. 2735 reflexions having $I > 2\sigma(I)$ were used in the calculations. Three standard reflexions were measured every 2 h. The data were corrected for background, Lorentz and polarization effects but not for absorption.

Structure determination and refinement

An overall temperature factor (B = 3·49 Å^2) and scale factor were determined (Wilson, 1942) and used to compute normalized structure amplitudes by the routine *NORMAL* included in *MULTAN* 78. In these calculations all the reflexions (3011) were used. The structure was solved with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The solution was based on 250 reflexions with $|E| \geq 1{\cdot}6$. The E map corresponding to the solution with the best figure of merit (ABS FOM = 1·235, PSI ZERO = 1·053, RESID = 21·30) revealed 25 non-hydrogen atoms out of 28 in the molecule. The remaining two C atoms belonging to the benzyl group and one of the terminal methyl groups were located from the resulting Fourier synthesis. Refinement was by full-matrix least squares minimizing $\sum w||F_o| - |F_c||^2$. A weighting scheme of type 3 from XRAY (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used. The weights were assigned as: $w = w_1 w_2$, where $w_1 = 1$ for $|F_o| \leq 35$ and $w_1 = 35/|F_o|$ for $|F_o| > 35$; $w_2 = 1$ for $\sin\theta \geq 0{\cdot}4$ and $w_2 = (\sin\theta)/0{\cdot}4$ for $\sin\theta < 0{\cdot}4$, Anisotropic refinement and a subsequent weighted difference synthesis located the H atoms. The positions of the H atoms attached to the phenyl C atoms were calculated on stereochemical grounds. The H atoms were included in the structure-factor calculations only. For the H atoms the isotropic thermal parameters were those of the bonded atoms plus one. A scale factor, heavy-atom coordinates and anisotropic thermal parameters (253 variables in all) were refined. Anisotropic thermal parameters (of the non-hydrogen atoms) are in the usual range: maximum values of U_{22} for Cl(3) and Cl(2) of 0·149 (2) and 0·127 (1) Å^2 were obtained, respectively. The final R = 0·064 and R_w = 0·069 for 2735 reflexions having $I > 2\sigma(I)$.

Scattering factors given by Cromer & Mann (1968) and (for H) by Stewart, Davidson & Simpson (1965) were used. An anomalous-dispersion correction was included for Cl (Cromer & Liberman, 1970).

The calculations were carried out on a Univac 1110 computer at the University Computing Centre in Zagreb with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Atom coordinates are listed in Tables 2 and 3.*

Table 2. *Final atomic coordinates* (× 10^4) *and istropic thermal parameters* (× 10^2) *for non-hydrogen atoms*

	x	y	z	U (Å^2)
Cl(1)	8331 (2)	2144 (0)	6067 (1)	10·26
Cl(2)	7150 (1)	1588 (0)	7648 (1)	9·21
Cl(3)	10030 (1)	1123 (1)	7751 (1)	9·25
O(1)	4969 (4)	344 (1)	3748 (3)	6·04
O(2)	5754 (3)	1229 (1)	4874 (3)	5·53
O(3)	3860 (4)	3837 (1)	5153 (4)	8·97
O(4)	4536 (4)	3682 (1)	3599 (3)	7·27
N(1)	3221 (4)	1847 (1)	3682 (2)	4·56
N(3)	3106 (4)	2532 (1)	5057 (3)	5·18
C(2)	2882 (4)	1948 (2)	4686 (3)	4·76
C(4)	3634 (4)	2824 (2)	4274 (3)	4·64
C(5)	3718 (4)	2406 (1)	3427 (3)	4·59
C(6)	3245 (4)	1248 (1)	3136 (3)	4·39
C(7)	4697 (4)	874 (1)	3905 (3)	4·56
C(8)	7251 (5)	956 (2)	5689 (4)	5·48
C(9)	8135 (5)	1434 (2)	6731 (4)	5·70
C(10)	2044 (4)	1074 (2)	2002 (3)	4·87
C(11)	1956 (5)	450 (2)	1388 (4)	5·84
C(12)	689 (5)	1506 (2)	1258 (4)	6·14
C(13)	2263 (5)	1445 (2)	5207 (4)	6·05
C(14)	604 (5)	1243 (2)	4281 (4)	5·61
C(15)	−597 (6)	1677 (2)	3716 (4)	6·60
C(16)	−2137 (6)	1495 (2)	2859 (5)	7·73
C(17)	−2483 (7)	860 (3)	2574 (5)	7·98
C(18)	−1285 (8)	430 (2)	3144 (6)	8·83
C(19)	251 (6)	615 (2)	3994 (5)	7·62
C(20)	4003 (4)	3493 (2)	4411 (4)	4·94
C(21)	4933 (8)	4337 (2)	3651 (6)	8·80

