

Microwave Spectrum, Dipole Moment, Planarity and Stability of *syn*-Oxalyl Fluoride. *Ab Initio* Computations of the *anti*–*syn* Equilibrium of Oxalyl Fluoride

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The microwave spectrum of oxalyl fluoride has been investigated in the gas phase in the 10.0–39.0 GHz spectral region at dry-ice temperature (–78 °C). The *syn* conformer having the two carbonyl groups and the two C–F bonds *syn* to each other was assigned. This rotamer has a *planar* equilibrium conformation.

Nine successively excited states of the torsional fundamental mode were assigned. The torsional fundamental frequency was determined to be 26(5) cm^{–1}. The rotational constants of the ground and of six torsionally excited states were used to determine the shape near the bottom of the potential well of the *syn* conformer. This shape is defined in terms of the dimensionless parameter z as $V(z) = 7.0 (\langle z^4 \rangle + 2.0 \langle z^2 \rangle)$ cm^{–1}. The full potential function has also been approximated by $V(\phi) = \sum \{1/2 V_n [1 - \cos(n\phi)]\}$ and the three first constants of the series determined to be $V_1 = 2.24$, $V_2 = 9.59$, and $V_3 = 0.26$ kJ mol^{–1}. The transition state lies 10.9(20) kJ mol^{–1} above the *anti* minimum for $\phi = 90(3)^\circ$. Absolute intensity measurements have been used to determine the Gibbs free energy difference at 195 K between *syn* and *anti* as $\Delta G^\circ = 1.7(5)$ kJ mol^{–1} (*anti* more stable than *syn*). The entropy difference, $\Delta S^\circ = 5.1(1)$ J K^{–1} mol^{–1} was found using statistical mechanics. The enthalpy difference is $\Delta H^\circ = H_{syn}^\circ - H_{anti}^\circ = 2.7(6)$ kJ mol^{–1}. The dipole moment of *syn*-oxalyl fluoride is $3.652(83) \times 10^{-30}$ C m.

The microwave work was assisted by *ab initio* computations at the MP2/6-31G* and MP2/6-311 + G* levels of theory. In the latter of these two formulations the *anti* conformer is computed to be 2.2 kJ mol^{–1} more stable than *syn* with a transition state lying 7.6 kJ mol^{–1} above the energy of the more stable *anti* conformer. These results are in good agreement with the experimental findings.

The structural and conformational properties of oxalyl fluoride have attracted the interest of several workers^{1–6} for obvious reasons: This molecule possesses two highly electronegative atoms, oxygen and fluorine, attached to the same carbon atom. The relative orientation of the two CFO groups is influenced by the electronegativity as well as other effects such as conjugation, dipole–dipole interaction and hybridisation of the carbon atoms. Oxalyl fluoride may exist either as planar *anti* or *syn* conformers as sketched in Fig. 1, or as some intermediate non-planar form(s).

Hencher and King¹ first addressed this problem in 1965 using infrared and Raman spectroscopy, and concluded that the spectra could be satisfactorily explained on the assumption that oxalyl fluoride is present in the planar *anti* form only. Durig *et al.*,² using the same methods, found that there are two rotamers in the gas, a more

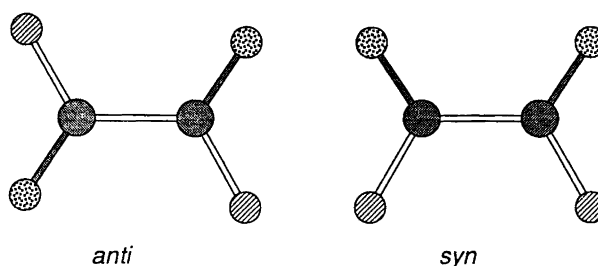


Fig. 1. The *anti* and *syn* conformers of oxalyl fluoride. The *syn* has been assigned in this work and shown to be 2.7(6) kJ mol^{–1} less stable than *anti*.

stable *anti* and a less stable *syn*. The torsional frequency of the *anti* form was observed at 54 cm^{–1} in their far-IR experiment.² Goubeau and Adelhelm,³ again employing vibrational spectroscopy, came to the same conclusion with regard to the existence of *anti* and *syn* as that of the American workers.² An electron-diffraction study was

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carried out by Borgers⁴ in 1968. It was concluded that two conformers are present. One of them is *anti*, whereas the conformation of the other rotamer was uncertain.⁴ A new electron-diffraction investigation was made by Friesen⁵ in 1981. He also found that *anti* is preferred, but he was unable to decide whether the second conformer is *syn* or *gauche*. An accurate structure was derived and the energy difference between *anti* and the other rotamer was estimated to be in the 3.7–8.9 kJ mol⁻¹ range.⁵ Very recently Davis *et al.*,⁶ utilizing Raman spectroscopy, determined the enthalpy difference between *syn* and *anti* in the gas phase to be in the 2.3–4.4 kJ mol⁻¹ range (*anti* most stable). These workers also made *ab initio* computations up to the MP2/6-31G* level of theory and found good agreement with their experimental results for the energy difference.

The *anti* conformer cannot be studied by microwave (MW) spectroscopy since it has no dipole moment for symmetry reasons. However, the *syn* (or a *hypothetical skew* or *gauche*) conformer should possess a sizeable dipole moment, and should thus be observable by this method provided it is present in detectable amounts. MW spectroscopy is ideally suited to determine beyond doubt whether the high-energy *syn* conformer is indeed completely planar as has previously been alleged,^{2,3,6} or if it has for example a potential hump at this planar conformation. A MW study of vibrationally excited states of the torsion around the C–C bond can give important information about the torsional potential function near the *syn* minimum. If the energy difference between *syn* and *anti* can be derived together with the torsional frequency of *syn*, there would now be sufficient experimental data to construct a full potential function and thereby obtain information about the transition state. Moreover, the dipole moment of *syn* can be determined accurately by the MW method and provide important information about the electronic distribution within oxalyl fluoride and the in-

fluence alleged conjugation might have on this compound. These were the motivations to carry out the present research.

