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The Crystal and Molecular Structure of Methyl 8-*tert*-Butoxy-6-hydroxy-7-nitrooctanoate, $C_{13}H_{25}NO_6$

BY W. J. VLOON

Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, *Amsterdam, The Netherlands*

AND D. HOTTENTOT, A. R. OVERBEEK AND C. H. STAM

Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, *Amsterdam, The Netherlands*

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Abstract

$C_{13}H_{25}NO_6$ is monoclinic with a = 10·301 (1), b = 26·909 (3), c = 12·547 (2) Å, β = 111·04 (1)°, Z = 8, space group $P2_1/c$. The structure was refined to an R of 0·051. The two molecules in the asymmetric unit have different conformations. The molecules are arranged in strings along [101] by OH···O hydrogen bonds of lengths 2·80 and 2·84 Å.

Introduction

The title compound was an intermediate in the attempted synthesis of a prostaglandin sulphur analogue. It was obtained by base-catalysed condensation of methyl 6-oxohexanoate and *tert*-butyl 2-nitroethyl ether (Vloon, 1976). In this reaction two chiral centres are generated. In the product only one of the two possible diastereomeric racemates was detected. The configuration of this racemate could not be established from chemical and spectroscopic considerations. Therefore an X-ray crystal structure determination was undertaken.

Crystal data

The crystals are monoclinic with space group $P2_1/c$ and two molecules in the asymmetric unit (Z = 8). The cell constants are: a = 10·301 (1), b = 26·909 (3), c = 12·547 (2) Å, β = 111·04 (1)°. 3715 reflections, 3304 of which were above the 2σ level, were collected on a Nonius CAD-4 single-crystal diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. No absorption correction was applied (μ = 0·91 mm^{-1}; crystal dimensions: 0·15 × 0·3 × 0·6 mm).

Structure determination and refinement

The phase problem was solved by *SIMPEL* (Schenk, Overbeek & van der Putten, 1976). Refinement was by block-diagonal least squares. Towards the end of the anisotropic refinement a difference synthesis revealed the H atoms which were included with isotropic temperature parameters. A weighting scheme w =

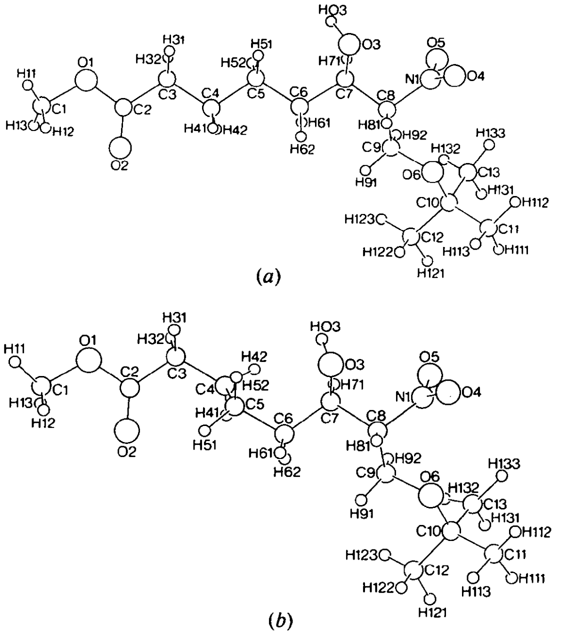

Fig. 1. Configurations of the two independent molecules. (*a*) Molecule *A*, (*b*) molecule *B*. (In order to bring out the similarity between the two molecules, molecule *A* of Table 1 has been inverted.)

