

Microwave Spectrum, Conformational Equilibrium and *Ab Initio* Computations for Ethyl Glycolate

K.-M. Marstokk and Harald Møllendal*

Department of Chemistry, The University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

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The microwave spectra of ethyl glycolate, HOCH₂COOCH₂CH₃, and one deuterated species, DOCH₂COOCH₂CH₃, have been investigated in the 26.5–39.5 GHz spectral region at –10 °C. Two conformers denoted *anti, Z, anti* and *anti, Z, gauche* were assigned. Each rotamer has an intramolecular hydrogen bond formed between the hydroxyl-group hydrogen atom and the carbonyl-group oxygen atom making the H–O–C–C(O)–C atoms coplanar. The orientation of the ethyl group is different in *anti, Z, anti* and in *anti, Z, gauche* owing to rotational isomerism around the O–Et bond. The heavy atoms form a plane in *anti, Z, anti*, while the ethyl group is rotated 96° from this plane in the *anti, Z, gauche* conformer. *Anti, Z, anti* is 1.9(5) kJ mol⁻¹ more stable than *anti, Z, gauche*. The microwave work has been assisted by *ab initio* computations at the 6–31G* level of theory.

The structural and conformational properties of ethyl esters in the free state have received some attention in the past. In a classical microwave (MW) study, Riveros and Wilson¹ found that ethyl formate exists in at least two rotameric forms around the O–Et bond; an *anti* form having a co-planar arrangement of the heavy atoms and a *gauche* form where the ethyl group is rotated 95° out of this plane. The *gauche* form was found to be 0.78(25) kJ mol⁻¹ less stable than *anti*. A low-resolution MW study by True and Bohn² of ethyl chloroformate and ethyl cyanoformate revealed the expected *anti* and *gauche* conformers produced by rotation around the O–Et bond. These two rotamers were found to have approximately the same energy. In addition, a third *gauche–gauche* rotamer characterized by a 45° rotation around the OC–O bond in addition to a 240° rotation around the O–Et bond was found. The *gauche–gauche* rotamer was determined to be 4–8 kJ mol⁻¹ less stable than *anti* and *gauche*.²

It was expected that the title compound (Fig. 1) would possess an intramolecular hydrogen (H) bond formed between the hydroxyl-group H atom and the carbonyl group in the gas phase, because this has been found in the only identified forms of the closely related molecules glycolic acid³ and methyl glycolate.⁴ The H bond is presumed to influence the electronic environment of the ester group, with possible conformational consequences. This work has been carried out to establish to what extent intramolecular H bonding might influence structural and conformational properties of ethyl esters.

Experimental

The sample used in this work was purchased from Aldrich-Chemie, Steinheim, Germany. The sample was purified by preparative gas chromatography. The MW spectrum was studied employing the Oslo spectrometer which is described in Ref. 5. The 26.5–39.5 GHz spectral region was investigated with the microwave absorption cell cooled to about –10 °C. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 2–3 Pa and the accuracy of the spectral measurements is presumed to be better than ±0.10 MHz. The deuteration of the hydroxyl group was achieved by conditioning the MW cell with heavy water and then introducing the normal species.

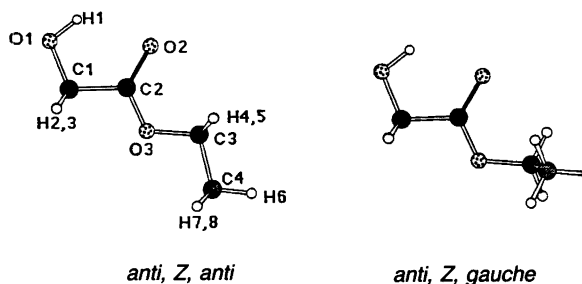


Fig. 1. Models of *anti, Z, anti* and *anti, Z, gauche* ethyl glycolate. *Anti, Z, anti* is 1.9(5) kJ mol⁻¹ more stable than *anti, Z, gauche*. *Anti, Z, anti* is converted into *anti, Z, gauche* by a 96° rotation around the O3–C3 bond.

*To whom correspondence should be addressed.

Table 1. Structure of *anti*, *Z*, *anti* and *anti*, *Z*, *gauche* conformers of ethyl glycolate as calculated by *ab initio* using the 6-31G* basis set.

