J. Org. Chem. **1992**, *57*, 5963-5967

Conformational Analysis of Furyl- and Thienylhydroxymethyl Radicals

Mauro A. Cremonini, Lodovico Lunazzi, and Giuseppe Placucci*

Department of Organic Chemistry "A. Mangini", The University, Risorgimento 4, Bologna, Italy

Maurizio Guerra*

C.N.R., I.Co.C.E.A., via della Chimica 8, Ozzano Emilia, Bologna, Italy

Received May 13, 1992

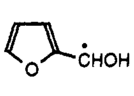
Low-temperature photolysis of ArCH$_2$OH derivatives (Ar = 2- and 3-furyl and -thienyl) in the presence of Bu^{t}OOBu^t yields the corresponding Ar$\dot{C}$HOH radicals which can be observed by means of EPR spectroscopy. Each radical displays *E* and *Z* rotational conformers due to restricted Ar–C$_\alpha$ rotation. The study of Ar$\dot{C}$HOMe radicals, as well as of 2-furyl- and 2-thienylhydroxymethyl radicals having a methyl group in position 3 of the ring, allowed us to identify the most stable of the two conformers. The temperature dependence of the a_{OH} hfs constant (assigned by deuterium substitution) has been interpreted on the basis of an averaging of ab initio a_{OH} hfs constant over the rotation about the $\dot{C}_\alpha$–O bond which also allowed us to obtain an estimate of the corresponding rotation barrier.

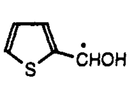
Introduction

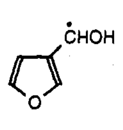
We have been recently investigating the conformational properties of thioaldehyde and aldehyde radical anions containing the furan and thiophene ring (ArCHS$^{\bullet-}$ and ArCHO$^{\bullet-}$, where Ar = 2- or 3-furyl and -thienyl moieties).[1] These radicals display restricted rotation about the Ar–$\dot{C}_\alpha$ bond, thus yielding pairs of rotational conformers of different stability. These conformers were identified and their *E* and *Z* structure assigned by making use of the EPR spectroscopy. The protonated forms of these furan- and thiophene-containing radical anions (i.e., the corresponding hydroxymethyl radicals Ar$\dot{C}$HOH) should also be amenable to EPR investigation and should, likewise, display rotational conformers. For, the protonated form of the benzaldehyde radical anion (i.e., phenylhydroxymethyl radical Ph$\dot{C}$HOH)[2-4] was found to have two different a_H hyperfine splitting constants for the two ortho (H-2 ≠ H-6) and meta (H-3 ≠ H-5) hydrogens. This is diagnostic of a restricted phenyl–$\dot{C}$ bond rotation which would generate pairs of rotational conformers in the case of aromatic rings with a lower symmetry than phenyl.

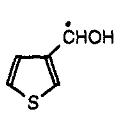
Results and Discussion

EPR Investigations. Radicals 1–4 were obtained when Bu^{t}OOBu^t solutions of the appropriate ArCH$_2$OH alcohols were photolized in the cavity of an EPR spectrometer: photolysis of the peroxide yields the Bu^{t}O$^\bullet$ radical which abstracts an hydrogen atom from the CH$_2$O moiety of the alcohol, yielding a stationary state of the radicals whose spectra can be thus detected.


1


2

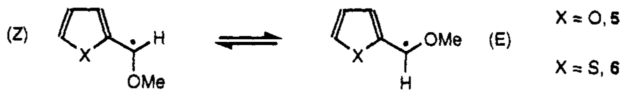

3


4

The EPR spectra of 1–4 appear as two superimposed traces, corresponding to the *E* and *Z* rotamers: a typical spectrum is that of radical 2 reported in Figure 1, together with the computer simulation. The relative proportions of the conformers, the a_H values, and the *g*-factors for radicals 1–4 are collected in Table I. The hyperfine splitting constants due to the OH hydrogens were assigned by deuterium substitution: in all the cases examined it was found that the smallest splitting disappears when observing the Ar$\dot{C}$HOD radical. A sample spectrum of a deuterium-substituted radical is shown in Figure 2 for radical 3a, i.e., radical 3 having the OH replaced by an OD group.

The largest splitting in radicals 1–4 belongs to the hydrogen bonded to the sp^2 carbon bearing the unpaired electron, the remaining ring splittings were assigned by analogy with the trends observed in the corresponding aldehyde radical anions.[1] No attempt was made to assign the *E*,*Z* structures to the rotamers of the 3-substituted radicals 3 and 4, whereas in the case of the 2-furyl and 2-thienyl radicals 1 and 2 a number of experiments were carried out for this purpose.