Experimental

Oxalyl fluoride was purchased from Lancaster Synthesis, Ltd., UK and checked by GC-MS, which revealed no detectable impurities. The MW spectrum was studied using the Oslo spectrometer which is described in Ref. 7. The 10.0–39.0 GHz spectral region was investigated with the microwave absorption cell cooled to dry-ice temperature (–78 °C). The pressure was about 3–9 Pa when the spectra were recorded. The accuracy of the spectral measurements is presumed to be better than ±0.05 MHz.

Results

Ab initio calculations. The *ab initio* computations were made at the MP2/6-31G* and MP2/6-311+G* levels of theory using the Gaussian 92 program package⁸ running on the Cray Y-MP computer in Trondheim and the IBM-RS6000 cluster in Oslo. The geometries of the various forms were fully optimized with one restriction, namely that the molecule retained C₂ symmetry. It was thus not assumed initially that *anti* and *syn* were completely planar, but the fully optimized structures refined to planar forms as indicated in Table 1.

The starting point in the computations of the transition state was a conformation that had the two CFO groups almost perpendicular to one another. This guess is quite natural considering the structure of the oxalyl fluoride molecule. The optimized conformations computed with both basis sets for the transition state came close to this suggestion (Table 1). It is also noted that the CCFO

Table 1. Calculated structures and energy differences obtained in the MP2/6-31G* and MP2/6-311+G* computations and structure determined in the electron-diffraction work.⁵

Basis:	MP2/6-31G*			MP2/6-311+G*			Exp. ^a
	<i>Syn</i>	<i>Anti</i>	Trans. state	<i>Syn</i>	<i>Anti</i>	Trans. state	
Structure ^b							
C–F	134.4	134.1	135.0	133.7	133.4	134.4	132.9(1)
C–C	152.8	152.6	151.4	153.5	153.4	152.0	153.6(3)
C=O	119.6	119.6	119.5	118.6	118.7	118.5	118.0(1)
F–C–C	111.8	109.5	109.9	112.1	109.5	109.8	109.8(1)
C–C=O	124.1	126.2	126.0	123.9	126.5	126.2	126.0(2)
F–C–C=O	180.0	0.0	88.9	180.0	0.0	87.8	0.0 ^c
F–C–C–F	0.0	180.0	–92.6	0.0	180.0	–93.9	180.0 ^c
Energy differences ^d /kJ mol ⁻¹	1.8	0.0	11.0	2.2	0.0	7.6	

^a Electron-diffraction structure taken from Friesen.⁵ This structure is presumed to be close to that of *anti*; see text. ^b Distances in pm; angles and dihedral angles in °. ^c Dihedral angles are measured from *anti* position (0°). ^d Assumed. ^e The absolute energy of *anti* was found to be –1116495.4 kJ mol⁻¹ in the MP2/6-31G* computation, and to be –1117135.4 kJ mol⁻¹ in the MP2/6-311+G* calculation.

group of atoms of the transition state is predicted to be very slightly pyramidal. The transition state was found typically⁹ to have one negative vibrational frequency (for the C–C torsion).

It is further noted that there are rather small differences in the structures calculated using the two basis sets. The MP2/6-311+G* structure has slightly shorter C–F and C=O bonds and a longer C–C bond than the MP2/6-31G* structure. The bond angles differ by less than 0.5°. There is also very good agreement for the *anti* conformer with the electron-diffraction structure⁵ included in this table, especially in the case of the largest basis set. The experimental structure⁵ is actually an average of the structures of *syn* and *anti* conformers but should be closer to *anti* than to *syn*, since the former rotamer is the predominating one. It is therefore more appropriate to compare the experimental structure⁵ with that calculated for *anti* than that computed for *syn*.

The energy differences with *anti* as the more stable form, are computed to be practically the same (about 2 kJ mol⁻¹) with both basis sets (Table 1). A much larger difference is seen for the transition state, which is calculated to lie about 3.5 kJ mol⁻¹ higher in energy in the MP2/6-31G* computation than in the MP2/6-311+G* calculation.

The predicted rotational constants and dipole moments are displayed in Table 2. The individual rotational constants calculated from the structures in Table 1 differ by less than 2.5% with the two basis sets. A larger difference exists for the theoretical dipole moment shown in Table 2. The dipole moment of the *syn* conformer is about 15% lower in the more elaborate computation. In Table 3 the vibrational frequencies computed using the larger 6-311+G* basis set in the MP2 procedure are listed. Some assignments of fundamentals to *anti* and *syn* of gaseous oxalyl fluoride which were given in the earlier studies^{2,6} as well as in the present one, are included in Table 3. It is seen that good agreement exists between the calculated and experimental fundamental frequencies. The largest discrepancy seen in this table is only 31 cm⁻¹ (for the COF rocking vibration of *anti*⁶). The two experi-

mental torsional fundamental frequencies are rather low, 54 cm⁻¹ (Ref. 2) and 26(5) cm⁻¹ (see below), respectively, which points to a very flexible molecule. The theoretical frequencies (Table 3) are too low by 17 cm⁻¹ in the case of *anti*, and by 14 cm⁻¹ in the case of *syn*.

MW spectrum and assignment. The first survey spectra taken in the 18–30 GHz spectral region revealed a rich, complex and intense spectrum typical for a *b*-type spectrum of a rather asymmetric ($\kappa \approx -0.26$) molecule with a relatively 'small' *A* rotational constant (Table 2). The strongest absorption lines occurring in this region had peak absorption coefficients of roughly 4.0×10^{-7} cm⁻¹ at dry-ice temperature. All lines were modulated at rather high Stark voltages, and many of them were presumably intermediate-*J* *Q*-branch transitions, as indicated by their unresolved Stark effects. A few lines with resolved Stark effects were also encountered. The first attempts to assign the spectrum in this region failed because the frequencies are quite sensitive to the *A* rotational constant, and the value initially used (from the MP2/6-31G* calculation done first) differed by as much as 2.6% from the experimental value (see Table 5 below). This was more than initially expected, and it delayed the assignments.

