

Microwave Spectrum, Conformation and Dipole Moment of Furan-3-carboxaldehyde

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The microwave spectrum of furan-3-carboxaldehyde has been investigated in the 10–39.5 GHz spectral region. One planar conformer, which has the carboxyl-group oxygen atoms *anti* to the ring oxygen atom, has been assigned in the ground and six vibrationally excited states. This conformer is at least 5 kJ mol⁻¹ more stable than any other rotameric form of the molecule. The dipole moment was determined to be (in units of 10⁻³⁰ C m): $\mu_a = 8.377(42)$, $\mu_b = 3.898(14)$, $\mu_c = 0.0$ (for symmetry reasons), and $\mu_{tot} = 9.239(42)$. Its gas-phase infrared spectrum has been recorded. *Ab initio* computations have been made for two selected conformations employing the MP2/6-31G* basis set.

Five-membered heterocycles possessing a carboxyl group in the 2- or 3-position have been found to display rotational isomerism, as shown in numerous studies made mostly in solution.¹ In all known cases¹ planar conformers are observed. In these planar forms the carboxyl-group oxygen atom is either *syn* or *anti* to the hetero atom of the five-membered ring. The two typical *syn* and *anti* conformers expected to be stable for furan-3-carboxaldehyde are shown in Fig. 1.

Several conformational studies have been made of the title compound in solution using NMR¹⁻⁴ and IR spectroscopy⁵ and dipole moment measurements.^{6,7} These studies all conclude that furan-3-carboxaldehyde exists almost exclusively in the *anti* conformation in solution. Theoretical calculations of the conformational properties have also recently been made.^{1,8} *Ab initio* computations⁸ at the 6-31G* level with full geometry optimization predict *anti* to be more stable than *syn* by 3.12 kJ mol⁻¹. The barrier height between the *anti* and *syn* conformers was calculated with this basis to be 37.27 kJ mol⁻¹ above *anti*.⁸

While no structural studies of free five-membered heterocycles with a carboxyl group in the 3-position have been reported, some studies are already available for the 2-substituted compounds. For example, a microwave (MW) study has shown that furan-2-carboxaldehyde⁹ exists, with the *anti* conformer 3.00(48) kJ mol⁻¹ more stable than *syn*. Only the *syn* conformer of pyrrol-2-carboxaldehyde was assigned in a MW work.¹⁰ Further conformers are, if they exist, at least 4.2 kJ mol⁻¹ less stable than *syn*.¹⁰ Thiophene-2-carboxaldehyde has been thoroughly investigated with MW,^{9a,11} electron diffraction¹¹ and vibrational spectroscopy.¹¹ It was found that *syn* is about 4 kJ mol⁻¹ more stable than *anti*.¹¹ The present work was carried out in

order to extend the gas-phase studies of this class of compounds.

Experimental

Microwave experiment. The spectra were studied using the Oslo spectrometer, which is described in Ref. 12. The 10.0–29.0 GHz spectral region was investigated extensively. Many measurements were also made in the 29.0–39.5 GHz spectral interval. The microwave absorption cell was cooled to about –15°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 in the 1–4 Pa range during the spectral measurements. The accuracy is presumed to be better than ±0.05 MHz.

IR experiment. The gas-phase IR spectrum in the 500–4000 cm⁻¹ region was taken at room temperature using a Bruker model IFS 88 spectrometer equipped with a multiple reflection cell. The path length was about 1.2 m, the vapour pressure roughly 100 Pa and the resolution 2 cm⁻¹.