The approach we followed was based on the comparison with analogous radicals where the OH hydrogen had been replaced by a methyl group. It was assumed that the greater steric effect of the OMe with respect to the OH moiety would modify the conformer ratio observed in 1 and 2: the proportion of the *E* conformer would conceivably become lower (hence that of the *Z* conformer higher) in radicals 5 and 6, respectively:



In the furan-containing radicals the conformer ratio is 80:20 in 1, but 60:40 in 5 (Table II). The a_{H_α} splitting of the minor conformer in both 1 and 5 is the same (13.65 G), and that of the major conformer is only slightly modified (14.45 G in 1 and 14.30 G in 5). As the proportion of the *major* conformer in 1 (80%) has *decreased* in 5 (60%), it seems reasonable to assign it the *E* structure. Also, in the thiophene-containing radicals 2 and 6 substitution of the OH with the OMe group changes the proportion of the conformers (from 65:35 in 2 to 75:25 in 6). Here too the largest splitting is not appreciably modified: 12.9 and 13.55 G for the major and minor conformer, respectively, in 2, to be compared with 13.0 and 13.6 G, respectively, in 6 (Table II). However, here the presence of the OMe moiety has *increased* the proportion of the *major* conformer (65% in 2 and 75% in 6), thus indicating that the *Z* structure should be assigned to the *major* conformer of 2.

To further confirm this conclusion an independent experiment was carried out by introducing a methyl group

---

[1] Borghi, R.; Cremonini, M. A.; Lunazzi, L.; Placucci, G.; Macciantelli, D. *J. Org. Chem.* **1991**, *56*, 6337.

[2] Fischer, H. *Z. Naturforsch.* **1965**, *20a*, 488.

[3] Wilson, R. *J. Chem. Soc. B* **1968**, 84.

[4] Paul, H.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 1575.

0022-3263/92/1957-5963$03.00/0

Table I. Hyperfine Splitting Constants (a_H in G) and g-factors of the Conformers of Radicals 1–4

radical	*Z*, *E* (%)	a_{H-2}	a_{H-3}	a_{H-4}	a_{H-5}	a_{CH}	a_{OH}	g-factor	t (°C)
1 (*E*)	80		8.00	1.20	6.25	14.45	0.25	2.0034_5	
1 (*Z*)	20		8.45	1.40	7.10	13.65	0.50	2.0034	−25
2 (*E*)	35		7.70	1.60	6.70	13.55	0.65	2.0040	
2 (*Z*)	65		7.73	1.70	7.33	12.90	0.70	2.0038	−35
3	30	9.15		1.40	0.57	15.95	0.60	2.0033	
	70	9.35		1.32	0.65	16.30	0.65	2.0033	−50
4	25	8.10		1.75	0.82	15.25	0.50	2.0037_5	
	75	8.30		1.58	0.85	15.40	0.50	2.0038	−17

Table II. Hyperfine Splitting Constants (a_H in G) of the Conformers of Radicals 5–8

radical	*Z*, *E* (%)	a_{H-3}	a_{Me-3}	a_{H-4}	a_{H-5}	a_{CH}	a_{OMe}	a_{OH}	t(°C)
5 (*E*)	60	7.90		1.15	6.25	14.30	1.15		
5 (*Z*)	40	8.35		1.40	7.25	13.65	1.15		−40
6 (*E*)	25	7.30		1.40	6.90	13.60	1.13		
6 (*Z*)	75	7.60		1.62	7.20	13.00	1.15		−55
7 (*E*)	30		7.75	1.20	6.40	14.20		0.40	
7 (*Z*)	70		7.80	1.50	7.40	13.20		0.00	+20
8 (*E*)	0								
8 (*Z*)	100		7.00	1.80	7.65	12.50		0.60	−50

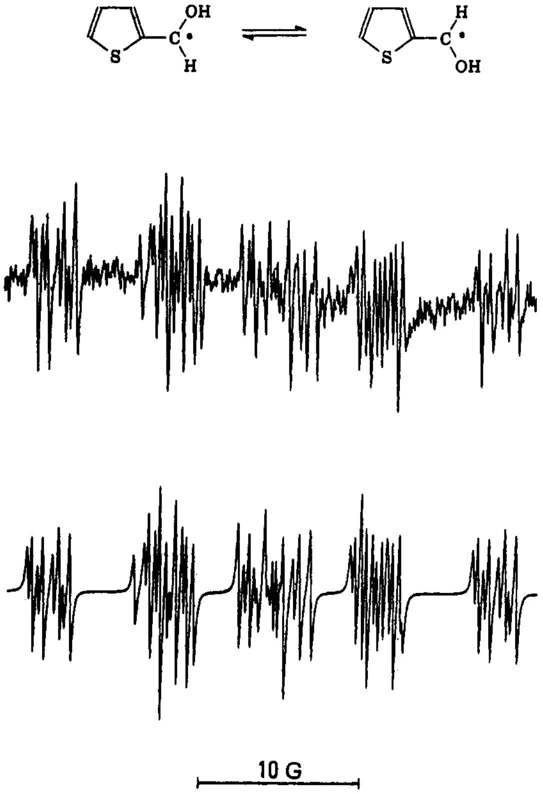


Figure 1. Experimental (top) EPR spectrum of radical **2**. The computer simulation shown underneath was obtained with the parameters of Table I and a line width of 0.16 G.

