

## ***Ab Initio* studies on the rotational equilibria of 2-substituted furan and thiophene carbonyl derivatives**

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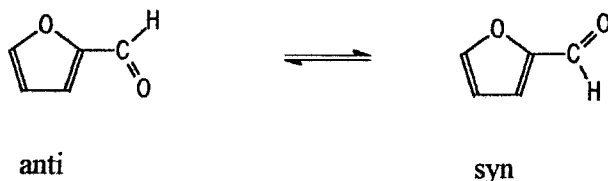
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**Summary.** The relative stabilities of syn- and anti-isomers of 2-substituted furan and thiophene carbonyl derivatives are investigated by the *ab initio* MO method. The energy differences between the rotamers are 1–3 kcal mol<sup>-1</sup> but the barriers to rotation are ca. 10 kcal mol<sup>-1</sup> so that free rotational mode is predicted to be a rather difficult process. Application of the self-consistent reaction field (SCRF) method to account for the solvent effect indicates that the isomer with a higher dipole moment (syn) is favored in solution. An electron withdrawing 2-substituent favors syn-isomers for furan carbonyls in contrast to thiophene carbonyls for which anti-isomers are favored. These trends are ascribable to a decrease in electrostatic repulsive and attractive interactions, respectively, in the syn forms of furan and thiophene carbonyls. Contribution of non-bonded repulsive interaction in the anti-isomer is important for the relative stability of the syn-isomer of furan carbonyl derivative. Solvent effects due to higher dielectric continuum are small on the absolute values of energy differences but can reverse the order of stability of the two isomers due to a greater stability acquired by an isomer (syn) with higher dipole moment in solution. The major factor determining stability, or instability, of syn-isomer is a repulsive electrostatic interaction between the two oxygen atoms for furan carbonyls and an attractive electrostatic interaction between the sulfur and oxygen atoms for thiophene carbonyls.

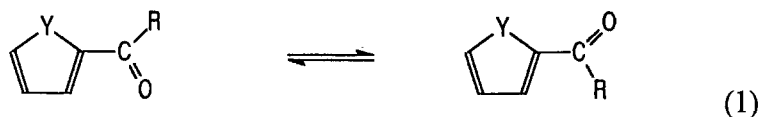
**Key words:** Rotational isomer – SCRF – Furan – Thiophene – Carbonyl derivatives

### **Introduction**

There has been numerous investigations of the rotational equilibrium between the two planar isomers, anti and syn, of 2-furanaldehyde [2].



The controversy surrounding the equilibrium stemmed from very small energy differences between the isomers, which made difficult for unambiguous assignments of the experimental, mostly spectral, results to separate isomers [3]. Moreover, the effects of solvent were large enough to reverse the order of stability between the two rotamers [3, 4]. The stability of an isomer depends strongly on electrostatic effects in the gas phase in contrast to much reduced electrostatic energies in a solvent with a high dielectric constant. The importance of solvent effects on the equilibrium involving internal rotation around carbon-carbon single bonds has prompted theoreticians to undertake theoretical investigations of the solvent effects on rotational equilibrium [5]. In order to account for solvent effects properly, both the specific or microscopic solvation interactions, such as hydrogen bonding and donor-acceptor complex formation between solute and solvent molecules, and the macroscopic effects due to bulk solvent continuum should be considered [6]. However, it has been reported that the quantum mechanical consideration of the macroscopic effect alone can provide a satisfactory prediction of the reversal in the most stable rotamers in solution. This quantum-mechanical model describes local orientational and electronic polarizations of the solvent in the electric field of the reactant molecules based on the classical Kirkwood-Onsager theory of electric polarization in liquids [7]. This method has been developed by several groups and is known as the self-consistent reaction field (SCRF) method [8]. In this work, to extend our understanding on the factors influencing the rotational equilibria and the barriers to the internal rotation around carbon-carbon single bonds between  $sp^2$ -type hybridized carbon atoms, we carried out *ab initio* studies on 2-substituted furan and thiophene carbonyl derivatives, Eq. (1).



Y	R
1 : O	a : CH <sub>3</sub>
2 : S	b : H
	c : Cl
	d : F

We adopted the SCRF method to account for the bulk solvent effects on the rotational equilibria and barriers.