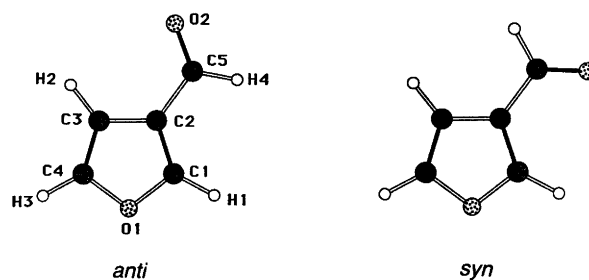


Fig. 1. The *anti* and *syn* conformers of furan-3-carboxaldehyde. Only *anti* was found in the gas-phase. This conformer is at least 5 kJ mol⁻¹ more stable than the hypothetical *syn* conformer.

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Table 1. Structures of *anti* and *syn* furan-3-carboxaldehyde calculated by the *ab initio* method using the MP2/6-31G* basis set.

Bond lengths/pm	Conformation	
	<i>anti</i>	<i>syn</i>
C1–O1	135.6	135.7
C1–C2	137.3	137.3
C2–C3	143.0	143.0
C3–C4	136.1	136.3
C4–O1	137.2	137.2
C2–C5	146.0	146.4
C5–O2	122.8	122.8
C1–H1	108.1	108.0
C3–H2	108.1	108.2
C4–H3	107.9	107.9
C5–H4	110.9	110.8
Angles/°		
O1–C1–C2	110.4	110.3
C1–C2–C3	106.3	106.2
C2–C3–C4	106.0	106.0
C3–C4–O1	110.7	110.5
C1–O1–C4	106.7	107.0
C2–C5–O2	123.4	123.7
H1–C1–C2	133.7	133.0
C2–C3–H2	126.4	127.5
C3–C4–H3	134.1	134.1
C2–C5–H4	115.8	115.7

Results

Ab initio calculations. In their theoretical study Benassi *et al.*⁸ found that the energy difference between the *syn* and the *anti* conformations increased when larger basis sets were employed. The largest basis set used by these authors⁸ was 6-31G*, which yielded an energy difference of 3.12 kJ

Table 2. Selected parameters of *anti* and *syn* furan-3-carboxaldehyde calculated by the *ab initio* method using the MP2/6-31G* basis set.

	Conformation	
	<i>anti</i>	<i>syn</i>
Rotational constants/MHz		
A	8245.1	8127.2
B	1975.9	1993.2
C	1593.9	1600.6
Dipole moments ^a /10 ⁻³⁰ C m		
μ_a	8.81	11.02
μ_b	4.32	2.74

Energy difference^b/kJ mol⁻¹

$$E_{\text{syn}} - E_{\text{anti}} = 2.6$$

^a1 debye = 3.33564 × 10⁻³⁰ C m. ^bThe total energy of the *anti* conformer was computed to be – 896 167.1 kJ mol⁻¹.

Table 3. Selected transitions of the ground-state MW spectrum of the *anti* conformer of furan-3-carboxaldehyde.