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP35546 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Positional* (×10³) *and isotropic thermal* (×10²) *parameters for* H *atoms*

	x	*y*	*z*	*U* (Å²)
H(5)	400	242	273	3·69
H(8)1	700	58	617	4·95
H(8)2	767	83	517	4·95
H(11)1	150	9	167	5·66
H(11)2	319	31	159	5·66
H(11)3	125	50	32	5·66
H(12)1	−34	125	73	5·52
H(12)2	53	183	193	5·52
H(12)3	95	180	59	5·52
H(13)1	293	107	550	5·21
H(13)2	217	158	600	5·21
H(15)	−34	218	395	5·22
H(16)	−308	185	241	6·31
H(17)	−370	71	191	7·15
H(18)	−155	−7	292	6·88
H(19)	119	26	444	6·08
H(21)1	580	442	453	7·37
H(21)2	529	446	290	7·37
H(21)3	387	464	346	7·37

Table 4. *Bond distances* (Å) *and angles* (°)

N(1)—C(2)	1·377 (7)	C(11)—H(11)1	1·01
N(1)—C(5)	1·367 (6)	C(11)—H(11)2	1·13
N(1)—C(6)	1·434 (5)	C(11)—H(11)3	1·12
C(2)—N(3)	1·305 (6)	C(12)—H(12)1	1·04
C(2)—C(13)	1·486 (8)	C(12)—H(12)2	1·11
N(3)—C(4)	1·385 (7)	C(12)—H(12)3	1·12
C(4)—C(5)	1·365 (7)	C(13)—C(14)	1·504 (6)
C(4)—C(20)	1·461 (6)	C(13)—H(13)1	0·98
C(5)—H(5)	0·97	C(13)—H(13)2	1·02
C(6)—C(7)	1·482 (5)	C(14)—C(15)	1·379 (7)
C(6)—C(10)	1·338 (5)	C(14)—C(19)	1·384 (7)
C(7)—O(1)	1·195 (5)	C(15)—C(16)	1·391 (7)
C(7)—O(2)	1·345 (5)	C(16)—C(17)	1·398 (9)
O(2)—C(8)	1·419 (5)	C(17)—C(18)	1·371 (9)
C(8)—C(9)	1·510 (6)	C(18)—C(19)	1·389 (8)
C(8)—H(8)1	1·07	C(20)—O(3)	1·193 (7)
C(8)—H(8)2	0·91	C(20)—O(4)	1·335 (7)
C(9)—Cl(1)	1·752 (6)	O(4)—C(21)	1·441 (7)
C(9)—Cl(2)	1·760 (6)	C(21)—H(21)1	0·99
C(9)—Cl(3)	1·765 (5)	C(21)—H(21)2	1·11
C(10)—C(11)	1·499 (7)	C(21)—H(21)3	1·13
C(10)—C(12)	1·491 (6)		
C(7)—O(2)—C(8)	117·2 (4)	Cl(2)—C(9)—C(8)	111·4 (4)
C(20)—O(4)—C(21)	116·3 (5)	Cl(3)—C(9)—C(8)	107·5 (4)
C(2)—N(1)—C(5)	107·2 (4)	C(6)—C(10)—C(11)	123·6 (4)
C(2)—N(1)—C(6)	125·5 (4)	C(6)—C(10)—C(12)	121·0 (4)
C(5)—N(1)—C(6)	126·9 (4)	C(11)—C(10)—C(12)	115·4 (3)
C(2)—N(3)—C(4)	105·2 (4)	C(10)—C(11)—H(11)1	117
N(1)—C(2)—N(3)	111·5 (4)	C(10)—C(11)—H(11)2	108
N(1)—C(2)—C(13)	122·5 (4)	C(10)—C(11)—H(11)3	109
N(3)—C(2)—C(13)	126·0 (5)	C(10)—C(12)—H(12)1	110
N(3)—C(4)—C(5)	110·6 (4)	C(10)—C(12)—H(12)2	110
N(3)—C(4)—C(20)	120·6 (4)	C(10)—C(12)—H(12)3	110
C(5)—C(4)—C(20)	128·7 (5)	C(2)—C(13)—C(14)	113·4 (4)
N(1)—C(5)—C(4)	105·5 (4)	C(2)—C(13)—H(13)1	115
N(1)—C(5)—H(5)	118	C(2)—C(13)—H(13)2	113
C(4)—C(5)—H(5)	136	C(14)—C(13)—H(13)1	108
N(1)—C(6)—C(7)	114·4 (3)	C(14)—C(13)—H(13)2	103
N(1)—C(6)—C(10)	120·3 (4)	H(13)1—C(13)—H(13)2	103
C(7)—C(6)—C(10)	125·2 (4)	C(13)—C(14)—C(15)	120·8 (4)
O(1)—C(7)—O(2)	122·2 (3)	C(13)—C(14)—C(19)	120·5 (4)
O(1)—C(7)—C(6)	128·7 (3)	C(15)—C(14)—C(19)	118·7 (4)
O(2)—C(7)—C(6)	109·2 (3)	C(14)—C(15)—C(16)	121·2 (5)
O(2)—C(8)—C(9)	105·8 (4)	C(15)—C(16)—C(17)	119·7 (5)
O(2)—C(8)—H(8)1	105	C(16)—C(17)—C(18)	118·8 (5)
O(2)—C(8)—H(8)2	107	C(17)—C(18)—C(19)	121·3 (6)
C(9)—C(8)—H(8)1	105	C(14)—C(19)—C(18)	120·3 (5)
C(9)—C(8)—H(8)2	119	O(3)—C(20)—O(4)	123·2 (5)
H(8)1—C(8)—H(8)2	114	O(3)—C(20)—C(4)	125·2 (5)
Cl(1)—C(9)—Cl(2)	108·0 (3)	O(4)—C(20)—C(4)	111·6 (4)
Cl(1)—C(9)—Cl(3)	109·7 (3)	O(4)—C(21)—H(21)1	107
Cl(1)—C(9)—C(8)	111·1 (4)	O(4)—C(21)—H(21)2	112
Cl(2)—C(9)—Cl(3)	109·1 (3)	O(4)—C(21)—H(21)3	110