## Calculations

All calculations were performed using Gaussian 92 [9]. In the gas phase, geometries of each isomers were fully optimized with 3-21G\* and 6-31 + G\*\* basis sets and electron correlation effects were considered at the second-order Moller-Plesset [10] (MP2) level of theory (MP2/6-31 + G\*\*//HF/6-31 + G\*\*). In order to account for the bulk solvent effects, the SCRF [8] computations were carried out by single point SCF calculation with dielectric constants of 32.6 (MeOH) and 78.5

(water). For the bulk solvent effects in water, MP2/6-31 + G\*\*//HF/6-31 + G\*\* level calculations were also performed. The barriers to internal rotations in the gas phase and in solution were determined at the HF/3-21G\*//HF/3-21G\* and HF/6-31 + G\*\*//HF/3-21G\* levels. The equilibrium state structures including the transition state (TS) were characterized by harmonic vibrational frequency calculations [11]. The most stable rotamer was determined based on the free energy differences  $\Delta G$ , which were calculated by considering temperature and entropy changes.

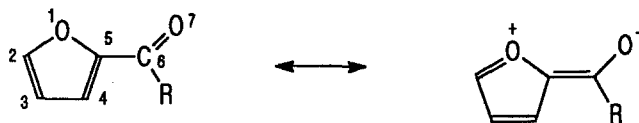
## Results and discussion

### Geometries

The optimized geometries at the HF/6-31 + G\*\* level are shown in Fig. 1. We note that the syn- and anti-isomers have the equilibrium geometries corresponding to the conventional structure, i.e., double bonds for C<sup>2</sup>-C<sup>3</sup> and C<sup>4</sup>-C<sup>5</sup>, but an essentially single bond for C<sup>5</sup>-C<sup>6</sup>, Eq. (1). The HF/6-31 + G\*\* bond lengths are in general in reasonable agreement with the experimental values shown in parenthesis [12].