Transition	Observed frequency ^a /MHz	Obs. – calc. frequency/MHz
3 _{0,3} ← 2 _{0,2}	10 642.73	0.04
3 _{1,2} ← 2 _{1,1}	11 272.73	0.02
3 _{1,3} ← 2 _{1,2}	10 126.69	0.00
4 _{0,1} ← 3 _{0,3}	14 112.77	0.02
4 _{1,3} ← 3 _{1,2}	15 009.35	0.01
4 _{1,4} ← 3 _{0,3}	18 864.93	0.02
4 _{1,4} ← 3 _{1,3}	13 483.53	0.00
5 _{1,4} ← 4 _{1,3}	18 726.62	0.02
5 _{2,4} ← 4 _{2,3}	17 812.76	–0.01
6 _{0,6} ← 5 _{0,5}	20 860.57	–0.01
6 _{1,6} ← 5 _{1,5}	20 151.07	0.04
6 _{2,5} ← 6 _{1,6}	23 481.86	0.00
7 _{0,7} ← 6 _{1,6}	20 786.38	–0.08
7 _{2,5} ← 6 _{2,4}	25 714.58	–0.01
7 _{6,1} ← 6 _{6,0}	25 037.69	–0.03
7 _{6,2} ← 6 _{6,1}	25 037.69	–0.03
8 _{2,7} ← 8 _{1,8}	26 489.32	0.02
9 _{0,9} ← 8 _{1,8}	28 461.61	0.00
10 _{1,9} ← 9 _{2,8}	25 228.79	–0.05
12 _{3,9} ← 12 _{2,10}	26 228.40	0.01
15 _{2,13} ← 15 _{1,14}	25 989.74	–0.01
16 _{3,13} ← 16 _{2,14}	24 682.27	0.01
19 _{3,16} ← 19 _{2,17}	28 054.94	0.01
22 _{4,19} ← 21 _{5,16}	20 835.78	–0.02
27 _{5,23} ← 26 _{6,20}	28 421.77	–0.03
31 _{5,26} ← 31 _{5,27}	23 391.21	0.01
33 _{7,27} ← 32 _{8,24}	26 989.26	–0.01
37 _{6,31} ← 37 _{6,32}	24 935.95	–0.02
40 _{9,31} ← 39 _{10,30}	27 281.20	0.03
43 _{7,36} ← 43 _{7,37}	26 022.65	0.06
49 _{8,41} ← 49 _{8,42}	26 711.16	–0.06
55 _{9,46} ← 55 _{9,47}	27 053.73	0.03
61 _{10,51} ← 61 _{10,52}	27 096.23	0.07
67 _{11,56} ← 67 _{11,57}	26 880.35	–0.03
Coalescing <i>P</i> - and <i>R</i> -branch transitions ^b		
29 _{1,1} ← 30 _{1,0}	26 554.31	–0.04
33 _{1,2} ← 34 _{1,1}	24 755.69	–0.03
37 _{1,3} ← 38 _{1,2}	22 937.78	0.00
42 _{1,4} ← 43 _{1,3}	17 258.92	0.03
46 _{1,6} ← 47 _{1,5}	28 916.83	0.00
52 _{1,7} ← 53 _{1,6}	19 398.92	–0.08
61 _{2,0} ← 62 _{1,9}	25 390.97	0.03
68 _{2,2} ← 69 _{2,1}	25 532.10	0.01
75 _{2,4} ← 76 _{2,3}	25 670.12	–0.02
82 _{2,6} ← 83 _{2,5}	25 806.03	–0.05
92 _{2,9} ← 93 _{2,8}	27 940.88	–0.12
63 _{1,6} ← 62 _{1,7}	20 074.45	0.10
67 _{1,7} ← 66 _{1,8}	22 012.64	0.06
71 _{1,8} ← 70 _{1,9}	23 950.67	0.00
78 _{2,0} ← 77 _{2,1}	23 776.92	–0.01
81 _{2,1} ← 80 _{2,7}	21 678.67	0.07
86 _{2,2} ← 85 _{2,3}	27 645.53	0.00
89 _{2,3} ← 88 _{2,4}	25 541.42	–0.03
96 _{2,5} ← 95 _{2,6}	25 375.55	–0.10

^a±0.05 MHz. ^bThe K_{-1} doublets coalesce for high values of J and K_{-1} . Subscripts of J quantum number refer to K_{-1} .

Table 4. Spectroscopic constants^{a,b} of the ground and first excited vibrational state of the C2–C5 torsional vibration of the *anti* conformer furan-3-carboxaldehyde.