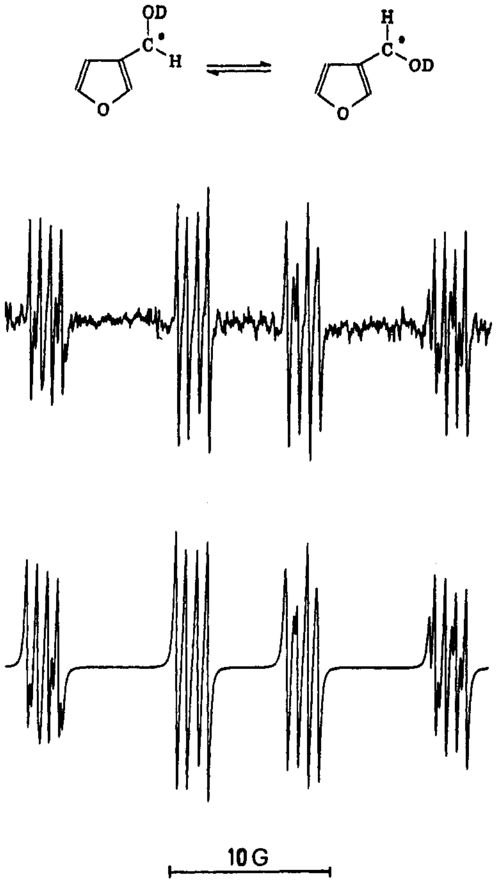
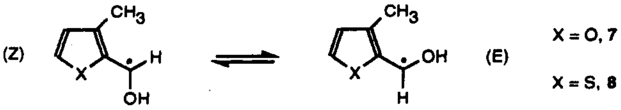


Figure 2. Experimental (top) EPR spectrum at 20 °C of the deuterated radical **3a** obtained by deuterium substitution of the OH hydrogen of radical **3**. The computer simulation shown underneath was obtained with the parameters for radical **3** of Table I, with the exception of the OH splitting which, on deuterium substitution, becomes lower than the line width of 0.17 G.



in position 3 of the five-membered ring to yield radicals **7** and **8** (Table II). The steric effect should again reduce the amount of the *E* conformer in **7** and **8** with respect to the unsubstituted radicals **1** and **2**, and the modifications of the conformer ratio should be even greater, owing to the rigidity of the methyl–aryl moiety which, contrary to the ArCOMe moiety, cannot relieve the steric congestion by being twisted out of the plane of the ring. Actually, the ratio observed in **7** is 30:70 but the a_{H_α} splitting for the *major* conformer of **7** (13.2 G) corresponds to that of the *minor* conformer of **1** (13.65 G) and, likewise, the splitting of the minor conformer in **7** to that of the major conformer in **1** (14.2 and 14.45 in **7** and **1**, respectively). Clearly the introduction of the methyl group in position 3 has reversed the stability of the conformers. Accordingly, to the more stable (80%) conformer of **1** the *E* structure has to be assigned since its proportion has decreased to 30% in **7**. In the thiophene-containing radical **8** only a single conformer is detectable, the one whose splitting is similar to that of the major conformer in **2**. As the latter has in-

