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Microwave Spectrum, Conformational Equilibrium, Intramolecular Hydrogen Bonding and *Ab Initio* Calculations for 2-Furanmethanethiol (Furfuryl Mercaptan)

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The microwave spectra of 2-furanmethanethiol and one deuterated species (mercapto group) have been investigated in the 26.0–39.5 GHz spectral region at −15 °C. Two conformers denoted *Skew 1* and *Skew 3* were assigned. In *Skew 1* the C=C–C–S dihedral angle is about 109° from *syn*, while this dihedral angle is approximately 111° from *syn* in *Skew 3*. These two *skew* forms are each stabilized by a weak intramolecular hydrogen bond which is formed between the hydrogen atom of the mercapto group and the π electrons of the furan ring in the case of *Skew 1*, and between the same hydrogen atom and the oxygen atom of the ring in the case of *Skew 3*. *Skew 3* is the most stable rotamer. It is 2.3(5) kJ mol^{-1} more stable than *Skew 1*. There is no indication of the stable coexistence of large fractions of further rotamers. The microwave work has been assisted by *ab initio* computations at the 6-31G** level of theory.

Several recent studies[1–8] of free molecules have shown that the mercapto group can participate in intramolecular hydrogen (H) bonding both as a proton donor and as an acceptor, depending on the other substituents which are present in the molecule. One example is allyl mercaptan, $H_2C=CH-CH_2SH$.[1] The C=C–C–S chain of atoms is *skew* (120° from *syn*) and the C–C–S–H link is *gauche* (60° from *syn*) in its preferred conformation, as shown in a microwave (MW) study.[1] This atomic arrangement allows a weak intramolecular H bond to be formed between the π-electrons of the double bond and the H atom of the mercapto group.

The π-electrons of the double bond were likewise found to be acceptor and the mercapto group donor in the most stable conformer of 3-butene-1-thiol, $HSCH_2CH_2CH=CH_2$.[2] However, the H bond is so weak in this rotamer that two high-energy S–C–C–C *anti* conformers, naturally without H bonds, were so abundant that they could be assigned with MW spectroscopy.[2] A similar situation exists in 3-mercaptopropionitrile, $HSCH_2CH_2C\equiv N$, where the preferred form has a S–C–C–C *gauche* conformation stabilized by a H bond between the mercapto group and the π-electrons of the triple bond. One *anti* conformer, which is unable to form this kind of bond, was also identified as a high-energy rotamer.[3]

In the three examples above π-electrons act as acceptor. There is also one example where pseudo-π-electrons take this role: In the one identified conformer of cyclopropanemethanethiol[4] the pseudo-π-electrons present along the edges of the cyclopropyl ring were seen to be acceptor for the H atom of the mercapto group.

However, in the compounds $HOCH_2CH_2SH$[5] and $CH_3CH(OH)CH_2SH$[6] the mercapto group is not a proton donor any more. In the internal H bond in these two compounds the sulfur atom is *acceptor* and the hydroxyl group is *donor* in the one S–C–C–O *gauche* conformer which has been identified for each of them.[5,6]

$HSCH_2CH_2SH$[7] is a special case. Electron-diffraction studies[7a,c] have shown that heavy-atom S–C–C–S *gauche* as well as *anti* forms exist with a small energy difference. The heavy-atom *gauche* rotamer is stabilized by an internal H bond where one mercapto group is proton donor and the other is acceptor.[7b,c] (The S–C–C–S *anti* conformer is of course without internal H bond.)

Similarly, a mixture of several conformers has also been found for $H_2NCH_2CH_2SH$.[8] One of the *high-energy* conformers was seen to be stabilized by a S–H···N hydrogen bond.

The molecules mentioned above all have alcohol counterparts in which the mercapto group(s) has been replaced by a hydroxyl group.[9] The corresponding alcohols also possess internal H bonds similar to those found for the thiols above,[9] but the mercapto group is clearly al-

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ways a less strong proton donor than the hydroxyl group is.[1–8] While most authors[9] assume that intramolecular H bonding stabilizes the alcohols, H bonding involving the mercapto group as donor is always weaker and can undoubtedly be said to represent borderline cases. The list of alcohols with internal H bonds is a long one,[9] whereas few thiols with this interaction have been studied. 2-Furanmethanethiol was therefore chosen for study because we wanted to extend our rather limited knowledge of thiols which may form intramolecular H bonds.