Distances/pm			Angles/°			Dihedral angles ^a /°		
<i>Conformer:</i>	<i>A</i> ^b	<i>G</i> ^c		<i>A</i> ^b	<i>G</i> ^c		<i>A</i> ^b	<i>G</i> ^c
O1-H1	95.1	95.1	H1-O1-C1	108.5	108.5	H1-O1-C1-H2	120.4	124.5
C1-O1	138.6	138.6	O1-C1-H2	110.8	110.6	H1-O1-C1-H3	-120.4	-116.4
C1-H2	108.6	108.5	O1-C1-H3	110.8	111.1	H1-O1-C1-C2	0.0	4.0
C1-H3	108.6	108.6	O1-C1-C2	111.3	111.3	O1-C1-C2-O2	0.0	-2.1
C1-C2	151.2	151.2	C1-C2-O2	122.9	122.8	O1-C1-C2-O3	180.0	178.4
C2-O2	119.1	119.1	C1-C2-O3	112.3	112.0	C1-C2-O3-C3	180.0	179.4
C2-O3	131.4	131.4	C2-O3-C3	117.8	118.7	C2-O3-C3-H4	58.8	-39.4
C3-O3	142.9	143.1	O3-C3-H4	108.7	109.0	C2-O3-C3-H5	-58.8	-156.0
C3-H4	108.1	107.9	O3-C3-H5	108.7	104.5	C2-O3-C3-C4	180.0	84.0
C2-H5	108.1	108.0	O3-C3-C4	107.4	111.3	O3-C3-C4-H6	180.0	175.7
C3-C4	151.3	151.7	C3-C4-H6	109.8	109.6	O3-C3-C4-H7	60.2	56.3
C4-H6	108.5	108.5	C3-C4-H7	110.8	110.6	O3-C3-C4-H8	-60.2	-64.7
C4-H7	108.4	108.4	C3-C4-H8	110.8	111.0			
C4-H8	108.4	108.3						

Hydrogen bond parameters^d*Anti*, *Z*, *anti*

Distances/pm	Angles/°
H1...O2	213.2
O1...O2	267.9
O1-H1...O2	115.1
O1-H1, C2-O2 ^e	17.4

Anti, *Z*, *gauche*

Distances/pm	Angles/°
H1...O2	213.3
O1...O2	267.8
O1-H1...C2	115.2
O1-H1, C2-O2 ^e	17.2

Sum of van der Waals radii^f

H...O	260
O...O	280

Substitution coordinates^g of hydroxyl group hydrogen atom/pm

	<i>Anti</i> , <i>Z</i> , <i>anti</i>			<i>Anti</i> , <i>Z</i> , <i>gauche</i>		
	a	b	c	a	b	c
Calc. from rotational constants	262.55(9) ^h	56.3(4) ^h	0.0 ^{h,i}	234.3(1) ^j	105.0(2) ^j	7.6(3) ^j
From <i>ab initio</i> ^d	275.4	73.1	0.0	246.5	106.6	2.3

^aMeasured from *syn*. ^b*Anti*, *Z*, *anti* conformer with *C*₁ symmetry. ^c*Anti*, *Z*, *gauche* conformer with *C*_s symmetry. ^dCalculated from the structure above. ^eAngle between the O1-H1 and C2-O2 bonds. ^fRef. 14. ^gEmploying Kraitchman's equations.¹⁰ ^hReported in Table 4 below. ⁱFor symmetry reasons. ^jReported in Table 6 below.

Results

Ab initio calculations. The calculations were made using the Gaussian 90 program package⁶ running on the Cray-X-MP/216 computer in Trondheim. The 6-31G* basis set was chosen. A large number of conformations is possible for ethyl glycolate. A full mapping of the potential surface of this molecule using high-level *ab initio* computations is beyond our present possibilities. The calculations were therefore restricted to three major tasks. Firstly, a full geometry optimization of *anti*, *Z*, *anti* and *anti*, *Z*, *gauche* (Fig. 1) was made. Both these conformers were found to be stable, as no imaginary vibrational frequencies were calculated for any of them. Their predicted geometries are listed in Table 1; further parameters of interest are collected in Table 2, and some results are referred to in the text below.