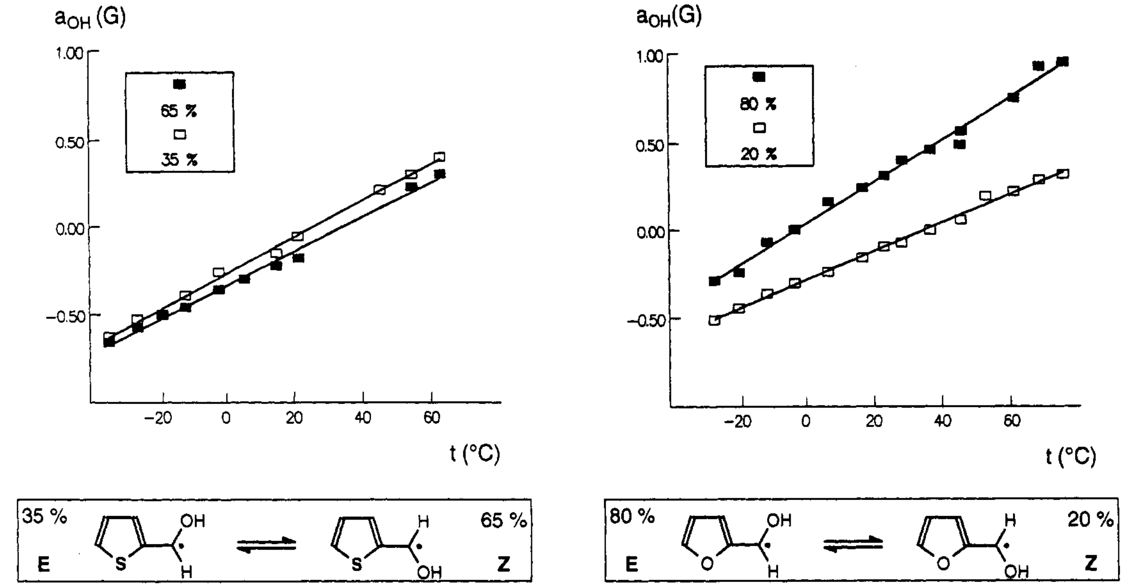


Figure 3. Temperature dependence of the a_{OH} splittings (G) for the two conformers of radical **2** (left hand side). On the right hand side the same dependence is shown for the conformers of radical **1**.

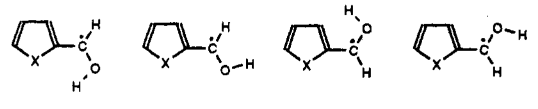
creased its proportion from 65% in **2** to 100% in **8** we must assign it the structure *Z*.

Both the approaches employed (i.e., methyl substitution for the hydrogen either of the OH group or of the ring position 3) indicate that structure *E* is that adopted by the major conformer in radical **1** and that the opposite structure *Z* is that corresponding to the major conformer in **2**. It is worthwhile to outline that in the case of **2** the *Z* structure for the major conformer corresponds to that observed for the major conformer of the analogous radical anion, whereas the *E* structure for the major conformer of **1** *does not* correspond to that observed in the corresponding radical anion, where the more stable conformer was found to have the structure *Z*. This difference might be due to the existence of a particularly stable ion pair in the radical anion of the 2-furan aldehyde: the presence of two contiguous oxygen atoms bearing a negative charge is expected to make particularly stable an ion pair in the *Z* configuration of the anion radical.

Another feature which is also related to the conformational behavior is the temperature dependence observed for the OH splittings of **1** and **2**. In the case of the thienyl-containing radical **2**, the variations of a_{OH} have similar slope for both the *E* and *Z* conformers (viz. 10.5 and 9.8 mG/K). On the other hand, in the case of the furan-containing radical **1** the slope for the major conformer (12.1 mG/K) is 1.5 times that for the minor one (8.2 mG/K), as shown in Figure 3.

The quasi linear dependence of the a_{OH} values upon the temperature is related to the height of the $\dot{C}$OH rotational barrier;[5] the larger the barrier, the lower is expected to be the slope of the line. The different slopes observed for the two conformers of **1** suggest that the minor conformer (which has the lower slope) has a larger rotational barrier than the major one. A possible explanation for this behavior (which would also explain the almost equal slopes observed for both conformers of **2**) is the occurence of an attractive hydrogen bond interaction between the OH group and the oxygen atom of the furan ring in the minor rotamer of **1**. This obviously requires that the latter has the *Z* structure, a conclusion which nicely agrees with the assignment previously made by methyl substitution. This type of stabilization should be, however, relatively small since it is not sufficient to make the *Z* more stable than the *E* conformer.

Scheme I. Ab Initio Computed Relative Energies (kcal/mol) of rotamers of 2-Furyl- and 2-Thienylhydroxymethyl Radical (UMP2/DZ+d//UHF/DZ+d Level of Theory)



	Z - syn	Z - anti	E - syn	E - anti
X = O	0.0	4.11	2.60	1.91
X = S	1.05	0.0	0.68	0.34

In order to obtain a better understanding of this phenomenon and to determine the values of the $\dot{C}$OH rotational barriers, ab-initio calculations were undertaken for radicals **1** and **2**.

Theoretical Calculations. Ab initio calculations (carried out at the UMP2/DZ+d//UHF/DZ+d level of theory) indicate that four stable conformers are available to both radical **1** and **2**. In particular, two energy minima occur for each of the *E* and *Z* structures in which the OH hydrogen is located in either the syn or in the anti position with respect to the ring moiety, the molecular skeleton being essentially planar. Energy stabilities relative to the most stable isomer are reported in Scheme I.