A survey spectrum was next taken in the 10–14 GHz region. The spectrum is much simpler here than in the 18–30 GHz region, and a *Q*-branch assignment was soon obtained. Finding the *R*-branch transitions was now easy. A portion of the ground-state spectrum is listed in Table 4.[†]

103 *b*-type transitions were ultimately measured for the ground vibrational state. A majority of these lines were *Q*-branch transitions. The maximum value of *J* was 25. *P*- and *R*-branch transitions involving considerably higher values of *J* are predicted to be present in the spectrum, but they are much weaker than the assigned ones and were not found in our search. A least-squares fit involving only quartic centrifugal distortion constants¹⁰ (Table 5) produced a root-mean-square deviation of the fit comparable to the experimental uncertainty. Inclusion of sextic centrifugal distortion constants¹⁰ yielded no improvement.

Excited torsional states. The ground-state spectrum was accompanied by several satellite spectra which could obviously be ascribed to vibrationally excited states of the torsional fundamental vibration. The rotational transitions of the successively excited states of this mode were seen to be separated by roughly constant intervals, with the intensities decreasing by about 20% upon excitation by one vibrational quantum. This behaviour is typical for a nearly harmonic vibration.¹¹

[†] The full ground-state spectrum and the spectra of the vibrationally excited states are available from the authors upon request, or from the Molecular Spectra Data Center, National Institute for Standards and Technology, Molecular Physics Division, Bldg. 221, Room B265, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 2. Calculated rotational constants and dipole moments obtained in the MP2/6-31G* and MP2/6-311+G* computations.

Basis:	MP2/6-31G*		MP2/6-311+G*	
	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>
Rotational constant ^a /MHz				
<i>A</i>	5747.8	5784.5	5835.0	5876.1
<i>B</i>	3601.1	3558.3	3585.3	3545.8
<i>C</i>	2214.0	2203.1	2220.8	2211.4
Dipole moment/10 ⁻³⁰ C m				
	4.70	0.0 ^b	4.03	0.0 ^b

^a Calculated from the structure in Table 1. ^b For symmetry reasons.

Table 3. Fundamental frequencies (cm^{-1}) obtained in the MP2/6-311+G* computations.

Symmetry:	D_{2h}			C_{2v}		
	Anti			Syn		
Conformer:	Calc.	Obs.	Species	Calc.	Obs.	Species
	37	54 ^a	A_u	12	26(5) ^b	A2
	258		B_u	260	249	A1
	422	414	A_g	430	415	A1
	458		A_u	463		B1
	531	500	A_g	515		B2
	677		B_u	674		B2
	808	803	A_g	807		A2
	811	830	B_g	807	825	A1
	1105		B_u	1080		B2
	1277	1290	A_g	1279	1267	A1
	1879		B_u	1864		B2
	1879	1869	A_g	1895	1892	A1

^a From Ref. 2. ^b This work, see below. All the other observed fundamentals but the two torsional modes are from Ref. 6.

Table 4. Selected translations of the MW spectrum of the ground vibrational state of oxalyl fluoride.

Transition	Observed	Obs. - calc.	
$J''_{K''-1, K''+1} \leftarrow J'_{K'-1, K'+1}$	frequency ^a /MHz	freq./MHz	
2 _{2,1}	← 1 _{1,0}	19949.49	-0.03
4 _{2,3}	← 3 _{1,2}	28224.58	0.01
5 _{1,4}	← 5 _{0,5}	18141.22	0.07
5 _{3,2}	← 5 _{2,3}	10928.07	0.01
6 _{1,6}	← 5 _{0,5}	29179.07	0.01
6 _{3,4}	← 6 _{2,5}	20499.50	-0.03
7 _{1,6}	← 7 _{0,7}	27878.99	0.05
7 _{3,4}	← 7 _{2,5}	23244.58	0.02
8 _{1,8}	← 7 _{0,7}	38083.18	-0.03
8 _{5,4}	← 8 _{4,5}	26069.88	-0.03
9 _{5,4}	← 9 _{4,5}	19276.71	-0.10
9 _{7,3}	← 9 _{6,4}	36926.68	0.06
10 _{4,7}	← 10 _{3,8}	31089.93	-0.05
10 _{6,4}	← 10 _{5,5}	26789.57	0.01
11 _{4,7}	← 11 _{3,8}	24001.30	0.00
11 _{6,6}	← 11 _{5,7}	31473.52	-0.03
12 _{3,9}	← 12 _{2,10}	38823.17	0.07
12 _{6,6}	← 12 _{5,7}	21587.50	-0.02
13 _{4,9}	← 13 _{3,10}	35968.72	0.08
13 _{7,6}	← 13 _{6,7}	28932.07	0.09
14 _{7,7}	← 14 _{6,8}	25851.77	-0.02
15 _{5,10}	← 15 _{4,11}	37782.57	0.03
15 _{7,9}	← 15 _{6,10}	38628.62	0.02
17 _{7,10}	← 17 _{6,11}	27771.48	0.03
18 _{9,9}	← 18 _{8,10}	35539.04	0.05
20 _{8,12}	← 20 _{7,13}	34092.80	0.02
21 _{9,12}	← 21 _{8,13}	31019.04	-0.02
22 _{10,12}	← 22 _{9,13}	33634.72	0.01
24 _{11,13}	← 21 _{10,14}	37709.86	0.00
25 _{11,14}	← 25 _{10,15}	35991.08	0.04

^a ± 0.05 MHz.

Nine excited states of the torsion were ultimately assigned, as shown in Table 5. The seven first excited states were fitted without problems to the Watson Hamiltonian¹⁰ including only quartic centrifugal distortion constants, just as for the ground state. However, in fitting the $\nu_T = 8$ and $\nu_T = 9$ excited states it was found that a few

of the high- K_{-1} transitions did not fit very well (off by typically 1–2 MHz), possibly because of higher-order interactions. These transitions were omitted in the final fits whose results are presented in Table 5. In this table it is seen that the rotational constants, the centrifugal distortion constants and the inertial defect $\Delta = I_c - I_a - I_b$ (I_a , I_b and I_c are the principal moments of inertia) vary rather smoothly with the vibrational quantum number. Again, this is typical for a near-harmonic mode. All centrifugal distortion constants vary much upon successive excitation. This also reflects a very flexible conformation.