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Table 1. *Fractional coordinates* ($\times 10^4$ *for* C, N, O; $\times 10^3$ *for* H) *with e.s.d.'s in parentheses*

	Molecule *A*			Molecule *B*		
	x	*y*	*z*	*x*	*y*	*z*
C(1)	13370 (4)	4796 (2)	4295 (4)	7941 (5)	190 (2)	4259 (4)
C(2)	11091 (4)	4484 (2)	3838 (3)	5710 (4)	583 (2)	3524 (4)
C(3)	9781 (4)	4337 (2)	2888 (3)	4557 (4)	756 (2)	2448 (4)
C(4)	8571 (4)	4231 (2)	3289 (3)	3285 (4)	971 (2)	2645 (4)
C(5)	7234 (4)	4091 (2)	2283 (4)	2397 (4)	575 (2)	2894 (4)
C(6)	6009 (4)	4024 (2)	2681 (3)	1096 (4)	784 (2)	3064 (4)
C(7)	4685 (4)	3849 (2)	1733 (3)	−31 (4)	978 (2)	1965 (3)
C(8)	3476 (3)	3797 (2)	2162 (3)	−1355 (4)	1121 (2)	2171 (3)
C(9)	3751 (4)	3405 (2)	3086 (4)	−1152 (4)	1525 (2)	3057 (4)
C(10)	2450 (4)	2971 (2)	4074 (4)	−2569 (4)	2058 (2)	3760 (4)
C(11)	1186 (5)	3109 (2)	4381 (5)	−4010 (5)	2007 (3)	3819 (6)
C(12)	3747 (5)	2921 (2)	5152 (4)	−1435 (5)	2065 (3)	4954 (5)
C(13)	2139 (5)	2506 (2)	3369 (5)	−2549 (6)	2516 (2)	3059 (6)
N(1)	2188 (3)	3646 (2)	1154 (3)	−2441 (3)	1303 (2)	1046 (3)
O(1)	12038 (3)	4651 (1)	3436 (2)	6718 (3)	349 (2)	3290 (3)
O(2)	11325 (3)	4456 (2)	4857 (2)	5808 (3)	654 (2)	4492 (3)
O(3)	4180 (3)	4201 (2)	824 (3)	−468 (3)	605 (2)	1107 (3)
O(4)	1198 (3)	3927 (2)	863 (3)	−3529 (3)	1079 (2)	650 (3)
O(5)	2201 (4)	3255 (2)	683 (3)	−2158 (4)	1658 (2)	596 (3)
O(6)	2546 (3)	3393 (2)	3383 (3)	−2476 (3)	1620 (2)	3118 (3)
H(11)	1358 (5)	500 (2)	389 (5)	846 (6)	−3 (3)	397 (5)
H(12)	1388 (5)	449 (2)	485 (4)	752 (6)	−1 (3)	471 (5)
H(13)	1313 (5)	506 (2)	479 (4)	835 (6)	49 (3)	473 (5)
H(31)	942 (6)	463 (2)	216 (5)	418 (6)	40 (2)	183 (5)
H(32)	995 (5)	399 (2)	240 (5)	510 (6)	101 (2)	216 (5)
H(41)	834 (6)	458 (2)	371 (5)	353 (6)	123 (2)	331 (5)
H(42)	871 (5)	394 (2)	381 (5)	272 (5)	122 (2)	206 (5)
H(51)	688 (5)	438 (2)	171 (5)	303 (5)	40 (2)	368 (4)
H(52)	756 (5)	377 (2)	200 (5)	206 (5)	31 (2)	224 (5)
H(61)	626 (5)	377 (2)	343 (4)	76 (6)	49 (2)	344 (5)
H(62)	575 (6)	440 (5)	300 (5)	142 (5)	106 (2)	364 (4)
H(71)	481 (5)	351 (2)	127 (5)	38 (5)	125 (2)	163 (5)
H(81)	325 (5)	419 (2)	244 (5)	−181 (5)	78 (2)	231 (5)
H(91)	444 (5)	351 (2)	381 (5)	−62 (5)	140 (2)	384 (5)
H(92)	384 (6)	306 (3)	279 (5)	−74 (5)	182 (2)	282 (4)
H(111)	112 (6)	288 (3)	487 (5)	−421 (6)	226 (3)	422 (5)
H(112)	29 (6)	316 (3)	357 (5)	−470 (6)	196 (2)	314 (5)
H(113)	138 (6)	345 (3)	483 (5)	−380 (6)	170 (3)	447 (5)
H(121)	355 (6)	262 (2)	566 (5)	−157 (5)	239 (2)	546 (5)
H(122)	390 (6)	326 (2)	556 (5)	−155 (6)	172 (2)	537 (5)
H(123)	462 (5)	290 (2)	494 (5)	−50 (6)	206 (2)	491 (5)
H(131)	197 (6)	223 (2)	375 (5)	−259 (6)	279 (2)	220 (6)
H(132)	288 (6)	239 (2)	313 (5)	−167 (6)	250 (2)	324 (5)
H(133)	139 (6)	249 (3)	247 (6)	−340 (6)	252 (2)	220 (6)
H(O3)	469 (6)	419 (2)	39 (5)	−2 (5)	67 (2)	68 (5)