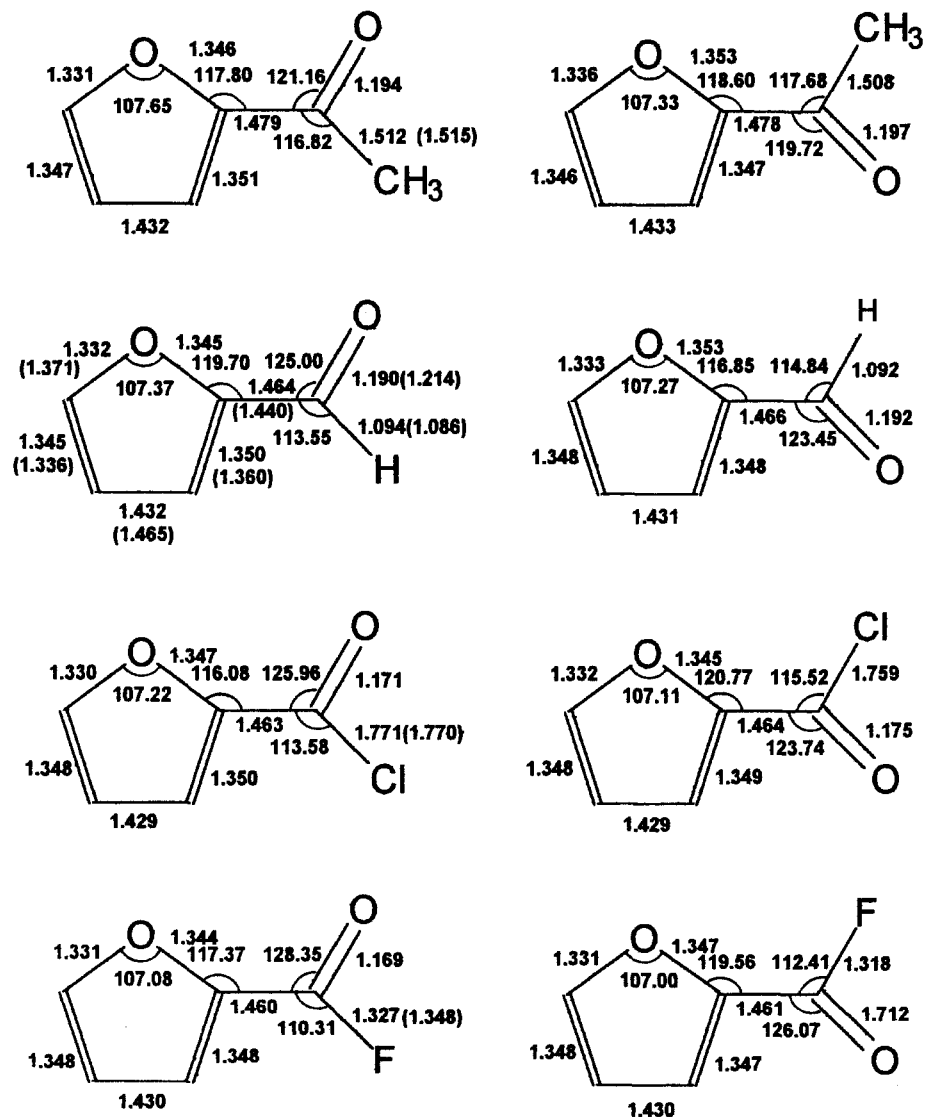
### Energetics

(i) *Furan carbonyl derivatives.* The energetics and dipole moments ( $\mu$ ) in the gas phase are summarized in Table 1. We note that the energy differences,  $\Delta E (= E_{\text{syn}} - E_{\text{anti}})$ , decrease as we raise the level of basis sets from 3-21G\* to 6-31 + G\*\*, however, incorporation of electron correlation at the MP2 level does not cause significant changes in energy differences. This is because the rotational equilibrium is a typical homodesmotic process [13] in which not only the number of electron pairs is held constant but also formal chemical bond types are conserved. In such simple processes, errors inherent in the calculations at the single-determinant level for the two isomeric species cancel largely and even simple levels of theory can provide an adequate description of the overall energetics [5b, 10b, 13]. The MP2/6-31 + G\*\*  $\Delta E$  values are correlated satisfactorily with the Taft's polar substituent constant  $\sigma^*$  [14] ( $\Delta E = a\sigma^* + b$ ) with a negative slope of  $a = -0.53$  and correlation coefficient of  $r = 0.95$ . This means that an electron acceptor substituent, R, is favorable for the stability of the syn form. For **1d** with substituent F, which is a strong inductive electron acceptor ( $\sigma_1 = 0.51$ ) [15],  $\Delta E$  and  $\Delta G$  are negative so that the syn form is more stable in the gas phase, in contrast to other compounds, **1a-c**, for which the anti-isomers are the more stable form. These results indicate that  $\Delta E$  and  $\Delta G$  are not related to the van der Waals radius of substituent R and hence steric repulsion due to the substituent, R, has very little effect on the relative stability of the rotamers as Arlinger et al. [2e] have reported earlier. The major factor determining the more stable isomer is thus electrostatic interaction between the two oxygen atoms. The positional charge densities in Table 2 reveal that both oxygen atoms are charged strongly negative so that in syn form the repulsive electrostatic interaction becomes maximized. As a result anti forms are favored for R = CH<sub>3</sub>, H and Cl. This is contrary to an attractive electrostatic interaction expected if resonance delocalization, scheme 1, occurs to any significant degree. The structures shown in Fig. 1 indicate that the C<sup>3</sup>-C<sup>4</sup> and C<sup>5</sup>-C<sup>6</sup> bonds



Scheme 1

have very little double-bond character supporting insignificant contribution of the resonance structure. For  $R = F$  (**1d**), there is a substantial electrostatic repulsion between  $O^1$  and  $F$  in the anti form (Table 2), albeit it should be somewhat weaker than that between two oxygen atoms in the syn form. However, in the anti form of **1d** in addition to the repulsive interaction between  $O^1$  and  $F$ , there is also a relatively strong repulsive non-bonded interaction between  $C^4$  and  $O^7$ ; I; in the