Relative intensity measurements, performed largely as described in Ref. 12, on carefully selected lines of the ground and first excited state yielded 28(7) cm^{-1} for the torsional fundamental. This is about 16 cm^{-1} higher than what was predicted in the MP2/6-311 + G* computations (Table 3).

An additional reason for assigning the satellite spectrum to excited states of the torsional mode is the fact that the inertial defect decreases upon excitation,¹¹ as shown in Table 5. The changes in the inertial defect upon excitation can be used to calculate the torsional vibration frequency provided it is well separated from other vibrational modes.¹¹ This criterion is met in the present case, as the lowest in-plane bending vibration is reported to be 249 cm^{-1} (Ref. 5) and computed at 260 cm^{-1} (Table 3), well above the 28(7) cm^{-1} determined by relative intensity measurements. From Ref. 13 one has that the torsional frequency ω_T in such cases is approximated by $\omega_T \approx 67.45 \times 10^{-20} \text{ m}^2 \text{ u cm}^{-1} / \delta\Delta$, where $\delta\Delta$ is taken as the change in the inertial defect between the first excited and ground state. From Table 5 one thus finds a torsional fundamental frequency as $\omega_T \approx 26 \text{ cm}^{-1}$, very close to 28(7) cm^{-1} obtained by relative intensity measurements. The uncertainty limit of the torsional fundamental obtained in this manner is hard to estimate, but $\pm 5 \text{ cm}^{-1}$ seems plausible. Our best estimate of the torsional frequency ω_T is thus $\omega_T = 26(5) \text{ cm}^{-1}$.

Table 5. Spectroscopic constants^{a, b} in the ground and vibrationally excited states of oxalyl fluoride.

Vibrational state:	$v_T=0$	$v_T=1$	$v_T=2$	$v_T=3$	$v_T=4$
No. of transitions:	103	103	107	94	77
R.m.s. dev. ^c /MHz:	0.041	0.062	0.063	0.060	0.088
A_v /MHz	5902.9095(26)	5900.0449(38)	5897.4039(39)	5894.9164(44)	5892.5260(81)
B_v /MHz	3588.5822(24)	3558.9553(36)	3531.1492(36)	3504.3795(42)	3478.2297(80)
C_v /MHz	2240.7582(23)	2254.8132(36)	2268.2233(36)	2281.3962(41)	2294.5331(78)
ΔJ /kHz	0.826(26)	1.158(39)	1.340(39)	1.542(43)	1.635(77)
ΔJK /kHz	-0.788(24)	-1.780(30)	-2.380(28)	-2.921(37)	-3.580(66)
ΔK /kHz	1.508(40)	2.194(59)	2.569(49)	2.894(69)	3.40(15)
δ_v /kHz	0.2972(26)	0.3504(31)	0.4067(31)	0.4487(36)	0.4754(53)
δ_K /kHz	1.410(20)	2.673(25)	3.618(26)	4.582(32)	5.724(50)
$(I_c - I_a - I_b)^d/10^{-20} \text{ m}^2 \text{ u}$	-0.90567(13)	-3.52545(19)	-6.00711(18)	-8.42307(19)	-10.81035(33)

^a A-reduction, I_r -representation.¹⁰ ^b Uncertainties represent one standard deviation. ^c Root-mean-square deviation. ^d Conversion factor $505\,379.05 \times 10^{-20} \text{ m}^2 \text{ u MHz}$.

All the strong lines as well as all transitions of intermediate intensities in this spectrum were assigned to the ground and the nine torsionally excited states of *syn*. It is ruled out that hypothetical *polar* conformations such as *skew* or *gauche* forms coexist with *syn* (and *anti*) to any significant extent.

Planarity of syn-oxalyl fluoride. The behaviour of the excited states described in the previous section strongly indicates that the torsional mode is nearly harmonic and that *syn*-oxalyl fluoride thus has a *planar* equilibrium conformation. This can be put in a more quantitative way following Gwinn and co-workers, who have shown that it is possible to define a potential function for the torsion of the form

$$V = A \langle z^4 \rangle + B \langle z^2 \rangle \quad (1)$$

where z is a dimensionless coordinate. If B is positive, the molecule is planar; if B is negative a potential hump exists at the planar conformation and the potential function of the *syn* conformer would be of the double-minimum type. The equilibrium conformation would in such a case be non-planar.

The Gwinn theory^{14,15} implies that rotational constants can be expanded in a power series of the expectation values of z^2 and z^4

$$\beta_v = \beta_0 + \beta_2 \langle z^2 \rangle_v + \beta_4 \langle z^4 \rangle_v \quad (2)$$

where β_v is the A_v , B_v or C_v rotational constant in the n th excited state of the torsion. β_0 , β_2 and β_4 are empirical parameters adjusted to give the best fit to the data. The values of $\langle z^2 \rangle_v$ and $\langle z^4 \rangle_v$ depend only on the value of the constant B of eqn. (1).

The rotational constants of successively excited states of the torsional vibration were least-squares fitted to eqn. (2) employing the computer programs described in Ref. 16 for a series of values of B . It was found that the value $B = 2.0$ yielded the best overall fit (Table 6). This positive value of B is thus another piece of evidence that

the *syn* conformer has a completely *planar* equilibrium conformation.

Initially, all excited states were utilized in the fitting procedure, but it turned out the $v_T = 7$, $v_T = 8$ and $v_T = 9$ did not fit well in the case of the B_v rotational constant (off by more than 1 MHz; Table 6). These states were therefore omitted in the final fits (Table 6). Such discrepancies are to be expected when a simple one-dimensional model like that in eqn. (1) is utilized for fitting and interaction with other vibrational modes occurs.