The most relevant aspect of the theoretical results is the large stability of the *Z*-syn isomer found in the case of **1**, due to a hydrogen bond interaction between the positively charged (+0.25e) OH hydrogen and the negatively charged (−0.46e) oxygen atom of the furan ring. In fact, the *Z*-syn isomer in **1** is computed to be much more stable (about 4 kcal/mol) than the corresponding anti isomer, whereas the anti isomer is found to be slightly more stable (<1 kcal/mol) than the corresponding syn isomer in both the *E* conformers, where the H-bond interaction is absent, as well as in the *Z* conformer of **2**, where the sulfur atom bears a very small negative charge (−0.08e). This confirms the hypothesis that a H-bond interaction is operative in **1**. Its magnitude, estimated for an isolated species, is, however, too large since the *Z*-syn isomer of **1** is computed to be more stable than the *E* conformer, apparently at variance

---

(5) Krusic, P. J.; Meakin, P.; Jesson, J. P. *J. Phys. Chem.* 1971, *75*, 3438. Sullivan, P. D. *J. Phys. Chem.* 1971, *75*, 2195. Ayscough, P. B.; McClung, R. E. D. *Mol. Phys.* 1971, *20*, 35.

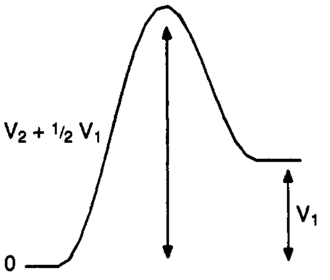
Table III. Best-Fit Coefficients of the Expansion of the Rotation Potential $V(\omega)$ and of the $a_{OH}(\omega)$ Computed at the UMP2/DZ+d//UHF/DZ+d and UHF/DZ+d Level of Theory, Respectively

radical	V_0	V_1	V_2	V_3	V_4	a_0	a_1	a_2	a_3	a_4
1*Z*	7.88	−3.71	−3.86	−0.40	0.08	13.42	0.18	−17.53	−0.15	−0.01
1*E*	2.43	−0.76	−1.95	0.07	0.21	13.29	−0.62	−16.70	0.84	−0.17
2*Z*	2.95	−1.13	−2.16	0.09	0.24	13.41	−0.49	−17.30	0.53	−0.08
2*E*	2.20	−0.30	−2.20	0.04	0.25	13.26	−0.70	−16.76	0.82	−0.15

Table IV. Temperature Coefficients $\Delta a_{OH}/\Delta T$ (mG/K) and a_{OH} (G) at Low and High Temperature for the *E* and *Z* Conformers of 2-Furyl- (1) and 2-Thienylhydroxymethyl (2) Radical

	$\Delta a_{OH}/\Delta T$		a_{O}H (−25 °C)		a_{OH} (60 °C)	
	expl	theor[a]	expl	theor[a]	expl	theor[a]
1*Z*	8.2	6.0	−0.50	−1.73	0.21	−1.22
1*E*	12.1	17.4	−0.27	2.54	0.76	4.02
2*Z*	9.8	16.7	−0.58	1.63	0.25	3.05
2*E*	10.5	16.4	−0.53	2.19	0.36	3.58

[a] Computed by using the expansion coefficients of $V(\omega)$ and $a_{OH}(\omega)$ as shown in Table III.



$$V = V_0 + \frac{1}{2} V_1 (1 + \cos \omega) + \frac{1}{2} V_2 (1 + \cos 2\omega) + \ldots$$

Figure 4. Energy profile of the potential for the $\dot{C}$–OH rotation in radicals 1 and 2.

Table V. Rotational Barrier ΔE (kcal/mol) about the C–OH Bond Estimated (A) from ab Initio Calculations at UMP2/DZ+d//UHF/DZ+d Level and (B) from a Theoretical Analysis of the Temperature Dependence of the a_{OH} hfs Constants

		(B)			
	(A) ΔE	ΔE^a	$V_1{}^b$	$V_2{}^b$	$\Delta a_0{}^c$
1*Z*	5.98	5.08		−2.88	0.91
		5.00	−1.47	−4.06	0.81
1*E*	2.27	3.58		−3.25	−0.58
2*Z*	2.68	4.29		−3.76	0.08
2*E*	2.29	3.83		−3.70	−0.43

[a] Estimated by changing the V_1 and/or V_2 coefficients of $V(\omega)$ to match the experimental $\Delta a_{OH}/\Delta T$. [b] Optimum value. [c] Correction to the constant coefficient a_0 of $a_{OH}(\omega)$ to make the theoretical $a_{OH}(T)$ equal to the experimental one.