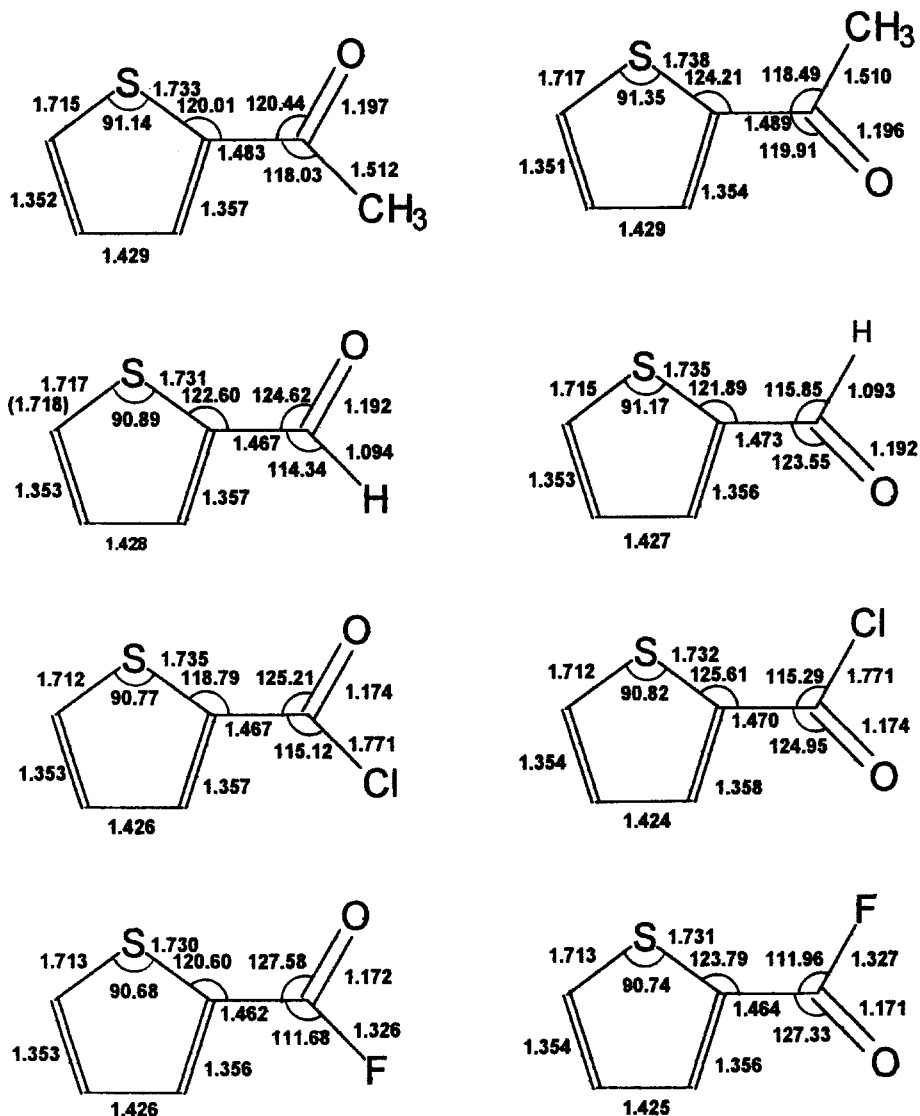


Fig. 1. Geometrical parameters optimized at the HF/6-31 + G\*\* level (experimental values are shown in parentheses)

anti form,  $-C^4 = C^5 - C^6 = O^7$  frame constitutes a *cis*-1,3-butadiene-like structure, whereas it forms a *trans*-1,3-butadiene-like structure in the syn form. A simple frontier MO (FMO) theory predicts that [16] the HOMO level is raised and the size of the  $\pi$ -lobe at  $C^1$  is enlarged when there is a  $\pi$ -donor like F at  $C^2$  of *cis*-butadiene, II. Our results indicated that the AO coefficients of  $C^4$  and  $O^7$  in the HOMO are +0.35 and -0.35 and +0.34 and -0.33 for **1d** ( $R = F$ ) and **1b** ( $R = H$ ), respectively. Since in the HOMO level of butadiene, the AO coefficients at terminal carbons,  $C^1$  and  $C^4$ , have opposite sign, the  $\pi$ -donor at  $C^2$  increases the repulsive non-bonded interaction between the two vicinal carbons [17] of the

**Table 1.** Electronic energies ( $E$ , hartrees), relative energies ( $\Delta E = E_{\text{syn}} - E_{\text{anti}}$ , kcal mol<sup>-1</sup>) and dipole moment ( $\mu$ , Debye) for furan derivatives

R	$E$				$\Delta E$ (syn-anti)				$\mu$
	3-21G*	6-31 + G**	MP2		3-21G*	6-31 + G**	MP2		
CH <sub>3</sub>	Syn	-378.26868	-380.42066	-381.57966		1.90	1.81		4.35
	Anti	-378.27501	-380.42370	-381.58254	3.97	(1.82) <sup>a</sup>	(1.73)		3.38
H	Syn	-339.43744	-341.37266	-342.38556		0.91	0.89		4.52
	Anti	-339.44227	-341.37411	-342.38698	3.03	(1.02)	(1.00)		3.62
Cl	Syn	-796.26683	-800.28060	-801.42537		-0.13	0.13		4.65
	Anti	-796.27003	-800.28039	-801.42558	2.00	(-0.01)	(0.25)		4.35
F	Syn	-437.78681	-440.25234	-441.43114		-0.16	-0.29		4.77
	Anti	-437.78652	-440.25208	-441.43067	-0.18	(-0.10)	(-0.23)		4.50