Theoretically, the title compound may form a number of conformations. In Fig. 1 five idealized, typical conformations of 2-furanmethanethiol initially thought to be stable are depicted. In the three *skew* rotamers the C2 = C1–C5–S dihedral angle is 120° from the two *syn* forms where this angle is 0°. The C2–C5–S–H6 dihedral angle is 60° in *Skew 1* and *Syn 1*, 180° in *Skew 2* and *Syn 2*, and −60° in *Skew 3*. Two types of intramolecular H bonds may be formed in this compound. An S–H···O hydrogen bond is possible in the *Skew 3* conformation, while an S–H···π bond is possible in *Skew 1* and *Syn 1*. No H bond is of course possible in the remaining two conformations, *Skew 2* and *Syn 2*.

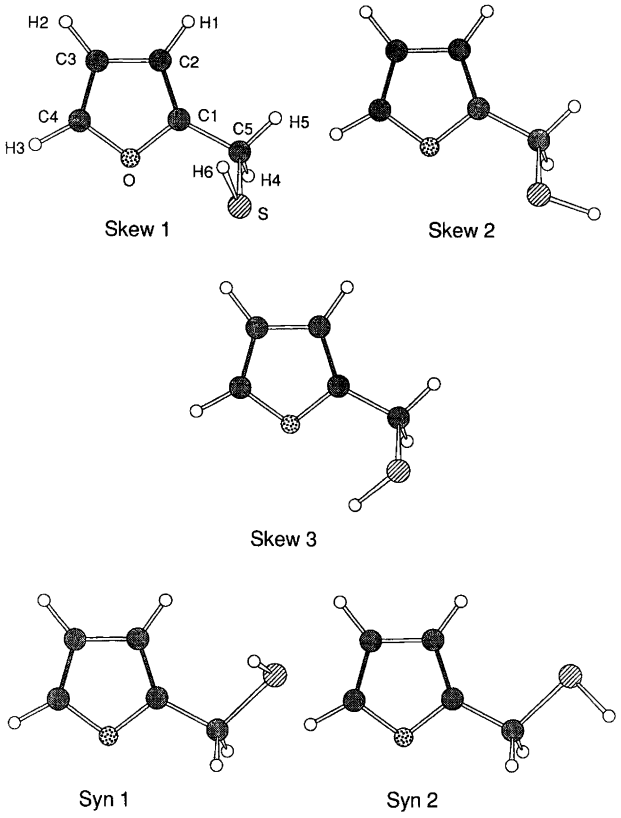

Fig. 1. The five idealized conformations of 2-furanmethanethiol. Atom numbering is given on the sketch of *Skew 1*. The computations indicate that the actual dihedral angle deviate somewhat from the idealized ones sketched in this figure. *Skew 3* and *Skew 1* was assigned in this work. *Skew 3* was found to be 2.3(5) kJ mol^{-1} more stable than *Skew 1*.

Very recently, the closely related alcohol, 2-furanmethanol, has been investigated in this laboratory by MW spectroscopy and *ab initio* computations.[10] Two conformers similar to *Skew 1* and *Skew 3* were found experimentally for this compound.[10] As already mentioned, alcohols and thiols often tend to make similar conformational choices. 2-Furanmethanethiol was hence guessed to prefer the same two rotamers, and this was indeed found in the present study, as shown below.

There exists a large body of literature for the title compound which deals mainly with its properties as a flavour agent. The structure of 2-furanmethanethiol has been the theme of only a few papers; one of which reports an electron-diffraction study[11] in which one conformer was identified. No information regarding the position of the H atom of the mercapto group was obtained in this work.[11] This rotamer was claimed to have a O–C1–C5–S dihedral angle of 39(4)° [corresponding to a C2 = C1–C5–S dihedral angle of 141(4)°].[11] This result is in disagreement with that presented in this study.

Experimental

Microwave experiment. The sample utilized in this work was purchased from Fluka A. G., Buchs, Switzerland. The compound, which was stated to be at least 97% pure, was checked by gas chromatography and found to be 100% pure. The MW spectrum was studied using the Oslo spectrometer, which is described in Ref. 12. The 24.0–39.5 GHz spectral region was investigated with the microwave absorption cell 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 about 3–4 Pa when the spectra were recorded. The accuracy of the spectral measurements is presumed to be better than ±0.10 MHz. The deuterated species were produced by conditioning the cell with heavy water and then introducing the parent species. In this manner roughly 30% deuteration was achieved.

Results

Ab initio *calculations.* 2-Furanmethanethiol has not previously been subject to high-level *ab initio* calculations. It was therefore decided to perform such computations in order to assist the MW work. The calculations were made at the 6-31G** level of theory using the Gaussian 92 program package[13] running on the Cray Y-MP computer in Trondheim. The starting points for the computations were the five idealized conformations depicted in Fig. 1, where the C = C–C–S dihedral angle is 0° (*syn* forms), or 120° (*skew* forms) and the H–S–C–C dihedral angle is 60, −60 or 180°, respectively.