No. of transitions:	239	115
R.m.s. deviation/MHz:	0.046	0.049
A/MHz	8238.727 6(16)	8167.270 2(29)
B/MHz	1976.138 83(42)	1976.439 79(66)
C/MHz	1593.971 14(34)	1596.835 15(57)
Δ_J /kHz	0.139 02(89)	0.139 6(13)
Δ_{JK} /kHz	0.748 2(92)	0.632 (14)
Δ_K /kHz	1.761 6(89)	-0.621 (14)
δ_J /kHz	0.030 99(17)	0.031 27(34)
δ_K /kHz	0.829 (14)	0.515 (26)
Φ_{JK} /Hz	-0.001 331(45)	-0.022 9(14)
$I_c - I_a - I_b$ /10 ⁻²⁰ m ² u	-0.025 955(26)	-1.092 365(47)

^aA-reduction *I*-representation.¹⁶ ^bUncertainties represent one standard deviation. ^cRoot-mean-square deviation. ^dFurther sextic centrifugal distortion constants fixed at zero. ^eConversion factor 505 379.05 × 10⁻²⁰ MHz m² u.

mol⁻¹. As will be shown below, this energy difference is clearly too small. In order to see if correlation effects influence the energy difference, *ab initio* computations have been made using the MP2/6-31G* basis set, which takes this effect into consideration. The geometries of *syn* and *anti* were completely optimized by the gradient method¹³ included in the standard calculation package.¹⁴ The computations were made using the Gaussian 90 program package¹⁴ running on the Cray-X-MP/216 computer in Trondheim. In Table 1 the optimized structural parameters are given, and some selected results are shown in Table 2. It is seen in the latter table that taking correlation into consideration did not improve the calculated energy difference between *syn* and *anti*. Calculation of vibrational frequencies is not implemented in the MP2/6-31G* basis set. In order to compare them with those obtained by relative intensity measurements, calculations were repeated using the 6-31G* basis set. Some of the calculated vibrational frequencies are given in the text below.

Assignment. The solution studies¹⁻⁷ and the *ab initio* results of Ref. 8, as well as those presented in Table 2, strongly indicated that the planar *anti* conformer is preferred by the

title molecule. The dipole moment predictions given in Table 2 indicated that the molecule should possess a sizable dipole moment along the *a*-inertial axis. Pile-ups of high-*K*₁ *R*-transitions separated by a frequency of approximately *B* + *C* were therefore expected to occur.¹⁵ Such a spectral feature was immediately seen in the broad-band spectra that were taken first. The assignments of the individual *a*-type *R*-branch transitions were made without problems. Extension to *b*-type *Q*-branch lines was made next. Finally, high-*J* *P*- and *R*-branch transitions were identified. A total of 239 transitions with a maximum value for *J* of 96 were ultimately measured. A portion of the spectrum* is shown in Table 3, while the spectroscopic constants (*A*-reduction *I*-representation)¹⁶ found from these transitions by the method of least-squares fitting are given in Table 4. One sextic constant has to be used in order to get a fit with a root-mean-square deviation comparable to the experimental uncertainty of ±0.05 MHz. Note the very good agreement between the rotational constants shown in Table 4 and those obtained in the theoretical computations (Table 2).

The inertial defect $\Delta = I_c - I_a - I_b$ shown in Table 4 is close to zero and almost the same as for furan-⁹ pyrrole-¹⁰ and thiophene-2-carboxaldehyde,^{9a,11} all of which have been shown to be planar.

Vibrationally excited states. The ground-state transitions were accompanied by satellite lines presumably belonging to vibrationally excited states. As shown in Tables 4–6, six excited states belonging to three different normal modes were ultimately assigned.

The most prominent excited state is probably associated with the torsion around the C2–C5 bond. As seen in Tables 4 and 5, the rotational constants and the inertial defect change rather linearly upon successive excitation of this vibration. This is typical for an out-of-plane mode that is rather harmonic, and presents additional evidence for a

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

Table 5. Spectroscopic constants^{a,b} in vibrationally excited states of the torsion around the C2–C5 bond of the *anti* conformer of furan-3-carboxaldehyde.