<sup>a</sup> Values in parentheses are Gibbs free energy differences

**Table 2.** Group charge densities ( $q$ )<sup>a</sup> for furan derivatives in electron unit

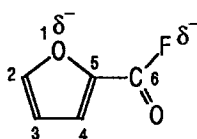
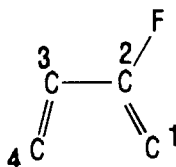
R		O <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>6</sup>	O <sup>7</sup>	R
CH <sub>3</sub>	Syn	-0.515	-0.425	-0.113	-0.014	0.202	0.625	-0.614	0.004
	Anti	-0.543	0.411	-0.102	0.030	0.191	0.635	-0.633	0.011
H	Syn	-0.518	0.436	-0.114	0.007	0.177	0.465	-0.604	0.151
	Anti	-0.537	0.420	-0.103	0.033	0.170	0.473	-0.615	0.160
Cl	Syn	-0.514	0.448	-0.110	0.053	0.158	0.621	-0.572	-0.082
	Anti	-0.519	0.438	-0.105	0.061	0.160	0.614	-0.595	-0.056
F	Syn	-0.513	0.443	-0.111	0.045	0.138	1.025	-0.613	-0.415
	Anti	-0.518	0.438	-0.107	0.056	0.133	1.032	-0.632	-0.403

<sup>a</sup> Group charge densities including the attached hydrogens by NBO\* calculations

\* (a) Glendenning ED, Reed AE, Carpenter E, Weinhold F NBO Version 3.1 in Gaussian 92

(b) Reed AE, Curtiss LA, Weinhold F (1988) Chem Rev 88:899

(c) Saunders WH, Saunders Jr WH, Van Verth JE (1995) J Org Chem 60:3452

**I****II**

*cis*-1,3-butadiene; as a result the anti-isomer becomes more destabilized relative to the syn-isomer. This type of interaction can also be considered for R = Cl, but Cl is a weaker  $\pi$ -donor ( $\sigma_R = -0.35$ ) [15] than F ( $\sigma_R = -0.59$ ) [15] in addition to a weaker acceptor ( $\sigma_I = 0.46$  and  $0.50$  for Cl and F, respectively) [15] with a lower negative charge on the Cl atom. Thus, for the anti form of R = Cl (**1c**) both repulsive electrostatic interactions, O<sup>1</sup>...Cl and C<sup>4</sup>...O<sup>7</sup>, are much weaker than those for R = F (**1d**); they are also weaker than the repulsive interaction between two oxygen atoms in the syn-isomer so that the anti form becomes more stable.

We have considered the bulk solvent effects by the SCRF calculations [8] with dielectric constants of  $\epsilon = 32.5$  and  $78.2$ . The results of  $\Delta E$  (= syn-anti) in Table 3 indicate that the syn-isomers become more favored in the higher dielectric media compared to the anti-isomers [5b]. Again the effects of electron correlation on the energy differences (MP2/6-31 + G\*\*) are small [18]. Correlation effects are seen to lead to a very small increase in the  $\Delta E$  values in favor of the anti form. There are

large decrease in the  $\Delta E$  values for R = CH<sub>3</sub>, H and Cl (**1a–c**) when the basis sets are improved to 6–31 + G\*\* from 3–21 G\*. In contrast to these relatively large changes in  $\Delta E$  for the three species, **1a–c**, there is practically no effects of basis sets on  $\Delta E$  for R = F. The reversal of relative stability of isomers in the higher dielectric media occurs only for furanaldehyde (R = H, **1b**) [3, 5b].