$0{\cdot}96 + F_o + 0{\cdot}0072F_o^2$ was applied. *R* converged to 5·1%. The final parameters are listed in Table 1.*

Results and discussion

The two molecules in the asymmetric unit have different conformations. These are depicted in Fig. 1, where the atomic numbering is also indicated.

Molecule *A* has an approximately planar straight zigzag part comprising C(1), O(1), C(2), O(2), C(3), ..., C(8), N(1) with deviations <0·14 Å from their best plane. A second approximately planar part involves C(7), C(8), C(9), O(6), C(10), C(11) with a largest deviation of 0·12 Å. The two sections are joined in the *gauche* conformation by C(7)—C(8). In molecule *B* the conformations about C(3)—C(4) and C(5)—C(6) are *gauche* rather than *anti* as in *A*. As a result the part C(1), O(1), C(2), O(2), C(3), ..., C(8), N(1) in *B* is not planar as a whole but consists of two approximately planar sections which are more or less parallel (angle between the best plane 12°). This is illustrated in the Newman projections of Fig. 2. From C(5) onward,

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33886 (16 pp.). Copies may be obtained through The Executive Secretary International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	Molecule *A*	Molecule *B*
C(1)–O(1)	1·446 (5)	1·450 (5)
C(2)–O(1)	1·333 (6)	1·338 (7)
C(2)–O(2)	1·212 (5)	1·196 (7)
C(2)–C(3)	1·482 (5)	1·500 (6)
C(3)–C(4)	1·535 (7)	1·535 (7)
C(4)–C(5)	1·527 (5)	1·511 (8)
C(5)–C(6)	1·532 (7)	1·540 (7)
C(6)–C(7)	1·511 (5)	1·525 (6)
C(7)–C(8)	1·537 (6)	1·529 (7)
C(7)–O(3)	1·423 (6)	1·417 (7)
C(8)–N(1)	1·507 (5)	1·518 (5)
N(1)–O(4)	1·211 (6)	1·204 (5)
N(1)–O(5)	1·209 (8)	1·200 (7)
C(8)–C(9)	1·514 (7)	1·512 (7)
C(9)–O(6)	1·424 (7)	1·418 (6)
C(10)–O(6)	1·454 (8)	1·451 (8)
C(10)–C(11)	1·535 (8)	1·520 (8)
C(10)–C(12)	1·510 (6)	1·517 (7)
C(10)–C(13)	1·496 (8)	1·519 (9)
C(1)–O(1)–C(2)	115·7 (3)	117·2 (4)
O(1)–C(2)–O(2)	122·4 (4)	121·4 (4)
O(1)–C(2)–C(3)	111·2 (4)	111·5 (5)
O(2)–C(2)–C(3)	126·5 (5)	127·0 (5)
C(2)–C(3)–C(4)	113·1 (4)	114·1 (4)
C(3)–C(4)–C(5)	111·5 (4)	112·8 (5)
C(4)–C(5)–C(6)	111·0 (4)	113·4 (5)
C(5)–C(6)–C(7)	113·0 (4)	114·1 (5)
C(6)–C(7)–C(8)	111·3 (4)	111·0 (4)
C(6)–C(7)–O(3)	112·0 (5)	111·3 (5)
O(3)–C(7)–C(8)	103·9 (3)	104·9 (3)
C(7)–C(8)–N(1)	107·8 (3)	108·5 (4)
C(7)–C(8)–C(9)	112·8 (3)	114·7 (4)
C(9)–C(8)–N(1)	108·0 (4)	107·6 (4)
C(8)–N(1)–O(4)	117·6 (5)	118·1 (5)
C(8)–N(1)–O(5)	118·5 (4)	118·1 (4)
O(4)–N(1)–O(5)	123·9 (4)	123·8 (4)
C(8)–C(9)–O(6)	106·5 (4)	107·3 (4)
C(9)–O(6)–C(10)	115·7 (4)	116·2 (4)
O(6)–C(10)–C(11)	102·3 (4)	102·8 (5)
O(6)–C(10)–C(12)	111·6 (4)	111·8 (5)
O(6)–C(10)–C(13)	110·4 (5)	108·6 (5)
C(11)–C(10)–C(12)	110·2 (5)	111·0 (5)
C(11)–C(10)–C(13)	109·7 (4)	109·1 (5)
C(12)–C(10)–C(13)	112·2 (5)	112·9 (5)