The geometries of the five conformations were fully optimized in the computations. They were all found to be

stable, as no imaginary vibrational frequencies[14] were computed for any of them. The optimized geometries are given in Table 1 together with other parameters of interest.

In order to see whether these five conformations are indeed the only ones predicted to be *stable* forms of 2-furanmethanethiol, searches for further stable rotamers were made starting with the C2 = C1–C5–S dihedral angle in the *anti* (180°) and *gauche* (60°) positions. However, no further stable forms with such dihedral angles were found. In fact, the Gaussian program refined to one of these five rotamers in all cases. It is therefore assumed that these five forms represent all the possible *stable* conformations of 2-furanmethanethiol.

A few remarks about the computed structures of the five rotamers (Table 1) are in order: The bond distances of the ring are the same as those found in the MW work[15] on furan to within about 2 pm, and the bond angles are also within 1°. The structure of the $-CH_2SH$ part of the molecule is close to that of methanethiol.[16]

The calculated conformations of the C2 = C1–C5–S chain of atoms deviate (Table 1) somewhat from the idealized cases shown in Fig. 1. This dihedral angle is computed to be as small as 102.7° in the hypothetical *Skew 2* conformer and 109.2 and 110.6° in *Skew 1* and *Skew 3*, respectively. These small dihedral angles should be compared to the 'normal' value of 124° found in allyl mercaptan,[1] which has a C = C–C–S link of atom, just as the title compound has. However, these small C2 = C1–C5–S dihedral angles have parallels in 2-furanmethanol,[10] and can perhaps be explained as resulting from steric repulsion between the sulfur and oxygen atoms. The S···O non-bonded distances are calculated to be about the same as the sum of the van der Waals radii of oxygen and sulfur (325 pm)[17] in these three conformations (Table 1). A dihedral angle of the 'normal' value of 120° would have made these distances shorter.

The hypothetical *syn* conformers are computed to have the C2 = C1–C5–S dihedral angle significantly different from co-planarity (10.3° for *Syn 1* and 29.5 for *Syn 2*, respectively) with the furan ring. It is noted that the distances between the S and C2 atoms are rather short in these two conformations (Table 1), so it is possible that non-bonded repulsion is important here, just as for the *skew* rotamers discussed above.

MW spectrum and assignment of Skew 3. The survey spectra revealed a rather weak spectrum. The peak intensities of the coalescing K_{-1}-doublets of the $J = 15 \leftarrow 14$ ^aR-transitions, which were the strongest lines observed, had intensities of roughly 2.0×10^{-7} cm^{-1} at −15°C.

According to the *ab initio* computations (Table 1), *Skew 3*, *Syn 1* and *Skew 1* were predicted to be close in energy. Furthermore, these three rotamers were each calculated to possess rather large components of the dipole moment along the ***a***-inertial axes. They were also predicted to be rather prolate asymmetric tops with the asymmetry parameter κ not far from −1.0. *a*-Type *R*-branch pile-ups typical of near-prolate asymmetric tops were therefore expected for all of them in the *R*-band spectral region. Moreover, the pile-ups of *Skew 3* and *Skew 1* were predicted to fall at nearly the same frequencies, since the rotational constants predicted for them were rather similar (Table 1), whereas the ^aR-pile-ups predicted for the hypothetical *Syn 1* form would fall at quite different frequencies, since the predicted rotational constants of this hypothetical conformation (Table 1) were somewhat different from those of *Skew 1* and *Skew 3*.

A series of pile-ups were immediately noted in the survey spectra. This led to a quick assignment of the *a*-type *R*-branch spectrum of *Skew 3*. The high-*J* ^bQ- and ^cQ-lines, which were predicted to be the strongest *b*- and *c*-type transitions, were searched for next, but not identified presumably because μ_b and μ_c are much smaller than μ_a, as predicted in Table 1. A portion* of the ground-state spectrum of *Skew 3* is listed in Table 2 and the spectroscopic constants (*A*-reduction *I*^{r}-representation)[18] of the ground vibrational state are found in Table 3. It was only possible to determine Δ_J and Δ_{JK} of the quartic centrifugal distortion constants from the available transitions. The remaining quartic constants were arbitrarily preset to zero.