Description and discussion of the structure

The structural formula is given in Fig. 1 and bond lengths and angles are in Table 4. The molecular packing is illustrated in Fig. 2.

The C—C lengths between C(sp^3) atoms range from 1·491 (6) to 1·510 (6) Å. Bond lengths in the phenyl ring are in the range 1·371 (9) to 1·398 (9) Å. There are two categories of C to O bond: the C—O bonds [O(2)—C(8) 1·419 (5), O(4)—C(21) 1·441 (7) Å] and the O—C=O bonds [O(2)—C(7) 1·345 (5), O(4)—C(20) 1·335 (7) Å]. The carbonyl bonds are 1·195 (5) and 1·193 (7) Å. The C—Cl distances range from 1·752 (6) to 1·765 (5) Å.

The chemistry and stereochemistry of the imidazole ring, as a constituent of histamine and of histidine residues of proteins and many other biologically useful compounds, *e.g.* haem, the oxygen-transfer coenzyme, have been widely studied. The geometry of the imidazole ring does not exhibit any new features (Tables 4, 5 and 6); it can be compared with those obtained from neutron diffraction at 293 K and 123 K for the imidazole molecule (Craven, McMullan, Bell & Freeman, 1977). The only exception is N(1)—C(2), 1·377 (7) Å, which is longer than in imidazole, 1·337 (3) (at 293 K), 1·342 (5) Å (at 123 K). The lengthening of N(1)—C(2) can be attributed to the presence and character of the two substituents attached to the atoms involved. Its value of 1·377 (7) Å is in agreement with that in 4-acetyl-5-methyl-2-phenylimidazole (Veronese, D'Angeli, Zanotti & Del Pra, 1977), 1·38 (2) Å.

Bond angles are in accordance with the given atom type and hybridization (Table 4).