with the experimental indications based on the change of the conformer ratio upon methyl substitution. The *Z*/*E* stability in 1 could be sizably reduced, or even reversed in solution, in that the strength of the H-bond is expected to decrease owing to intermolecular interactions. On the other hand, the computed *Z*/*E* relative stability in 2 is in agreement with experimental findings. Information on the magnitude of the H-bond interaction and on the *E*/*Z* relative stability in 1 can be obtained by comparing the experimental a_{OH} values, and their quasi linear temperature dependence ($\Delta a_{OH}/\Delta T$), with the corresponding values evaluated theoretically from a Boltzmann weighted average of the ab initio a_{OH} hfs constants over the rotational motion about the C_α–O bond. The expansion coefficients of the ab initio potentials $V(\omega)$ relative to the more stable isomer ($\omega = 0°$) and of the ab initio $a_{OH}(\omega)$ hfs constants employed in the calculations are collected in Table III. The theoretical values of the rotationally averaged a_{OH} hfs constants, $\langle a_{OH}(T) \rangle$, evaluated at low (−25 °C) and high (60 °C) temperature, along with the corresponding gradient $\Delta a_{OH}/\Delta T$, are reported in Table IV. The experimental trends are well reproduced by these calculations. For, the slope of $\langle a_{OH} \rangle$ with temperature is computed to be much higher in the *E* than in the *Z* conformer in 1, whereas it is computed to be similar in the *E* and *Z* conformers of 2. This confirms the importance of the H-bond interaction in 1. Interestingly, $\langle a_{OH} \rangle$ and its slope are computed to be lower than experiment in the *Z* conformer of 1, in which the H-bond interaction is operative, while they are computed to be higher than experiment in all the other cases. This suggests that, in general, ab initio calculations underestimate the rotation barrier about the $\dot{C}_\alpha$–O bond, except for that in the *Z* isomer of 1 where a too strong H-bond interaction causes an anomalous overestimate of the rotation barrier. Indeed, the rotation barriers rise by about 0.75 kcal/mol with addition of electron correlation, i.e., on going from UHF/DZ+d to UMP2/DZ+d//UHF/DZ+d, so that it is likely that geometry optimisation at higher level (i.e., with inclusion of electron correlation at second-order Möller–Plesset perturbation theory–UMP2–) and/or estimate of electron correlation at higher orders could provide higher values of rotation energy barriers. Calculations at higher levels of theory are very expensive when carried out on such large systems as those investigated here; thus the rotation barriers were estimated by varying the leading terms of the expansion coefficients of $V(\omega)$ and of $a_{OH}(\omega)$ reported in Table III, so that the theoretical slope of $\langle a_{OH}(T) \rangle$ with temperature exactly matches the experimental dependence. It is evident from Table III that in all the radicals the leading terms of $V(\omega)$ are the 1-fold term, which gives the syn/anti relative stability, and the 2-fold term, which determines the height of the rotation barrier (see Figure 4). The leading term of $a_{OH}(\omega)$ is the 2-fold term, which is related to the delocalization of spin density to the OH hydrogen through a hyperconjugative mechanism. The ab initio $a_{OH}(\omega)$ values are found to be similar in all the radicals (see Table III); thus, acceptable variations of a_2 cannot improve the agreement between theory and experiment, since $\langle a_{OH}(T) \rangle$ is lower than experiment in the *Z*-syn isomer of 1, whereas the opposite trend occurs in the other cases. Preliminary calculations also showed that a variation in either V_1 or a_2 improves the slope of $\langle a_{OH} \rangle$ but worsens the a_{OH} splitting and vice versa and that the slope of $\langle a_{OH} \rangle$ with temperature is more sensitive to a change in V_2 than in V_1. Thus, the optimum rotation barriers, obtained by varying only the V_2 term, are collected in Table V: their trend corresponds to the expectation. In particular, the rotation barrier decreases by 0.9 kcal/mol in the *Z* conformer of 1, whereas it increases by 1.3 kcal/mol in the corresponding *E* conformer and by about 1.5 kcal/mol in both conformers of 2. This suggests that the energy of the transition state to rotation should be underestimated by 1.3–1.5 kcal/mol at the UMP2/DZ+d//UHF/DZ+d level as the H-bond interaction is not expected to affect the transition-state energy. Thus, the H-bond interaction in 1 was determined by varying both the V_1 and V_2 terms, with the constrain that the transition-state energy with respect to the less populated isomer (i.e., *Z*-anti where the H-bond is absent) is kept 1.3 kcal/mol higher than that computed at the UMP2/DZ+d//UHF/DZ+d level. Interestingly, a sizable variation of the *Z*/*E* relative stability does not significantly affect the optimum value of the rotation barrier, as previously observed. This confirms the reliability of the rotation barrier determined from the best fit of the slope of a_{OH} with temperature. From the optimum V_1 value one can estimate a decrease of the H-bond energy by 2.28 kcal/mol. This means that the *E* conformer in **1** turns out to be more stable (0.37 kcal/mol) than the corresponding *Z* conformer, in agreement with experimental conclusions. Finally, it should be noted that the correction to the constant a_0 term, made in order to exactly reproduce the experimental hfs constants, is now very small (<6%). Even a minor departure of the optimized geometries from the actual structure in the ground state might be responsible for the little residual discrepancy between experimental and theoretical hfs constants, in that the correction needs to be positive or negative for the *Z* and for the *E* conformers, respectively.