The pile-ups are very crowded because the ground-state spectrum was accompanied by several vibrationally excited states. In addition, many high-K_{-1} transitions also fall at frequencies separated by only a few megahertz. The first and second excited states of what is presumed to be the torsion vibration around the C1–C5 bond were assigned; their spectroscopic constants are found in Table 4. This fundamental is computed to be the lowest one. Relative intensity measurements performed largely as described in Ref. 19 yielded 72(20) cm^{-1} for this vibration, compared to 70 cm^{-1} calculated by *ab initio* (not given in Table 1). The second lowest fundamental frequency was computed to be 135 cm^{-1}, but no assignment was made owing to the crowded nature with many overlapping lines in the pile-ups, where the assignments had to be started.

The deuterated species (mercapto group) was studied to locate the position of the H atom of the mercapto group. The assignment of this spectrum was straightforward. The substitution coordinates[20] were calculated as $|a| = 188.874(83)$, $|b| = 142.24(10)$ and $|c| = 15.9(10)$ pm. These values are in reasonable agreement with those predicted for *Skew 3* (Table 1) and represent conclusive evidence that *Skew 3* has indeed been assigned and not confused with *Skew 1* or *Skew 2*, which would have rotational constants close to those of *Skew 1*, but strikingly different coordinates for the H atom of the mercapto group, as can be seen in Table 1.

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

Table 1. Structure[a] rotational constants, principal-axes coordinates of the H atom of the mercapto group and dipole moments of five selected rotamers of 2-furanmethanethiol as calculated by *ab initio* using the 6-31G** basis set.

Conformation:	*Skew 1*	*Skew 2*	*Skew 3*	*Syn 1*	*Syn 2*
Distances/pm					
H3–C4	106.8	106.8	106.8	106.8	106.8
C3–C4	133.8	133.9	133.8	133.7	133.7
C3–H2	107.0	107.0	107.0	107.0	107.0
C2–C3	144.0	143.9	144.1	144.2	144.1
C1–C2	134.3	134.2	134.1	134.1	134.1
C1–O	134.4	134.6	134.7	134.8	134.7
C1–C5	148.5	148.8	148.7	149.5	149.5
C5–S	183.1	183.6	183.1	181.6	182.6
C5–H4	108.3	108.2	108.2	108.2	108.1
C2–H1	107.1	107.1	107.1	106.9	107.0
C5–H5	108.1	108.0	108.1	108.5	108.4
S–H6	132.7	132.8	132.7	132.8	132.7
O–C4	134.8	134.4	134.7	134.7	134.6
Angles/°					
H3–C4–C4	133.0	133.0	133.1	133.2	133.2
C4–C3–H2	126.8	126.8	126.7	126.7	126.8
C4–C3–C2	105.6	105.6	105.7	105.8	105.8
C3–C2–C1	106.0	106.0	106.0	105.9	105.9
C2–C1–O	110.2	110.2	110.2	110.2	110.3
C2–C1–C5	132.3	132.7	133.2	135.1	134.5
C1–C5–S	114.9	110.9	114.7	114.9	110.7
C1–C5–H4	110.2	109.7	110.4	109.6	108.7
C3–C2–H1	127.5	127.6	127.5	127.6	127.6
C1–C5–H5	109.4	109.0	109.3	110.1	110.3
C5–S–H6	97.4	97.1	97.4	97.7	97.0
C1–O–C4	107.5	107.5	107.5	107.5	107.5
Dihedral angels[b]/°					
H3–C4–C3–H2	0.1	0.1	0.1	−0.1	0.0
H3–C4–C3–C2	180.1	180.1	180.0	179.9	179.9
C4–C3–C2–C1	0.0	0.1	0.0	0.0	−0.1
C3–C2–C1–O	0.1	0.0	0.1	−0.1	0.0
C3–C2–C1–C5	180.1	179.9	179.6	179.0	178.3
O1–C1–C5–S	−70.8	−77.4	−69.9	−169.6	−152.3
O1–C1–C5–H4	47.1	42.9	53.3	−45.4	−31.4
C4–C3–C2–H1	179.9	180.3	180.3	179.6	180.0
O1–C1–C5–H5	165.7	162.3	172.0	71.9	87.2
C1–C5–S–H6	−60.1	173.7	62.0	65.8	196.9
C2–C1–C5–S	109.2	102.7	110.6	10.3	29.5
Non-bonded distances[c]/pm					
O···S	334.1	332.9	331.5	401.9	393.0
O···H6	368.5	431.9	289.2	415.6	476.6
S···C2	384.9	373.9	386.1	329.4	323.6
C1···H6	294.7	370.3	296.1	299.9	368.0
Rotational constants[d]/MHz					
A	6 197.9	6 169.9	6 212.7	6 980.1	6 831.3
B	1 280.4	1 289.7	1 292.4	1 253.3	1 275.9
C	1 177.1	1 195.6	1 174.4	1 079.7	1 102.8
Principal axis coordinates[16] of the H6 atom/pm					
|*a*|	206.8	339.5	201.2	226.8	339.4
|*b*|	53.1	8.5	143.6	66.3	30.4
|*c*|	141.4	24.4	25.4	125.7	36.9
Dipole moment[e]/10^{-30} C m					
μ_a	5.42	2.17	5.58	3.99	1.34
μ_b	5.38	3.78	1.02	0.24	2.21
μ_c	0.10	4.53	2.53	2.31	3.13
Energy difference[f,g]/kJ mol^{-1}	1.1	4.9	0.0	3.0	7.9