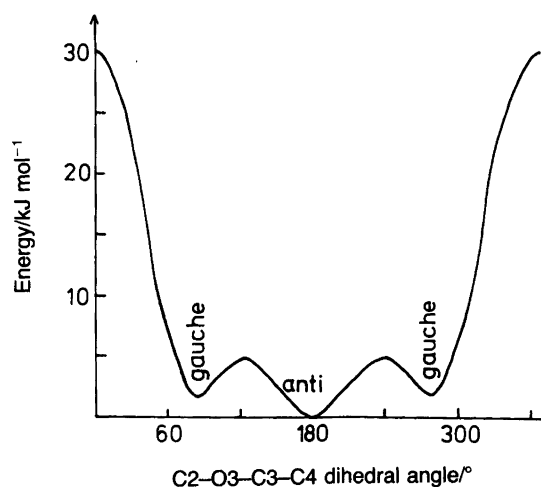


Fig. 2. Potential function for torsion around the O3-C3 bond calculated by the *ab initio* method using the 6-31G* basis set.

Table 2. Selected parameters obtained in the *ab initio* calculations with the 6–31G* basis set.

Energy difference ^a $E_{anti, Z, gauche} - E_{anti, Z, anti} = 1.8 \text{ kJ mol}^{-1}$		
	<i>Anti, Z, anti</i>	<i>Anti, Z, gauche</i>
Rotational constants/MHz		
A	8394.7	7114.9
B	1293.4	1412.7
C	1144.3	1310.3
Dipole moments ^b /10 ⁻³⁰ C m		
μ_a	10.67	9.66
μ_b	2.49	4.19
μ_c	0.0 ^c	0.85

^aThe total energy of *anti, Z, anti* was calculated as $-999\,536.35 \text{ kJ mol}^{-1}$. ^bComponents of the total dipole moment along the principal inertial axes. 1 debye = $3.335\,64 \times 10^{-30} \text{ C m}$. ^cFor symmetry reasons.

The *anti, Z, anti* rotamer was calculated to have a symmetry plane (C_1 symmetry). The HOCCOO atoms are practically coplanar in *anti, Z, gauche* which has C_s symmetry. *Anti, Z, anti* is converted into *anti, Z, gauche* by a 96° rotation around the O3–C3 bond (the O–Et bond). The energy difference is calculated to be only 1.8 kJ mol^{-1} with *anti, Z, anti* as the more stable, as seen in Table 2. Secondly, the barrier to rotation around the O3–C3 bond was calculated, because *anti, Z, anti* is transformed into *anti, Z,*

Table 3. MW spectrum of the ground vibrational state of the *anti, Z, anti* conformer of ethyl glycolate.

Transition	Observed frequency ^a /MHz	Obs. – calc. frequency/MHz
11 _{5,6} ← 10 _{5,5}	26 540.07	–0.01
11 _{5,7} ← 10 _{5,6}	26 540.07	0.00
12 _{2,11} ← 11 _{2,10}	28 824.00	–0.04
12 _{3,10} ← 11 _{3,9}	28 990.72	–0.03
12 _{7,5} ← 11 _{7,4}	28 943.37	0.00
12 _{7,6} ← 11 _{7,5}	28 943.37	0.00
13 _{0,13} ← 12 _{0,12}	30 621.04	–0.04
13 _{1,13} ← 12 _{1,12}	30 213.85	0.04
13 _{4,10} ← 12 _{4,9}	31 395.11	–0.06
13 _{8,5} ← 12 _{8,4}	31 353.58	–0.04
13 _{8,6} ← 12 _{8,5}	31 353.58	–0.04
14 _{2,12} ← 13 _{2,11}	34 437.79	0.05
14 _{3,12} ← 13 _{3,11}	33 836.68	–0.14
14 _{7,7} ← 13 _{7,6}	33 772.86	0.00
14 _{7,8} ← 13 _{7,7}	33 772.86	0.00
14 _{10,4} ← 13 _{10,3}	33 761.43	0.00
14 _{10,5} ← 13 _{10,4}	33 761.43	0.00
15 _{0,15} ← 14 _{0,14}	35 147.55	–0.04
15 _{1,15} ← 14 _{1,14}	34 808.85	0.07
15 _{3,13} ← 14 _{3,12}	36 259.91	0.04
15 _{6,9} ← 14 _{6,8}	36 198.43	–0.10
15 _{6,10} ← 14 _{6,9}	36 198.43	–0.10
15 _{10,5} ← 14 _{10,4}	36 174.57	0.03
15 _{10,6} ← 14 _{10,5}	36 174.57	0.03
16 _{1,16} ← 15 _{1,15}	37 100.62	–0.02

^a±0.10 MHz.