The A constant [eqn. (1)] was then adjusted to reproduce the torsional fundamental frequency of 26 cm^{-1} . This was achieved with $A = 7.0 \text{ cm}^{-1}$. The potential function derived in this manner is $V = 7.0 (\langle z^4 \rangle + 2.0 \langle z^2 \rangle) \text{ cm}^{-1}$. It is sketched in Fig. 2 and is presumed to give a rather accurate description of the potential function near the *syn* bottom.

Dipole moment. The dipole moment determined in the ordinary manner¹⁷ is given in Table 7. The theoretical MP2/6-311+G* dipole moment comes rather close to the experimental value, while the MP2/6-31G* model is somewhat too high (Table 2).

Energy difference between syn and anti and the full potential function. Five of the six previous works²⁻⁶ claim that two conformers, *syn* and *anti*, are stable.

Davis *et al.*⁶ found that *anti* is more stable than *syn*, with an upper enthalpy difference limit of about 4.4 kJ mol⁻¹, whereas Friesen⁵ found a much higher upper limit. The upper limit of Davis *et al.*⁶ must be somewhat too high because *syn* has a comparatively strong MW spectrum and must consequently be present in the gas phase with a larger fraction than that which 4 kJ mol⁻¹ roughly implies.

Fortunately, it is possible to estimate the energy difference between *anti* and *syn* even if *anti* has no dipole moment and therefore no rotational spectrum. The key to this is *absolute* intensity measurements and the assumption that only *one* additional conformation, the *anti*, coexists with *syn*.¹⁸

Table 5. continued.

$v_T=5$ 85 0.073	$v_T=6$ 72 0.070	$v_T=7$ 55 0.067	$v_T=8$ 31 0.062	$v_T=9$ 34 0.091
5890.2068(52)	5887.9583(68)	5885.7455(59)	5883.6158(75)	5881.479(10)
3452.4410(51)	3426.8121(68)	3401.1510(63)	3375.2589(80)	3348.854(10)
2307.7806(51)	2321.2708(69)	2335.1212(64)	2349.4789(79)	2364.451(10)
1.783(53)	1.952(84)	2.236(78)	2.90(10)	2.83(12)
-4.124(35)	-4.732(38)	-5.506(50)	-6.52(11)	-7.47(10)
3.773(80)	4.178(85)	4.54(13)	5.51(28)	6.08(23)
0.5176(33)	0.5444(37)	0.5844(39)	0.6099(77)	0.6746(81)
6.806(30)	8.102(33)	9.721(39)	11.752(86)	14.152(94)
-13.19378(23)	-15.59401(29)	-18.03032(27)	-20.52384(31)	-23.09773(41)

Table 6. Comparison of calculated and observed rotational constants (MHz) using $B=2.0$.

v_T	A_v^a	Calc. - obs. ^b	B_v^a	Calc. - obs. ^b	C_v^a	Calc. - obs. ^b
0	5902.922	0.012	3588.628	0.046	2240.759	0.000
1	5900.000	-0.044	3558.587	-0.368	2254.828	0.015
2	5897.421	0.018	3531.060	-0.089	2268.259	0.036
3	5895.004	0.088	3504.854	0.475	2281.255	-0.141
4	5892.594	0.068	3478.192	-0.038	2294.746	0.213
5	5890.262	0.055	3452.195	-0.246	2308.002	0.221
6	5888.003	0.045	3426.866	0.054	2320.988	-0.283
7 ^c	5885.592	-0.154	3399.196	-1.955	2335.455	0.334
8 ^c	5883.634	0.019	3377.453	2.194	2346.499	0.020
9 ^c	5880.923	-0.556	3345.455	-3.399	2363.679	-0.772

Calculated rotational constants/MHz

$$A_v^a = 5904.535(70) - 5.56(16) \langle z^2 \rangle_v - 0.605(44) \langle z^4 \rangle_v$$

$$B_v^a = 3604.92(27) - 54.62(74) \langle z^2 \rangle_v - 8.09(23) \langle z^4 \rangle_v$$

$$C_v^a = 2233.29(13) + 24.20(35) \langle z^2 \rangle_v + 4.79(11) \langle z^4 \rangle_v$$

^a Calculated rotational constants using the $v_T=0$ through $v_T=6$ torsional states; see text. ^b obs. means the experimental rotational constants listed in Table 5. ^c Omitted from least-squares fit; see text. The values of the calculated rotational constants have been obtained using the equations appearing on the bottom of this table.

In the limit of no power saturation, the peak absorption coefficient α_{\max} is given by¹⁹

$$\alpha_{\max} = 3.85 \times 10^{-14} a i F_v \sigma (ABC)^{0.5} \mu^2 \lambda \nu^2 g_I [\exp(-E_{J_r}/kT)] / [T^{2.5} (\Delta\nu)_1] \quad (3)$$

Here a is the fraction of molecules belonging to the *syn* conformer, i is the fraction belonging to the isotopic species under study, F_v is the fraction of molecules in a given vibrational state, σ is the symmetry number, A , B and C are the rotational constants (in MHz) of that vibrational state, μ is the dipole moment (in Debye units), λ is the line strength of the rotational transition, ν is the peak absorption frequency (in MHz), g_I is the reduced nuclear weight, E_{J_r} is the lowest energy level involved in the MW transition, k is Boltzmann's constant, T is the absolute temperature and $(\Delta\nu)_1$ is the line breadth in MHz at a pressure of 1 Torr and a temperature of 300 K. The line breadth at another temperature and pressure, p (in Torr), $\Delta\nu$, is given by $\Delta\nu \approx 300 p (\Delta\nu)_1/T$.