[a] See Fig. 1 for definition. [b] Measured from *syn*=0°. [c] Sum of van der Waals radii:[17] O···S 325 pm; S···C (half-thickness of aromatic molecule) 355 pm; O···H 260 pm; H···C (half-thickness of aromatic molecule) 290 pm. [d] Calculated from the structures given above in this table. [e] 1D=3.33564×10^{-30} C m. [f] The total energy of conformer *Skew 3* was calculated to be −1 747 351.11 kJ mol^{-1}. [g] Energy difference between *Skew 3* and each of the other four conformations.

Table 2. MW spectrum of the ground vibrational state of *Skew 3* of 2-furanmethanethiol.

Transition $J''_{K''-1,K''+1} \leftarrow J''_{K'-1,K'+1}$			Observed frequency[a]/MHz	Obs. − calc. frequency/MHz
$10_{0,10}$	←	$9_{0,9}$	24430.36	−0.08
$10_{1,10}$	←	$9_{1,9}$	24098.14	−0.06
$10_{3,7}$	←	$9_{3,6}$	24815.57	0.13
$10_{6,4}$	←	$9_{6,3}$	24770.99	0.01
$10_{6,5}$	←	$9_{6,4}$	24770.99	0.01
$11_{2,9}$	←	$10_{2,8}$	27582.13	−0.01
$11_{4,8}$	←	$10_{4,7}$	27268.20	0.08
$11_{7,4}$	←	$10_{7,3}$	27246.43	0.01
$11_{7,5}$	←	$10_{7,4}$	27246.43	0.01
$11_{9,2}$	←	$10_{9,1}$	27242.29	0.12
$11_{9,3}$	←	$10_{9,2}$	27242.29	0.12
$12_{1,12}$	←	$11_{1,11}$	28882.04	−0.02
$12_{3,10}$	←	$11_{3,9}$	29766.72	−0.04
$12_{8,4}$	←	$11_{8,3}$	29721.92	−0.02
$12_{8,5}$	←	$11_{8,4}$	29721.92	−0.02
$12_{10,2}$	←	$11_{10,1}$	29717.99	−0.03
$12_{10,3}$	←	$11_{10,2}$	29717.99	−0.03
$13_{0,13}$	←	$12_{0,12}$	31539.84	−0.06
$13_{2,11}$	←	$12_{2,10}$	32702.86	0.02
$13_{4,9}$	←	$12_{4,8}$	32242.06	−0.04
$13_{5,8}$	←	$12_{5,7}$	32220.95	−0.03
$13_{5,9}$	←	$12_{5,8}$	32220.95	0.02
$13_{7,6}$	←	$12_{7,5}$	32204.34	0.00
$13_{7,7}$	←	$12_{7,6}$	32204.34	0.00
$13_{10,3}$	←	$12_{10,2}$	32195.40	0.02
$13_{10,4}$	←	$12_{10,3}$	32195.40	0.02
$13_{12,1}$	←	$12_{12,0}$	32192.47	0.00
$13_{12,2}$	←	$12_{12,1}$	32192.47	0.00
$14_{1,13}$	←	$13_{1,12}$	35182.43	−0.12
$14_{2,13}$	←	$13_{2,12}$	34505.60	0.03
$14_{4,10}$	←	$13_{4,9}$	34731.78	−0.04
$14_{6,8}$	←	$13_{6,7}$	34691.78	0.01
$14_{6,9}$	←	$13_{6,8}$	34691.78	0.01
$14_{9,5}$	←	$13_{9,4}$	34675.51	0.00
$14_{9,6}$	←	$13_{9,4}$	34675.51	0.00
$14_{12,2}$	←	$13_{12,1}$	34669.39	0.01
$14_{12,3}$	←	$13_{12,2}$	34669.39	0.01
$15_{1,14}$	←	$14_{1,13}$	37639.04	0.07
$15_{3,12}$	←	$14_{3,11}$	37364.63	−0.02
$15_{4,12}$	←	$14_{4,11}$	37216.75	0.00
$15_{7,8}$	←	$14_{7,7}$	37164.31	0.03
$15_{7,9}$	←	$14_{7,8}$	37164.31	0.03
$15_{9,6}$	←	$14_{9,5}$	37153.88	0.03
$15_{9,7}$	←	$14_{9,6}$	37153.88	0.03
$15_{11,4}$	←	$14_{11,3}$	37148.33	0.00
$15_{11,5}$	←	$14_{11,4}$	37148.33	0.00
$15_{14,1}$	←	$14_{14,0}$	37143.56	0.03
$15_{14,2}$	←	$14_{14,1}$	37143.56	0.03
$16_{0,16}$	←	$15_{0,15}$	38591.09	0.03
$16_{1,16}$	←	$15_{1,15}$	38408.88	0.09