Table 4. Ground-state spectroscopic constants^{a,b} of the *anti, Z, anti* conformer of ethyl glycolate.

Species:	Parent	Deuterated ^c
No. of transitions:	72	51
R.m.s. deviation ^d /MHz:	0.062	0.123
A ₀ /MHz		
	8285.41(43)	8245.0(11)
B ₀ /MHz		
	1278.354 3(21)	1256.532 7(59)
C ₀ /MHz		
	1132.130 4(24)	1114.193 6(64)
Δ_J /kHz		
	0.043 7(41)	0.095(11)
Δ_{JK} ^e /kHz		
	0.222 3(90)	0.331(17)
$I_a + I_b - I_c$ /10 ⁻²⁰ u m ²		
	9.935 5(40)	9.914(10)

^aA-reduction, *I*-representation.¹⁰ ^bUncertainties represent one standard deviation. ^cDeuteration has taken place in the hydroxyl group. ^dRoot-mean-square deviation. ^eFurther centrifugal distortion constants preset at zero. ^fConversion factor $505\,379 \times 10^{-20} \text{ MHz u m}^2$.

gauche by rotation around this bond with minor relaxations of other structural parameters. In the computations of the barrier (sketched in Fig. 2) the two transition states were located using the built-in procedure provided with the program.⁶ The transition state at 0° (360°) corresponding to the *anti, Z, syn* conformation was found to be 30.2 kJ mol^{-1} higher in energy than *anti, Z, anti*, while the transition state at 56.1° (236.1°) was 4.9 kJ mol^{-1} higher in energy. The shape of this barrier (Fig. 2) is fairly similar to that determined for ethyl formate.¹

Thirdly, an unsuccessful effort was made to calculate the fully optimized structure and energy for a conformation similar to the *gauche-gauche* conformer reported by True and Bohn² for ethyl chloroformate and ethyl cyanoformate. In these computations we started with the C1–C2–O3–C3 dihedral angle at 45° and the C2–O3–C3–C4 dihedral angle at 240° as indicated by them.² When full geometry relaxation was allowed, the program refined to the *anti, Z, gauche* conformer, and not the hypothetical *gauche, Z, gauche* rotamer that was sought after.

MW spectrum and assignment of the anti, Z, anti conformer. According to the theoretical predictions (Table 2) the *anti, Z, anti* conformer was predicted to have a rather large *a*-axis dipole moment component. The strongest transitions expected for this conformer were thus the *a*-type *R*-branch lines. These transitions were readily assigned, and some of them* are found in Table 3. These lines are quite weak. For example, the low- $K_{-1} J = 13 \leftarrow 12$ transitions have peak absorption coefficients of only ca. $5 \times 10^{-8} \text{ cm}^{-1}$, in spite of the fact that the *a*-axis dipole moment component is quite large (Table 2). The weakness of the

* The complete spectra of the parent and deuterated species are available from the authors upon request, or from The National Institute of Standards and Technology, Microwave Data Center, Molecular Physics Division, Bldg. 221, Rm. B265, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 5. MW spectrum of the ground vibrational state of the *anti*, *Z*, *gauche* conformer of ethyl glycolate.