If a can be estimated from intensity measurements, it should be possible to calculate the energy difference between two conformers from it. Fortunately, this is feasible

in the present case since α_{\max} as well as all the parameters but a , on the right-hand side of eqn. (3) are available as follows: In our case $i=0.98$ because the spectrum of the ¹²C species is the only one assigned. σ is 2 because of the C_{2v} symmetry of *syn*. g_I is 3/4 for the absorption lines of $K_{-1}, K_{+1} eo \leftrightarrow oe$ parity used to determine the energy difference (Table 8), since a 180° rotation exchanges two pair of bosons (the ¹²C and ¹⁶O pairs) and one pair of fermions (the F pair).²⁰

α_{\max} was measured for the three rotational transitions listed in Table 8. These transitions were selected because they are well separated from other lines. Measurement of α_{\max} cannot be made directly, so the cell was calibrated using OCS as standard and employing the intensity values given in Ref. 21. Unfortunately, it is not possible to get very accurate values for a_{\max} this way because of numerous systematic sources of errors such as reflections in the cell, base-line inaccuracy, and non-linearity of the detector system, to mention but a few. However, it is expected that the uncertainties quoted in Table 8 are realistic.

The line breadth, $(\Delta\nu)_1$, is another quantity that is difficult to determine accurately, as indicated in Table 8. $\Delta\nu$

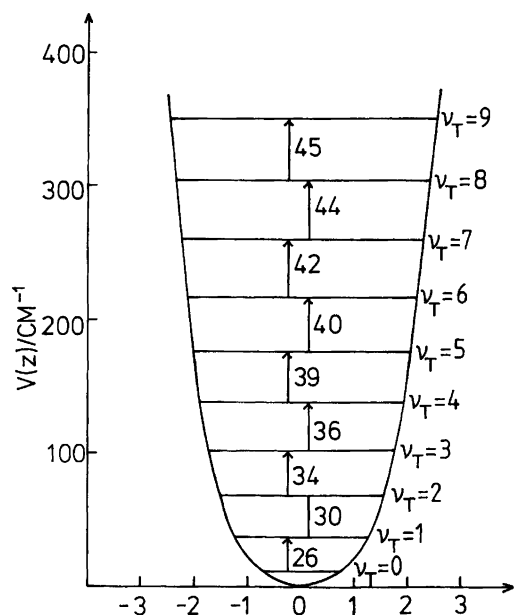


Fig. 2. Potential function $V=7.0 (\langle z^4 \rangle + 2.0 \langle z^2 \rangle)$ presumed to describe the bottom of the potential well near its *syn* minimum rather accurately. The ground state lies 12 cm^{-1} above the bottom. Eigenstates of the first 10 torsional states are indicated. Microwave spectra of these states have been assigned.

was measured at dry-ice temperature (195 K) and a pressure of a few Pa. $(\Delta\nu)_1$ was then calculated from $\Delta\nu = 300 p (\Delta\nu)_1/T$. Finally, an accurate determination of F_ν is problematic. In our derivation it was assumed that $F_\nu = \Pi(1 - \exp(h\nu_i/kT))$ for the ground vibrational state.²² The low-frequency torsional vibration weighs heavily in this calculation where 26 cm^{-1} was used. A major part of the uncertainty of F_ν stems from this frequency. Furthermore, the five fundamentals already assigned in the Raman work⁶ were used. The fundamental frequencies not assigned in Ref. 6 were taken from the theoretical calculation (Table 3) and used to compute the remaining quantities in this expression. In this manner $F_\nu = 0.13(1)$ was computed, where the uncertainty is an estimated one standard deviation. The ground-state rotational constants (Table 5) were employed; λ was calculated using these constants, ν was the measured frequency of the absorption peak under study and μ was taken from Table 7. In this manner a was calculated for three selected transitions with the results shown in Table 8.

The average value of a is 0.26, meaning that roughly 26% of the gas is the *syn* conformer at 195 K. The Gibbs free energy difference can now be calculated to be $\Delta G^\circ = 1.7 \text{ kJ mol}^{-1}$ at this temperature with *anti* as the most stable conformer. One standard deviation of $\pm 0.5 \text{ kJ mol}^{-1}$ has been estimated taking the various sources of error into consideration.

The entropy difference, ΔS° , between *syn* and *anti* was assumed to be well approximated by²³

Table 7. Stark coefficients^a and dipole moment^a of the *syn* conformer of oxalyl fluoride.

Transition	$ M $	$\Delta\nu \text{ E}^{-2}/10^{-6} \text{ MHz V}^{-2} \text{ cm}^2$	
		Obs.	Calc.
$4_{1,4} \leftarrow 3_{0,3}$	1	0.824(10)	0.800
$7_{3,4} \leftarrow 7_{2,5}$	7	7.13(15)	6.03
	6	5.28(15)	4.40
	5	3.56(10)	3.02
$5_{4,1} \leftarrow 5_{3,2}$	5	-3.47(5)	-3.87
	4	-2.30(4)	-2.43

Dipole moment/ 10^{-30} C m
 $\mu = 3.652(83)$

^a Uncertainties represent one standard deviation. $1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$.

$$\Delta S^\circ = R \ln[(ABC)^{0.5} \Pi(1 - \exp(h\nu_i/kT)_{anti}) / (ABC)^{0.5} \Pi(1 - \exp(h\nu_i/kT)_{syn})] \quad (4)$$

The symbols in the numerator are for *anti*; those in the denominator are for *syn* and have already been defined. In calculating ΔS° experimental values were used in the cases where available. The rest were taken from the theoretical predictions (most elaborate computations) in Tables 2 and 3. The torsional frequencies of *anti* and *syn* weigh heavily in eqn. (4).

In this manner $\Delta S^\circ = 5.1(1) \text{ J mol}^{-1} \text{ K}^{-1}$ is found with *syn* favoured by entropy, mostly because it has the lowest torsional frequency; $26(5) \text{ cm}^{-1}$ compared to 54 cm^{-1} for *anti*.² Use of the Gibbs-Helmholtz equation then yields for the enthalpy difference $\Delta H^\circ = H^\circ_{syn} - H^\circ_{anti} = 2.7(6) \text{ kJ mol}^{-1}$.

Our result is in satisfactory agreement with that reported in the Raman work,⁶ but falls in the lower range of the estimate of the enthalpy difference. Friesen's result⁵ is too high. Our finding is in good agreement with the theoretical predictions (Table 1).