[a] ±0.10 MHz.

The dipole moment could not be obtained for any of the two conformers assigned in this work because the low-J transitions are too weak. However, the total dipole moment has been measured in benzene solution and found to be 5.04×10^{-30} C m.[21] This is not widely different from the *ab initio* value predicted for *Skew 3* (6.21×10^{-30} C m) calculated from the entries in Table 1.

Table 3. Ground-state spectroscopic constants[a,b] of *Skew 3* of 2-furanmethanethiol.

Species:	Parent	Deuterated
No of transitions:	131	85
R.m.s. dev.[c]/MHz:	0.042	0.056
A_0/MHz	6008.41(20)	5867.50(37)
B_0/MHz	1296.2353(10)	1284.3576(19)
C_0/MHz	1179.6156(11)	1164.4548(23)
Δ_J/kHz	0.2428(18)	0.2378(37)
Δ_{JK}[d]/kHz	0.4194(29)	0.3553(50)

[a] *A*-reduction, I^r-representation.[18] [b] Uncertainties represent one standard deviation. [c] Root mean-square deviation. [d] Further quartic constants preset at zero.

Assignment of Skew 1. The ^aR-pile-ups of this conformer were assigned simultaneously with their counterparts for *Skew 3* because they fall rather close to one another in frequency. This results because the rotational constants are rather similar, as are their μ_a dipole-moment components (Table 1). The intensities of the transitions belonging to *Skew 1* are roughly 35% of the intensities of the corresponding transitions of *Skew 3*. The frequency difference between the *a*-type transitions of *Skew 3* and *Skew 1* are so small that initially it was not certain that *Skew 1* had been assigned and not confused with a large-amplitude vibration of *Skew 3*. However, *Skew 1* was calculated (Table 1) to have a sizable μ_b, and its strongest *b*-type transitions were readily identified, whereas no *b*-type lines were found for *Skew 3* (see above). This was one important piece of evidence that these transitions indeed do not belong to *Skew 3*. A total of 184 transitions were ultimately assigned for this rotamer; a portion of the spectrum is given in Table 5. The spectroscopic constants are listed in Table 6. Vibrationally excited states of this conformer were noted, but no assignments were made.

The deuterated species (mercapto group) was assigned in a straightforward manner. Only ^aR-transitions were assigned; the ^bQ-transitions were too weak to be identified with certainty. The spectroscopic constants are found in Table 6. The substitution coordinates[20] for the H atom of the mercapto group is calculated to be $|a| = 200.88(15)$, $|b| = 60.16(48)$ and $|c| = 135.49(24)$ pm; values that are

Table 4. Spectroscopoic constants[a,b] of *Skew 3* of 2-furanmethanethiol in vibrationally excited states of the C1–C5 torsional vibration.

Vibrational state:	1st ex. C1–C5 torsion	2nd ex. C1–C5 torsion
No. of transitions:	105	68
R.m.s. dev.[c]/MHz:	0.048	0.057
A_v/MHz	6010.99(25)	6015.65(33)
B_v/MHz	1294.5710(12)	1293.1859(19)
C_v/MHz	1178.9798(14)	1178.5293(21)
Δ_J/kHz	0.2434(23)	0.2418(36)
Δ_{JK}[d]/KHz	0.6940(39)	0.8087(68)

[a-d] Comments as for Table 3.

Table 5. MW spectrum of the ground vibrational state of *Skew 1* of 2-furanmethanethiol.