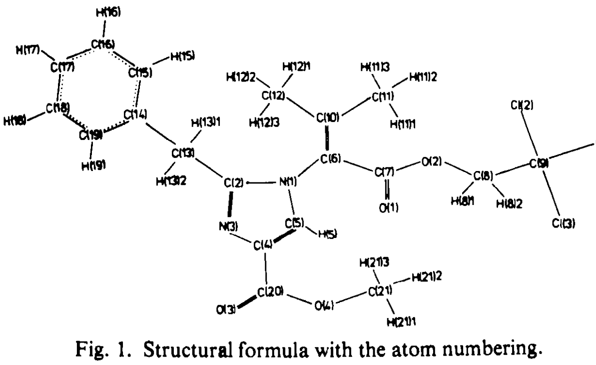

Fig. 1. Structural formula with the atom numbering.

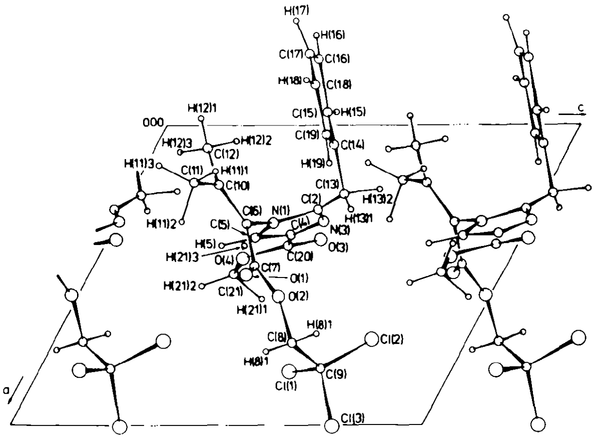

Fig. 2. A view of the crystal structure along **b**. A right-handed coordinate system has been chosen so that the positive direction of **b** is away from the reader.

Table 5. *Displacements* (Å) *from the least-squares plane through the imidazole ring*

Atoms included in the calculations of the least-squares plane are denoted by asterisks.

N(1)*	−0·005 (4)	C(2)	0·005 (5)
C(2)*	0·005 (5)	H(5)	−0·010
N(3)*	−0·003 (4)	C(13)	−0·036 (6)
C(4)*	−0·001 (5)	C(20)	−0·016 (5)
C(5)*	0·004 (5)		

Table 6. *Torsion angles* (°)

N(1)–C(2)–C(13)–C(14)	−68·4 (6)
C(2)–C(13)–C(14)–C(15)	−52·2 (8)
N(3)–C(4)–C(20)–O(4)	178·2 (3)
C(4)–C(20)–O(4)–C(21)	179·8 (3)
C(7)–C(6)–N(1)–C(2)	−78·5 (5)
C(11)–C(10)–C(6)–N(1)	−178·1 (5)
O(2)–C(7)–C(6)–N(1)	−7·7 (6)
C(8)–O(2)–C(7)–C(6)	−177·7 (4)
Cl(1)–C(9)–C(8)–O(2)	−58·6 (5)

The relative orientation of the imidazole ring to the benzyl group is defined by the torsion angle N(1)–C(2)–C(13)–C(14), −68·4 (6)°. As regards the substituents at N(1), the trichloroethyl acetate is in a *trans* orientation to the benzyl group [C(7)–C(6)–N(1)–C(2) −78·5 (5)°] whereas the α-isopropylidene group is *cis* [C(11)–C(10)–C(6)–N(1) −178·1 (5)°].

Molecular packing is realized through close contacts involving two Cl atoms and C atoms belonging to the methyl groups of the 4-methoxycarbonyl [C(21)···Cl(2) 3·476 (9), $\angle$C(21)–H(21)2–Cl(2) 108°] and the α-isopropylidene substituent [C(12)···Cl(1) 3·597 (6) Å, $\angle$C(12)–H(12)2–Cl(1) 123°]. These intermolecular distances (3·476, 3·597 Å) are close to those required for C–H···Cl hydrogen-bond formation (Vinogradov & Linnell, 1971) and also to those found in 4-imidazoleacetic acid hydrochloride (3·441, 3·642 Å) (Jones & Pauling, 1976). However, the angles involving these atoms are not favourable for the formation of hydrogen bonds. The shortest intermolecular contact appearing between a methyl group (in the α-isopropylidene) and a carbonyl O atom is C(11)···O(3), 3·191 (8) Å.

The authors thank MSc Milenko Bruvo for collecting the intensities at the Department of General and Inorganic Chemistry, Faculty of Sciences, University of Zagreb, and M. Kovačević, J. J. Herak and B. Gašpert for the crystals and for helpful comments.

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