Fortunately, it is now possible to derive a rough, one-dimensional potential function $V(\phi)$ where ϕ is the torsional angle. $V(\phi)$ is expanded in a series as follows:²³

$$V(\phi) = \sum \left(\frac{1}{2} V_n (1 - \cos(n\phi)) \right) \quad (5)$$

This series is expected to converge rapidly, i.e. only a few V_n terms are necessary to describe the potential accurately.²⁴

At the *anti* ($\phi = 0^\circ$) and *syn* ($\phi = 180^\circ$) minima one has²⁴

$$\frac{\partial V_n}{\partial \phi} = \sum \left(\frac{1}{2} n^2 V_n \cos(n\phi) \right) 4 \pi^2 \nu^2 G_{tt}^{-1} \quad (6)$$

where G_{tt}^{-1} represents the diagonal element of the torsion of the G^{-1} matrix at two minima, and ν is the torsional frequency for *anti* and *syn*. Using Polo's method²⁵ and the

Table 8. Intensities of peak absorption coefficients, line breadths at a pressure of 1 Torr and 300 K, and fractions of molecules belonging to *syn*.^a

Transition	Peak abs. coeff., ^b $\alpha_{\max}/10^{-8} \text{ cm}^{-1}$	Line breadth, $(\Delta\nu)_1/\text{MHz Torr}^{-1}$	Fraction of <i>syn</i> , <i>a</i>
$5_{3,2} \leftarrow 5_{2,3}$	5.1(6)	13(1)	0.24
$5_{2,3} \leftarrow 5_{1,4}$	5.0(6)	11(1)	0.24
$7_{3,4} \leftarrow 7_{2,5}$	8.2(7)	12(1)	0.29
Average:			0.26

^a Uncertainties represent one standard deviation. ^b Peak absorption coefficient.

MP2/6-311+G* structures in Table 2 one finds $G_{\text{tt}}^{-1} = 0.3592$ for *syn* and $1.107 \times 10^{-45} \text{ kg m}^2 \text{ radian}^{-1}$ for *anti*, respectively. The three first coefficients in eqn. (5) are then calculated to be $V_1 = 2.24$, $V_2 = 9.59$ and $V_3 = 0.46 \text{ kJ mol}^{-1}$, respectively, when $\Delta H^\circ = 2.7 \text{ kJ mol}^{-1}$ is taken to be the energy difference between the two bottoms of the potential.

The full potential can now be drawn as shown in Fig. 3. This potential is not expected to be as accurate near the bottom of the *syn* conformer as that in Fig. 2. The maximum (transitional state) is located at 90° and

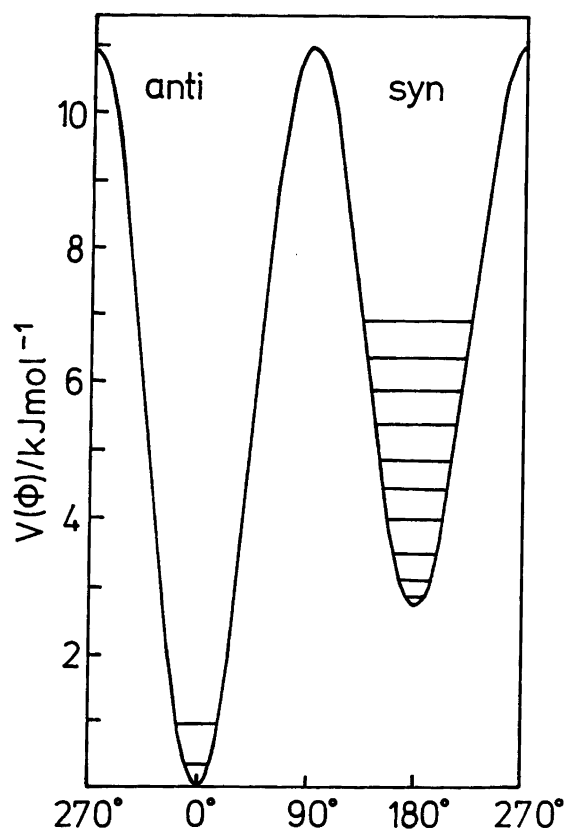


Fig. 3. Full potential function $V(\phi) = \sum (\frac{1}{2} V_n (1 - \cos(n\phi)))$ calculated using $V_1 = 2.24$, $V_2 = 9.59$, and $V_3 = 0.46 \text{ kJ mol}^{-1}$. This simple potential function which covers the whole torsional motion, indicates that the transition state lies $10.9(20) \text{ kJ mol}^{-1}$ above the *anti* minimum (8.2 kJ mol^{-1} above the *syn* minimum) with $\phi = 90(3)^\circ$. The observed eigenstates are indicated. Those of *anti* are from the IR article,² while those of *syn* were made in this work.

10.9 kJ mol^{-1} (above the *anti* bottom). It is of course difficult to assign uncertainty limits to these two numbers, but the transitional state is presumed to fall within $\pm 3^\circ$ from 90° and the energy of the transitional state is estimated to be uncertain by $\pm 2 \text{ kJ mol}^{-1}$. There is good agreement with the values found for these two parameters in the *ab initio* computations in Table 1. It should be noted that the transitional state found here is much less than the 51.8 kJ mol^{-1} given previously.²

Structure of syn-oxalyl fluoride. It has already been remarked that the structure of oxalyl fluoride given by Friesen⁵ more closely resembles that of *anti* than that of *syn*, and that the MP2/6-311+G* structure of *anti* (Table 1) is very close to its experimental counterpart.⁵ Presumably, the MP2/6-311+G* structure of *syn* is also close to the 'real' structure. There is some important evidence supporting this view: It is seen from Tables 2 and 5 that the experimental rotational constants of *syn* are close (roughly 1%) to those calculated from the MP2/6-311+G* structure (Table 1). This is as good an agreement as one can possibly get because the experimental rotational constants are 'contaminated' by zero-point vibration, and the theoretical values are an approximation of the equilibrium structure. A 'methodological' difference of roughly 1% is therefore to be expected. The good agreement seen here is one indication that the MP2/6-311+G* structure is close to the 'real' structure.