Vibrational state:	2nd excited	3rd excited	4th excited
No. of transitions:	27	17	17
R.m.s. deviation/MHz:	0.087	0.115	0.040
A_v /MHz	8098.878 (10)	8032.893 (18)	7967.57(50)
B_v /MHz	1976.729 8(24)	1976.978 5(68)	1977.205 3(56)
C_v /MHz	1599.706 1(21)	1602.590 2(69)	1605.461 6(56)
δ_J /kHz	0.018 4(26)	-0.022 (14)	— ^d
$I_c - I_a - I_b$ /10 ⁻²⁰ m ² u	-2.145 38(48)	-3.194 4(22)	-4.244 9(55)

^{a-c}Comments as for Table 4. ^dThe other quartic centrifugal distortion constants were preset at the ground-state values shown in Table 4. ^eAs Table 4.

Table 6. Spectroscopic constants^{a,b,d} of the first excited states of the two lowest bending vibrations of the *anti* conformer of furan-3-carboxaldehyde.

Vibrational state:	In-plane bending	Out-of-plane bending
No. of transitions:	44	39
R.m.s. deviation ^c /MHz:	0.056	0.038
A_v /MHz	8302.600 6(47)	8240.357 3(39)
B_v /MHz	1978.240 99(82)	1976.307 07(50)
C_v /MHz	1593.656 41(81)	1594.984 83(50)
$I_c - I_a - I_b$ /10 ⁻²⁰ m ² u	0.780 33(12)	-0.193 557(72)

^{a-c}Comments as for Table 5.

planar equilibrium conformation of the molecule,¹⁷ The changes in the inertial defect upon successive excitations are also rather similar to those found in the other three cases.⁹⁻¹¹ Relative intensity measurements made as described in Ref. 18 yielded 125(15) cm⁻¹ for this vibration, as compared to 146 cm⁻¹ calculated using the 6-31G* basis.

The vibrationally excited states listed in Table 6 are presumed to be the lowest in-plane and lowest out-of-plane bending vibrations, respectively. These assignments are based upon the changes of the inertial defects upon excitation.¹⁷ Relative intensity measurements¹⁸ yielded 206(20) cm⁻¹ for the in-plane bending frequency, and 275(25) cm⁻¹ for the out-of-plane bending vibration. The *ab initio* values were 211 and 301 cm⁻¹, respectively.

Dipole moment. The dipole moment was determined following standard procedures.¹⁹ The results are shown in Table 7. The total dipole moment of the free molecule agrees well with those determined in solution.^{6,7} The calculated total dipole moment for *anti* (Table 2) as well as its components along the principal inertial axes agree very well with that determined experimentally. The dipole moments determined in the solution studies^{6,7} are also close to the present results.

Conformer assignment. Accidentally, the rotational con-

Table 7. Stark coefficients^a and dipole moments^a of the *anti* conformer of furan-3-carboxaldehyde.

Transition	M	$\Delta v E^{-2}/10^{-6}$ MHz V ⁻² cm ²	
		Obs.	Calc.
5 _{1,4} ← 4 _{1,3}	1	10.8(2)	10.8
	2	6.98(8)	6.93
	4	-8.54(10)	-8.43
4 _{1,3} ← 3 _{1,2}	1	-7.59(7)	-7.66

Dipole moment/10⁻³⁰ C m

$\mu_a = 8.377(42)$ $\mu_b = 3.898(14)$ $\mu_{tot} = 9.239(42)^b$

^aUncertainties represent one standard deviation, 1 debye = 3.33564 × 10⁻³⁰ C m. ^bThe component of the dipole moment along the *c*-inertial axis was assumed to be zero for symmetry reasons.

stants of *syn* and *anti* are predicted to be quite similar, as shown in Table 2. Both conformers are also predicted to have large components of their dipole moment along the *a*-axes. A unambiguous assignment of the observed conformer as the *anti* conformer, and not the *syn*, cannot therefore be claimed exclusively on the basis of the rotational constants and dipole moment. Additional evidence is needed. Fortunately, this is available. The numerous solution studies¹⁻⁷ and the relative stabilities as calculated with high-level *ab initio* techniques above and in Ref. 8 are two pieces of evidence. In addition, there is much better agreement between the observed (Table 4) and calculated rotational constants (Table 2) for *anti* than for *syn*. The same is seen for the dipole moment and its components along the *a*- and *b*-principal inertial axes. The above evidence convinces us that *anti*, and not *syn*, has indeed been assigned.