Transition	Observed frequency ^a /MHz	Obs. – calc. frequency/MHz
10 _{3,7} ← 9 _{3,6}	27 222.72	–0.05
10 _{5,6} ← 9 _{5,5}	27 196.78	0.01
10 _{5,5} ← 9 _{5,4}	27 196.78	0.01
10 _{7,3} ← 9 _{7,2}	27 192.14	0.03
10 _{7,4} ← 9 _{7,3}	27 192.14	0.03
11 _{0,11} ← 10 _{0,10}	29 590.73	–0.04
11 _{1,11} ← 10 _{1,10}	29 246.90	0.01
11 _{2,10} ← 10 _{2,9}	29 849.78	–0.02
11 _{6,5} ← 10 _{6,4}	29 914.57	0.04
11 _{6,6} ← 10 _{6,5}	29 914.57	0.04
12 _{1,11} ← 11 _{1,10}	33 134.43	–0.01
12 _{3,10} ← 11 _{3,9}	32 664.02	–0.02
12 _{6,6} ← 11 _{6,4}	32 635.74	0.01
12 _{6,7} ← 11 _{6,6}	32 635.74	0.01
12 _{8,4} ← 11 _{8,3}	32 630.97	–0.01
12 _{8,5} ← 11 _{8,4}	32 630.97	–0.01
13 _{1,13} ← 12 _{1,12}	34 533.89	0.10
13 _{3,11} ← 12 _{3,10}	35 390.74	–0.04
13 _{5,8} ← 12 _{5,7}	35 364.30	0.02
13 _{5,9} ← 12 _{5,8}	35 364.30	0.03
13 _{7,6} ← 12 _{7,5}	35 353.49	–0.01
13 _{7,7} ← 12 _{7,6}	35 353.49	–0.01
14 _{4,10} ← 13 _{4,9}	38 106.30	0.08
14 _{6,8} ← 13 _{6,7}	38 079.49	0.00
14 _{6,9} ← 13 _{6,8}	38 079.49	0.00
14 _{8,6} ← 13 _{8,5}	38 071.69	0.02
14 _{8,7} ← 13 _{8,6}	38 071.69	0.02

^a±0.10 MHz.

spectrum presumably results from a large value for the partition function, which is inversely proportional to the peak absorption intensity,⁷ as well as the presence of at least two rotameric forms.

No searches for *b*-type transitions were made, because μ_b is predicted to be considerably less than μ_a (Table 2). The spectroscopic constants (*A*-reduction *I'*-representation)⁸ are collected in Table 4. Note that $I_a + I_b - I_c = 9.9355(40) \times 10^{-20} \text{ u m}^2$. This value is very similar to that found for several other molecules that contain a symmetry plane and six out-of-plane *sp*³-hybridized hydrogen atoms.⁹

The ground-state transitions were accompanied by satellite lines presumably originating from vibrationally excited states of this conformer, but they were very weak and no assignments were made.

The hydroxyl-group deuterated species was studied in order to locate exactly the position of the H atom of the said group using Kraitchman's equations.¹⁰ The assignments were again made in a straightforward manner for the ³*R*-transitions. The spectroscopic constants are collected in Table 4, whereas Kraitchman's substitution coordinates¹⁰ are reported in Table 1. It is seen in Table 4 that the value of $I_a + I_b - I_c$ is nearly the same as for the parent species. This is expected for a molecule that possesses a symmetry plane containing the substituted H atom. The principal-axes coordinates of the hydroxyl-group H atom (Table 1) show beyond doubt that the hydroxyl-group H atom is

directed towards the carbonyl-group oxygen atom, with the formation of an internal H bond. A similar finding was made for *anti*, *Z*, *gauche* below.

The dipole moment could not be determined for either *anti*, *Z*, *anti* or *anti*, *Z*, *gauche* because the transitions are too weak.

Assignment of anti, Z, gauche. This conformer was also predicted (Table 2) to possess a large dipole moment component along the *a* principal inertial axis. The ³*R*-branch transitions were readily assigned, and some of them are presented in Table 5. These lines were approximately as weak as the *a*-type *R*-branch lines belonging to *I*. The rotational constants derived from the transitions in Table 5 are listed in Table 6.

Searches were also made for a hypothetical conformation similar to *gauche-gauche* of ethyl chloroformate and ethyl cyanofornate.² However, no such species was seen, and it is presumed that such a form, if it exists, is a high-energy rotamer of the molecule. It is also recalled that we were not able to 'find' this conformation in the *ab initio* computations reported above.

Internal energy difference. The internal energy difference between *anti*, *Z*, *anti* and *anti*, *Z*, *gauche* was determined by relative intensity measurements, observing the precautions of Ref. 11. The strongest ones of the *a*-type *R*-branch transitions of both rotamers were used for this purpose. The μ_a dipole moment components of Table 2 were employed, since no experimental values are available. The statistical weight of *anti*, *Z*, *gauche* was assumed to be 2. In this manner an internal energy difference of 1.9(5) kJ mol^{–1} was determined with *anti*, *Z*, *anti* as the most stable conformer.