Transition $J''_{K''-1,K''+1} \leftarrow J''_{K'-1,K'+1}$			Observed frequency[a]/MHz	Obs.−calc. frequency/MHz
$10_{1,9}$	←	$9_{1,8}$	25100.17	0.00
$10_{3,8}$	←	$9_{3,7}$	24688.21	−0.04
$11_{0,11}$	←	$10_{0,10}$	26781.78	−0.05
$11_{3,8}$	←	$10_{3,7}$	27183.48	0.03
$11_{7,4}$	←	$10_{7,3}$	27132.88	−0.02
$11_{7,5}$	←	$10_{7,4}$	27132.88	−0.02
$12_{0,12}$	←	$11_{0,11}$	29158.90	0.05
$12_{2,11}$	←	$11_{2,10}$	29512.25	0.07
$13_{3,11}$	←	$12_{3,10}$	32110.13	0.24
$13_{8,6}$	←	$12_{8,5}$	32066.03	0.01
$13_{8,5}$	←	$12_{8,4}$	32066.03	0.01
$13_{10,3}$	←	$12_{10,2}$	32062.05	−0.09
$13_{10,4}$	←	$12_{10,3}$	32062.05	−0.09
$14_{4,10}$	←	$13_{4,9}$	34575.28	0.04
$14_{7,7}$	←	$13_{7,6}$	34537.99	0.04
$14_{11,3}$	←	$13_{11,2}$	34527.64	0.02
$14_{11,4}$	←	$13_{11,3}$	34527.64	0.02
$15_{0,15}$	←	$14_{0,14}$	36245.85	0.02
$15_{3,13}$	←	$14_{3,12}$	37058.28	−0.03
$15_{6,9}$	←	$14_{6,8}$	37014.55	−0.03
$15_{6,10}$	←	$14_{6,9}$	37014.55	−0.03
$15_{12,3}$	←	$14_{12,2}$	36992.94	−0.03
$15_{12,4}$	←	$14_{12,3}$	36992.94	−0.03
$16_{1,16}$	←	$15_{1,15}$	38402.18	0.02
$18_{3,16}$	←	$18_{2,17}$	25763.27	0.00
$19_{4,15}$	←	$19_{3,16}$	32182.82	−0.06
$22_{2,21}$	←	$22_{1,22}$	27760.59	−0.06
$25_{1,24}$	←	$25_{0,25}$	28841.33	0.01
$26_{3,24}$	←	$26_{2,25}$	30498.05	0.17
$28_{4,24}$	←	$28_{3,25}$	27615.54	−0.05
$31_{2,29}$	←	$31_{1,30}$	28613.02	0.02
$33_{2,31}$	←	$33_{1,32}$	32161.51	0.09
$34_{4,30}$	←	$34_{3,31}$	24398.99	−0.02
$37_{3,34}$	←	$37_{2,35}$	27400.86	−0.12
$39_{3,36}$	←	$39_{2,37}$	30728.60	−0.06
$40_{5,35}$	←	$40_{4,36}$	33199.99	0.00
$43_{4,39}$	←	$43_{3,40}$	27166.86	−0.04
$45_{5,40}$	←	$45_{4,41}$	30087.00	−0.02
$48_{4,44}$	←	$48_{3,45}$	34090.76	−0.08
$53_{6,47}$	←	$53_{5,48}$	37402.82	0.00
$56_{5,51}$	←	$56_{4,52}$	35673.28	−0.02
$59_{6,53}$	←	$59_{5,54}$	35027.57	−0.01
$62_{6,56}$	←	$62_{5,57}$	36115.21	0.04
$64_{6,58}$	←	$64_{5,59}$	37812.38	0.03

[a] ±0.10 MHz.

fairly close to the predicted ones (Table 1). This is additional, conclusive evidence that the spectrum in Table 5 is correctly assigned to *Skew 1*.

Searches for further rotamers. The assignments reported above include all the strongest transitions of the spectrum and many weak ones too. However, this spectrum has a rich background of mostly very weak transitions which have not been assigned. Many, or perhaps all of these undoubtedly belong to vibrationally excited states of *Skew 1* and *Skew 3* which were not assigned. As shown in Table 1, all the remaining three conformations predicted to be stable, possess sizable dipole moments and would have rather prominent spectra provided they were present in high concentrations. Attempts to assign these remaining weak transitions to any of these three hypothetical rotamers failed. It is felt that they are present in small concentrations, if they exist at all. It is concluded that *Skew 3* and *Skew 1* undoubtedly make up most of the gas phase of 2-furanmethanethiol. It is impossible to tell from this experiment exactly how much of the gas is these two conformers, but it is suggested that these *Skew 3* and *Skew 1* together make up at least 80% of the gas at −15°C.