Table 3. *Hydrogen bonds*

	O···O	O–H	H···O	∠O–H···O
O(2)(*A*)···H–O(3)(*B*)	2·84 Å	0·85 Å	2·04 Å	157°
O(3)(*A*)–H···O(2)(*B*)	2·80	0·89	1·93	166

B is virtually identical to *A*. (In Fig. 1, *A* of Table 1 has been inverted to bring out the similarity between the two molecules.)

The configurations around the two chiral centres C(7) and C(8) are *SS* (and *RR*) for both molecules, as can be seen from the Newman projections along C(7)–C(8) (Fig. 2).

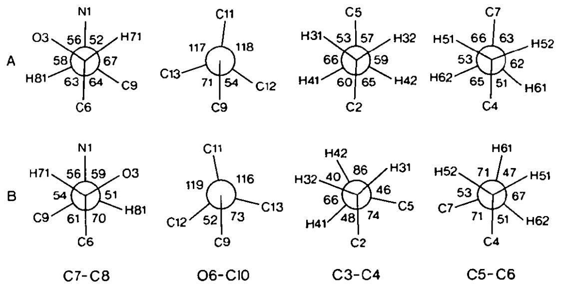

Fig. 2. Some Newman projections.

The bond lengths and angles are listed in Table 2. The only significant differences between the two molecules are in the angles which are always more responsive to differences in packing and conformation.

The methyl carboxylate groups have the usual geometry. The parts C(1)O(1)O(2) are planar within a few thousandths of an ångström. C(3) and C(4) deviate significantly from these planes: 0·03 and −0·22 Å for *A* and 0·09 and −0·07 Å for *B*. The C=O bond is synplanar with respect to $O-CH_3$ and C(3)–C(4).

The *tert*-butoxy groups show some typical features. In both molecules the angle O(6)C(10)C(11), involving the $C-CH_3$ bond *anti* with respect to O(6)–C(9), is 7 or 8° smaller than the other two $O-C-CH_3$ angles. This must be due to the interaction of the H atoms at C(12) and C(13) with those at C(9). A similar behaviour is found in *tert*-butoxycarbonylsarcosylglycine benzyl ester (Itoh, Yamane & Ashida, 1976) and *tert*-butoxycarbonyl-glycyl-L-alanine (Gadret, Leger & Carpy, 1977). In agreement with this is the fact that in both *A* and *B* C(12)C(10)C(13) is larger than C(11)C(10)C(12) and C(11)C(10)C(13), and also that C(9)O(6)C(10) (average 116°) is somewhat larger than the corresponding angle in the methoxy group which is usually 113–114°.

A and *B* are connected by hydrogen bonds between O(2)(*A*) and O(3)(*B*) and between O(3)(*A*) and O(2)(*B*). This gives rise to strings of hydrogen-bonded molecules along [101] in which *A* and *B* alternate. The dimensions of the two hydrogen bonds are given in Table 3.

The packing of the molecules is governed by the hydrogen bonds and by normal van der Waals contacts.

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