Conclusions

The presence of two conformational isomers in arylhydroxymethyl radicals (the aryl moiety being a thiophene or a furan ring) has been detected by EPR spectra. In the 2-substituted derivatives assignment of the more stable rotamers, due to the restricted Ar–$\dot{\mathrm{C}}_\alpha$ rotation, has been achieved, whereas the *E*-form is more stable in the case of the furan and the *Z*-form is more stable in the case of the thiophene-containing radical. The a_{OH} hfs constants and their temperature dependence were well reproduced by averaging the ab initio a_{OH} hfs constants over thermally populated levels of the restricted rotation about the $\dot{\mathrm{C}}_\alpha$–O bond: the corresponding rotation barriers were estimated. The existence of an intramolecular hydrogen bond accounts for the higher $\dot{\mathrm{C}}$OH rotation barrier observed for the *Z* with respect to the *E* conformer of the radical containing the furan ring.

Experimental Section

Material and Spectral Measurements. The alcohols used as precursors of the radicals **1**–**4** are commercially available and were purified before use. The ethers[6,7] used as precursors of radicals **5** and **6** were obtained from the alcohol precursors of **1** and **2**, respectively, by reaction with NaH and $\mathrm{CH_3I}$ in anhydrous ether. The alcohol precursors of radicals **7** and **8** had been reported in refs 8 and 1, respectively.

The EPR spectra were obtained by photolyzing saturated $\mathrm{Bu^tOOBu^t}$ solutions (two phases were occasionally observed) of the appropriate precursor within the cavity of a Varian E-3 spectrometer, using Suprasil quartz tubes sealed in vacuo and a 500-W high-pressure Hg lamp. Addition of cyclopropane to reach lower temperatures resulted in weaker signals. The temperature was monitored by inserting a thermocouple in the place of the sample before and after each spectral determination.

Computational Details. Ab initio unrestricted Hartee–Fock (UHF) calculations have been performed on 2-furyl- (**1**) and 2-thienylhydroxymethyl (**2**) radicals with the GAUSSIAN 82 system of programs[9] employing a quite flexible basis set. The basis set (DZ+d) consists of Dunning's full double-ζ (DZ) contraction of Huzinaga's primitives, supplemented with d-functions (d) on the sulfur atom.[10] Geometries were optimized as a function of the rotation angle ω about the C_α–O bond at 15° intervals keeping the structural parameters of the ring moiety fixed to those determined experimentally for furan[11] and thiophene.[12] Rotation barriers have been computed by taking into account electron correlation energy estimated by using second-order Möller–Plesset perturbation theory (UMP2).[13] Theoretical hyperfine coupling constants have been estimated at the UHF/DZ+d level from a statistical averaging of the computed $a_{\mathrm{OH}}(\omega)$ values over the thermally populated rotational states[14]

$$\langle a_{\mathrm{OH}}(T)\rangle = \textstyle\sum_m \langle\psi_m|a_{\mathrm{OH}}(\omega)|\psi_m\rangle e^{-E_m/KT} / \sum_m e^{-E_m/KT} \qquad (1)$$

The eigenfunctions ψ_m and eigenvalues E_m have been taken as solutions of the hamiltonian *H* for the hindered rotor

$$H = -h^2\partial^2\psi_m/8\pi^2 I\partial^2\omega + V(\omega) \qquad (2)$$

where *h* is the Planck constant and *I* is the reduced moment of inertia for rotation about the C_α–O bond; its value has been computed from the optimized geometries to be 1.319, 1.365, 1.317, and 1.303 10^{-40} g cm^2 for **1**-*E*, **1**-*Z*, **2**-*E*, and **2**-*Z* conformers, respectively. According to the symmetry properties of $V(\omega)$ ($V(\omega) = V(-\omega)$), the potential $V(\omega)$ has been expanded in periodic even and odd functions of the angle ω. The coefficients V_k have been

$$V(\omega) = 1/2\textstyle\sum_k V_k(1 + \cos k\omega) \qquad k = 0, 1, ..., n \qquad (3)$$

determined by means of a least-squares fitting of the ab initio rotation energy values. An expansion up to a 4-fold term is sufficient to fit the energy values with accuracy.