Table 6. Ground-state spectroscopic constans[a,b] of *Skew 1* of 2-furanmethanethiol

Species:	Parent	Deuterated
No. of transitions:	184	56
R.m.s. dev.[c]/MHz:	0.061	0.115
A_0/MHz	5997.4795(40)	5847.18(80)
B_0/MHz	1284.6619(12)	1265.8653(42)
C_0/MHz	1181.1226(12)	1169.0272(45)
Δ_J/kHz	0.2319(30)	0.2517(81)
Δ_{JK}/kHz	0.3639(36)	0.356(11)
Δ_K/kHz	9.50(22)	9.50[d]
δ_J/kHz	0.001307(35)	0.001307[d]
δ_K/kHz	−0.6866(54)	−0.6866[d]

[a-c] Comments as for Table 3. [d] Kept fixed at this value in the least-squares fit.

Energy difference. The internal energy difference between *Skew 1* and *Skew 3* was obtained from relative intensity measurements[19] made on selected ^aR-transitions. The ratios between the calculated μ_a dipole-moment components given in Table 1 were used, as no experimental dipole moments of the two conformers have been obtained. In this manner an internal energy difference of 2.3(5) kJ mol^{-1} was found with *Skew 3* as the most stable conformer. The standard deviation of ±0.5 kJ mol^{-1} has been estimated by taking into account the uncertainty of the calculated dipole moment, as well as other sources of error. The energy difference obtained in the 6-31G** computations is 1.1 kJ mol^{-1} (Table 1), and is thus in good agreement with the experimental value.

Structure. It is seen from Tables 3 and 6 that the experimental rotational constants of *Skew 3* and *Skew 1* are close to those calculated from the 6-31G** structure (Table 1). In fact, the agreement is almost perfect in the cases of the *B* and *C* rotational constants and deviate by about 3% in the cases of the *A* rotational constants. Moreover, the structural parameters of the furan ring and the $-CH_2SH$ substituent are very similar to their experimental counterparts in furan[15] and methanethiol,[16] as already mentioned. There is also good agreement between the substitution coordinates of the H atom of the mercapto group and those obtained in the *ab initio* computations. No experimental data are at hand that could really improve the 6-31G** structures of these two conformers. The *ab initio* structures shown in Table 1 are

therefore adopted as *plausible* structures for the *Skew 3* and *Skew 1* conformers of 3-furanmethanethiol.

The *ab initio* structures of Table 1 deviate from the electron-diffraction structure[11] in one important respect: The C2 = C1–C5–S dihedral angles are about 110° (Table 1) in the two identified *skew* forms, whereas the electron-diffraction result[11] was 141(4)°, which is not compatible with the present result.

Some remarks about the H bonds in *Skew 1* and *Skew 3* are warranted. It is seen in Table 1 that the distance between H6 and C1 is 295 pm in *Skew 1*. This is almost the same as the sum of the van der Waals radius of H and the half-thickness of aromatic carbon (290 pm),[17] and this is indicative of a weak interaction between the H6 atom and the π-electrons of the ring.

In *Skew 3* the H6···O non-bonded distance is 289 pm compared to 260 pm, which is the sum of the van der Waals radii of oxygen and hydrogen,[17] and the S–H6···O atoms form an angle of 96°. Such a long distance and non-linearity of the S–H···O linkage indicate that covalent forces are of little importance for the stabilization of this conformer. However, it is interesting to note that the C1–O and S–H6 bonds are only 5° from being parallel. The bond dipoles of these two bonds are thus almost anti-parallel, a situation which is very favourable for electrostatic interaction. It is therefore suggested that this electrostatic stabilization is an important reason why *Skew 3* is the most stable conformer of the molecule.

Discussion

Conformational data are now available for two congeners of 2-furanmethanethiol, namely 2-furanmethanol[10] and 2-furanmethanamine.[22] All identified conformers of these three molecules prefer *skew* conformations stabilized by weak H bonds. There are probably several reasons why these three compounds display the same conformational preferences. The choice to have the C = C–C–X (X = O, N, S) chain of atoms in a *skew* conformation is probably caused largely by electronic interaction between the π-electrons of the double bond, the electrons of the methylene group and the electrons of the X atom, just as explained in the case of allyl alcohols.[23] This model[23] predicts that C = C–C–X *syn* forms should also be stable, and this is in agreement with the theoretical predictions (Table 1), although no *syn* forms have been found experimentally.

Once the heavy-atom *skew* conformation have been established, the H atom of the mercapto as well as of the hydroxyl group binds itself either to the electronegative oxygen atom of the ring or to the π-electrons of the C1 = C2 bond. 2-Furanmethanamine can use both the H atoms of the amino group for internal H bonding at the same time, one of which is bonded to the oxygen atom while the other is bonded to the π-electrons of the C1 = C2 bond in the most stable conformer of this molecule.[22]

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