Searches for *syn*. The spectral assignments reported above include all strong and intermediate-intensity transitions. Many of the weakest transitions have also been assigned.

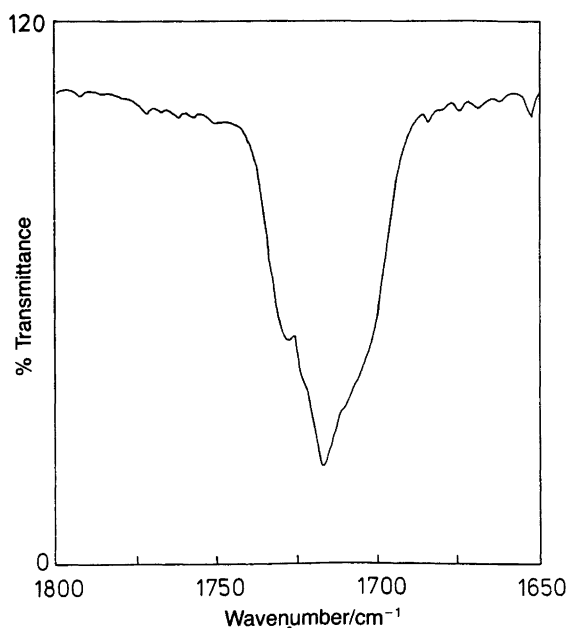


Fig. 2. Gas-phase infrared spectrum of furan-3-carboxaldehyde in the carbonyl group stretching region. The absorption maximum is at 1718 cm⁻¹.

Searches were made for the *a*-type *R*-branch lines of the hypothetical *syn* conformation amongst the remaining weak, unassigned transitions, because it is predicted to possess a large μ_a (Table 2). The *a**R*-transitions should be easy to assign, provided this rotamer were present. However, our searches were unsuccessful. It is concluded that if *syn* exists, it cannot be present with a concentration higher than 10% of the total in the gas at -15°C . The energy difference between *anti* and the hypothetical *syn* is then conservatively estimated to be at least 5 kJ mol^{-1} . The theoretical computations (Table 2) definitely underestimate the energy difference between *syn* and *anti* in this case.

The gas-phase IR spectrum in Fig. 2 of the carbonyl stretching frequency corroborates the microwave data, at least to a certain extent, as there is no obvious splitting of this band that can be associated with two conformers.

Structure. As already noted, the calculated rotational constants in Table 2 are in remarkably good agreement with the experimentally observed ones. Moreover, the furan part is calculated (Table 1) to have a structure that is very close to that of furan itself,²⁰ whereas the geometry of the C₂C₅H₄O₂ part is very similar to that of *anti*-acrolein.²¹ On this basis we suggest the theoretical structure to be the best available approach to the structure of the *anti* conformer of furan-3-carboxaldehyde.

Discussion

The C1–C2–C5–O2 chain of atoms takes the *anti* conformation in the stable conformer of furan-3-carboxaldehyde, as shown above. Interestingly, the corresponding chain of atoms in propenal (acrolein) also strongly prefers the *anti* conformation.²¹ In fact, in propenal the *anti* conformer is present in a concentration of 98%, while *syn* is present in 2% concentration at room temperature.²¹ 2-Methylpropenal²² and *trans*-2-butenedial²³ also take the *anti* form.

There is probably no simple explanation why furan-3-carboxaldehyde strongly prefers *anti* instead of *syn*. Benassi *et al.*⁸ have pointed out that the relative stability of these conformers is a balance between conjugative interactions between the formyl group and the ring and local electrostatic interactions between the atoms of the formyl group and those of the ring, a view that is shared by us.

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