The hamiltonian *H* has been set up in the basis of the even ϕ^{e} and odd ϕ^{o} eigenfunctions of the free rotor[15]

$$\phi^{\mathrm{e}}{}_0 = (2\pi)^{-1/2} \qquad (4)$$

$$\phi^{\mathrm{e}}\lambda = \pi^{-1/2} \cos \lambda\omega \qquad (5)$$

$$\phi^{\mathrm{o}}{}_\lambda = \pi^{-1/2} \sin \lambda\omega \qquad (6)$$

According to the symmetry properties of $V(\omega)$ ψ_m has been separated in the even $\psi^{\mathrm{e}}{}_m$ and odd $\psi^{\mathrm{o}}{}_m$ expansions by diagonalizing the $\mathbf{H}^{\mathrm{e}}$ and $\mathbf{H}^{\mathrm{o}}$ matrices, respectively, in which the matrix **H** can be partitioned. The diagonal matrix elements are

$$H^{\mathrm{i}}{}_{\lambda\lambda} = h^2\lambda^2/8\pi^2 I + V_0 + \sum_{k\neq 0} V_k/2 + (2\delta_{\mathrm{ie}} - 1)(1 - \delta_{\mathrm{o}\lambda})V_{2\lambda}/4 \qquad i = \mathrm{e, o} \quad (7)$$

and the off-diagonal matrix elements are

$$H^{\mathrm{i}}{}_{\lambda\lambda'} = (1 + (2^{1/2} - 1)(\delta_{\mathrm{o}\lambda} + \delta_{\mathrm{o}\lambda'}))(V_{|\lambda-\lambda'|} + (2\delta_{\mathrm{ie}} - 1)V_{\lambda+\lambda'})/4 \qquad i = \mathrm{e, o} \quad (8)$$

The periodic function $a_{\mathrm{OH}}(\omega)$ has been expanded in a Fourier series

$$a_{\mathrm{OH}}(\omega) = \textstyle\sum_k a_k \cos k\omega \;\; k = 0, 1, ... \qquad (9)$$

An expansion up to the 4-fold term is sufficient to accurately reproduce the computed a_{OH} values by means of a least-squares procedure. Expectation values over even and odd functions are

$$\langle\psi^{\mathrm{i}}{}_m|\cos k\omega|\psi^{\mathrm{i}}{}_m\rangle = 2^{1/2}\, c^{i}{}_{m0}\, c^{i}{}_{mk}\, \delta_{\mathrm{ie}} + \sum_{\lambda=1}^{\lambda_{\max}-k} c^{i}{}_{m\lambda} c^{i}{}_{m\lambda+k} + (\delta_{\mathrm{ie}} - 0.5)\sum_{\lambda=1}^{k-1} c^{i}{}_{m\lambda} c^{i}{}_{mk-\lambda} \quad i = \mathrm{e, o} \quad (10)$$

An expansion up to the 60th term ($\lambda_{\max} = 60$) is sufficient to obtain complete convergence.

Acknowledgment. This work was carried out with the financial support of MURST and CNR (Rome).

---

(6) Schaft, H.-D.; Wolters, E. *Chem. Ber.* **1978**, *111*, 639.

(7) Takahashi, K.; Sone, T.; Matsuki, Y.; Hazato, G. *Bull. Soc. Chim. Jpn.* **1963**, *36*, 108. Krishnaswamy, N. R.; Kumaz, Ch. S. R.; Prasanna, S. R. *J. Chem. Res., Synop.* **1991**, 166; *J. Chem. Res., Miniprint* **1991**, 1801.

(8) Leonardi, A.; Cazzulani, P.; Nardi, D. *Boll. Chim. Farm.* **1982**, 121.

(9) Binkley, J. S.; Frisch, M. J.; Raghavechari, K.; De Frees, D. J.; Schlegel, H. B.; Whitside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, 1983.

(10) Dunning, T. H.; Hay, J. P. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1976.

(11) Bak, B.; Christensen, D.; Dixon, W. B.; Hansen-Nygaard, L.; Rastrup-Andersen, J.; Scottländer, M. *J. Mol. Spectrosc.* **1962**, *9*, 124.

(12) Bak, B.; Christensen, D.; Hansen-Nygaard, L.; Rastrup-Andersen, J. *J. Mol. Spectrosc.* **1961**, *7*, 58.

(13) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(14) Fessenden, R. W. *J. Chim. Phys. Phisicochim. Biol.* **1964**, *61*, 1570.

(15) Guerra, M. *J. Am. Chem. Soc.* **1992**, *114*, 2077.