There are some interesting features in the MP2/6-311+G* *syn* structure (Table 1): This conformer has a short C=O distance (118.6 pm) and a rather long C-C distance (153.5 pm) for two sp^2 -hybridized carbon atoms attached to one another. A short C=O distance of 118–119 pm is typical for the COF group and has been found in the *anti* [119.4(13) pm] and *syn* [119.5(5) pm] conformers of fluoracetyl fluoride (CH_2FCFO),²⁶ as well as in acetyl fluoride (CH_3CFO) [118.5(2) pm],²⁷ formyl fluoride (CHFO) [118.4(4) pm],²⁸ as well as in the *anti* form (Table 1) of oxalyl fluoride itself.⁵ A rather long C-C distance of 153–154 pm has been determined experimentally in several OXC–CXO type molecules, where X is an electronegative substituent, e.g. in the *anti* forms of oxalyl fluoride [153.6(3); Table 1],⁵ oxalyl chloride [153.4(5) pm],²⁹ oxalyl bromide [154.6(8) pm],³⁰ and oxalic acid [154.4(4) pm].³¹ This distance is a little shorter in glyoxal, OHC–CHO, where it is 152.6(3) pm in *anti*³² and 151.4 pm in *syn*.³³ The MP2/6-311+G* structure of

syn thus closely resembles experimental structures of its congeners in an expected manner. The MP2/6-311 + G* structure of *syn* (Table 1) is then taken to be a *plausible* structure for oxalyl fluoride. Any experimental structure that might be determined in the future is predicted to deviate little from it.

Discussion

Investigations of five OXC-CXO type molecules have now been made. It has been found that OHC-CHO^{32,33} and OFC-CFO prefer *planar syn* and *anti* forms. Only the *anti* form was seen for oxalic acid.³¹ In contrast, OCIC-CCIO²⁹ and OBrC-CBrO³⁰ both take *anti* and *gauche* conformers. (The existence of the *gauche* form of oxalyl chloride was not found in recent *ab initio* computations^{6,34} made at high levels of theory, and its existence has been questioned³⁴). The geometries of these five molecules imply that the carbon atoms are undoubtedly *sp*²-hybridized in all conformers. In the *syn* and *anti* forms conjugation is expected to be important. However, this effect does not produce a short C-C bond in any of these molecules, as mentioned in the previous section. The long C-C bond is paralleled with low torsional frequencies in the title compound, 54 and 26(5) cm⁻¹ for *anti* and *syn*, respectively.

In addition, conjugation does not have any noticeable effect on the dipole moment of the *syn* conformers. The predicted dipole moments using Smyth's tabulation³⁵ of bond moments which are added vectorially, are (in units of 10⁻³⁰ C m) 15.3 for *syn*-glyoxal and 4.1 for *syn*-oxalyl fluoride compared to the experimental values of 16.0(6)³⁶ and 3.652(83) (Table 7), respectively. Conjugation thus seems to have rather limited influence on geometry and electrical properties of the OXC-CXO type molecules regardless of whether the substituent X is electropositive such as hydrogen, or electronegative such as the halogens and the hydroxyl group in oxalic acid.

The fact that oxalyl chloride²⁹ and oxalyl bromide³⁰ takes the alleged³⁴ *gauche* conformation in addition to *anti* is presumably a result of steric repulsion between the two halogen atoms which would be prominent in a planar *syn* conformer. The *gauche* forms thus represent the best compromise. In this conformation the non-bonded distances of the halogen atoms are approximately equal to twice their respective van der Waals radii.^{29,30}

The existence of *syn* forms in glyoxal and oxalyl fluoride may reflect the small van der Waals radii of the hydrogen and fluorine atoms. In *syn* oxalyl fluoride the non-bonded distance between the two fluorine atoms is calculated to be 252 pm from the MP2/6-311 + G* structure in Table 1, compared to 270 pm which is twice the van der Waals radius³⁷ of fluorine. This indicates that steric repulsion is not very prominent in *syn*, and this conformer is therefore 'allowed' instead of *gauche*. The situation in glyoxal is even better in this respect. The energy difference between the *syn* and *anti* (most stable)

conformers of glyoxal is 13.4(12) kJ mol⁻¹ (Ref. 38) in contrast to 2.7(6) kJ mol⁻¹ for oxalyl fluoride. The question is how this significant difference can be explained. Obviously, several factors contribute. One is perhaps the polarisation of the C-C bond, which would be widely different in the two cases owing to the great differences in electronegativity of fluorine and hydrogen atoms. It is impossible to say how important this effect is, but it can undoubtedly be large, and is perhaps dominant.

Another factor that seems to be of importance is the complicated interplay of bond dipole-dipole interactions that exists in the two conformers. In glyoxal the C-H and C=O bond dipoles would attract one another in the *anti* conformer, while in the *syn* form a large repulsion will exist between the two polar³⁵ carbonyl-group bond dipoles. The repulsion in this conformer of glyoxal between the two C-H bond dipoles³⁵ is of course much less. The definite preference of the *anti* form of glyoxal thus conforms well with this dipole-dipole interaction picture.

The situation in oxalyl fluoride is different in that bond dipole-dipole repulsion prevails in both conformers. In the *anti* form the carbonyl groups and the C-F bond dipoles strongly repel each other, while in the *syn* form two C-F bonds and two carbonyl groups repel one another at the same time producing an even more significant destabilization than in *anti* because the bond moment of the carbonyl group is considerably larger than that of the C-F bond.³⁵ The repulsive bond-dipole forces in *syn*-oxalyl fluoride are thus stronger than in *anti*. The *anti*-*syn* equilibrium is thus under influence of dipole repulsion which is more prominent in *syn* than in *anti*. This may explain partly why *anti* is 2.7(6) kJ mol⁻¹ more stable than *syn*.

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