The uncertainty, which represents one standard deviation, was estimated to be ±0.5 kJ mol^{–1}. It is not easy to estimate this uncertainty, because many factors contribute to it. The *ratio* of the *a*-axis dipole moment components is used in the derivation of the energy difference, and it is presumed that the theoretical ratio taken from Table 2 is accurate to within 15%. Uncertainties associated with the base line contribute another 10–20% to the peak absorption intensities. The linewidths are also uncertain by at least 20%. There are also other sources of uncertainty. In

Table 6. Ground-state spectroscopic constants^{a,b} of the *anti*, *Z*, *gauche* conformer of ethyl glycolate.

Species:	Parent	Deuterated ^c
No. of transitions:	55	48
R.m.s. deviation ^d /MHz:	0.050	0.056
<i>A</i> ₀ /MHz	6915.34(65)	6814.26(57)
<i>B</i> ₀ /MHz	1412.094 0(23)	1390.738 5(27)
<i>C</i> ₀ /MHz	1306.326 7(24)	1284.517 2(27)
Δ_J /kHz	0.262 6(47)	0.252 0(64)
Δ_{JK} /kHz	–1.215(15)	–1.219(17)
$I_a + I_b - I_c/10^{-20} \text{ u m}^2$	44.103 9(75)	44.115 0(69)

^{a–d}Comments as for Table 4.

the estimate of the standard deviation of $\pm 0.5 \text{ kJ mol}^{-1}$ efforts have been made to treat all these sources of error in a realistic manner. It is noteworthy that the experimental energy difference is identical with the computed one (Table 2) within the experimental uncertainty limit.

Structure. The experimental rotational constants shown in Tables 4 and 6 are close to those obtained by *ab initio* computations (Table 2). The substitution coordinates for the hydroxyl group H atom shown in Table 1 are also fairly close to the experimental ones listed in the same table. Moreover, the *ab initio* structures of the HOCH_2COO moieties in *anti*, *Z*, *anti* as well as *anti*, *Z*, *gauche* shown Table 1 are close to the r_g -structure of glycolic acid.^{3a} Likewise, the computed structures of the $\text{CH}_3\text{CH}_2\text{O}$ moieties (Table 1) are close to those determined for ethyl alcohol¹² and ethyl methyl ether.¹³ For these reasons it is presumed that the theoretical structures of *anti*, *Z*, *anti* and *anti*, *Z*, *gauche* are good approximations to the real structures of these two conformers, and that no experimental data are at hand that could significantly improve the *ab initio* structures.

Discussion

The theoretical structures of *anti*, *Z*, *anti* and *anti*, *Z*, *gauche* (Table 1) reveal quite normal bond angles and distances. The dihedral angles of *anti*, *Z*, *anti* are all normal, which reflects that no important strain is present in this rotamer. However, in *anti*, *Z*, *gauche* the C2-O3-C3-C4 dihedral angle takes the unusual value of 96° (measured from *anti*, *Z*, *anti*; 84° measured from *anti*, *Z*, *syn*) instead of 120° . This is almost the same as that found for ethyl formate,¹ ethyl chloroformate² and ethyl cyanoformate.² The 24° deviation from the normal situation is presumably caused by steric repulsion between the HOCH_2COO part of the molecule and the methyl group, just as suggested by Riveros and Wilson¹ in the case of ethyl formate. This repulsion is not so strong in *anti*, *Z*, *gauche* that it ruptures the internal H bond and makes the H-O-C(O)O atoms significantly non-planar. This can be seen from the H1-O1-C1-C2 , O1-C1-C2-O2 and O1-C1-C2-O3 dihedral angles (Table 1), which take values only slightly different from those expected for a completely planar arrangement of these five atoms.

Not only are the structures of the *anti*, *Z*, *gauche* and *anti*, *Z*, *anti* conformers of ethyl glycolate very similar to their counterparts in ethyl formate¹ and ethyl chloroformate,² as well as ethyl cyanoformate;² also the energy dif-

ferences are in all cases found to be small. The title compound differs from the other esters^{1,2} in that the acid part is larger, more bulky and contains an intramolecular H bond that might perturb the electron distribution of the carbonyl group. Nevertheless, these differences seem to have a rather small effect on the conformational equilibrium.

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