The energy difference,  $\Delta E$  ( $= E_{\text{syn}} - E_{\text{anti}}$ ), in the higher dielectric medium seems to depend on two factors:  $\Delta E$  and  $\Delta\mu$  ( $= \mu_{\text{syn}} - \mu_{\text{anti}}$ ), in the gas phase. In a higher dielectric medium, an isomer with a higher dipole moment is favored due to a stronger solute–solvent interaction [5b]; as a result the syn form can be more stable than the anti-isomer in solution when gas phase  $\Delta E$  is relatively small and  $\Delta\mu$  is large. When the  $\Delta E$  value is relatively large ( $\Delta E \gg 0$ ) in the gas phase, it is difficult to reverse the order ( $\Delta E < 0$ ) in the higher dielectric medium even if  $\Delta\mu$  is large as for R = CH<sub>3</sub>. If  $\Delta\mu$  is large enough, the reversal of the order can occur even though  $\Delta E$  has a moderate value, as for R = H. If  $\Delta\mu$  is small, despite the small  $\Delta E$  the order of relative stability will not reverse as for R = Cl. These energy differences between the two rotamers,  $\Delta E$ , are very small so that in the gas phase as well as in solution the difference in the concentration of the two isomers in equilibrium will not differ significantly. Interconversion between the two isomers takes place by rotation around the C<sup>5</sup>–C<sup>6</sup> bond. We have determined the rotational barriers,  $\Delta E^\ddagger$  ( $= E_{\text{TS}} - E_{\text{syn}}$ ), as shown in Table 4.

The transition state corresponds to a structure formed by 90° rotation around C<sup>5</sup>–C<sup>6</sup> from the planar syn-isomer (Fig. 1). Reference to this table reveals that

**Table 3.** Calculated bond lengths (in Å) for furan derivatives

R		$d(\text{O}^1\text{--C}^2)$	$d(\text{C}^2\text{--C}^3)$	$d(\text{C}^3\text{--C}^4)$	$d(\text{C}^4\text{--C}^5)$	$d(\text{O}^1\text{--C}^5)$	$d(\text{C}^5\text{--O}^6)$	$d(\text{C}^6\text{--O}^7)$	$d(\text{C}^6\text{--R})$
CH <sub>3</sub>	Syn	1.331	1.347	1.432	1.351	1.346	1.479	1.194	1.512
	Anti	1.336	1.346	1.433	1.347	1.353	1.478	1.197	1.508
H	Syn	1.332	1.345	1.432	1.350	1.345	1.464	1.190	1.094
	Anti	1.333	1.348	1.431	1.348	1.353	1.466	1.192	1.092
Cl	Syn	1.330	1.348	1.429	1.350	1.347	1.463	1.171	1.771
	Anti	1.332	1.348	1.429	1.349	1.345	1.464	1.175	1.759
F	Syn	1.331	1.348	1.430	1.348	1.344	1.460	1.169	1.327
	Anti	1.331	1.348	1.430	1.347	1.347	1.461	1.172	1.318

**Table 4.** Calculated rotational barrier ( $\Delta E^\ddagger$ , kcal mol<sup>-1</sup>)<sup>a</sup> in gas and aqueous phase for furan derivatives

R	$\epsilon$	
	1.00	78.54
CH <sub>3</sub>	7.33	8.46
H	9.23	11.20
Cl	9.30	10.67
F	9.32	10.98

<sup>a</sup>  $\Delta E^\ddagger = E(\text{TS}) - E(\text{syn})$



**Table 5.** Electronic energies ( $E$ , hartrees), relative energies ( $\Delta E = E_{\text{syn}} - E_{\text{anti}}$ , kcal mol<sup>-1</sup>) and dipole moment ( $\mu$ , Debye) for thiophene derivatives

$\epsilon$	Level	$E$										$\Delta E$ (syn-anti)					
		CH <sub>3</sub>	H	Cl	F	CH <sub>3</sub>	H	Cl	F	CH <sub>3</sub>	H	Cl	F				
1.0	HF/3-21G*	Syn	-699.51391	-660.68325	-1117.51229	-759.03261	-0.70	-1.27	-0.58	0.05							
		Anti	-699.51279	-660.68123	-1117.51137	-759.03269											
	HF/6-31 + G**	Syn	-703.08442 (4.02) <sup>a</sup>	-664.03685 (4.34)	-1122.94418 (4.53)	-762.91614 (4.65)	-0.86	-1.42	-0.97	-0.38							
		Anti	-703.08305 (3.00)	-664.03458 (3.42)	-1122.94264 (4.23)	-762.91554 (4.40)	(-0.61) <sup>b</sup>	(-1.33)	(-0.84)	(-0.29)							
	MP2/6-31 + G**	Syn	-704.19624	-665.00213	-1124.04147	-764.04724	-1.34	-1.44	-0.73	-0.14							
		Anti	-704.19442	-664.99984	-1124.04030	-764.04701	(-1.09)	(-1.35)	(-0.60)	(-0.05)							
32.63	HF/3-21G*	Syn	-699.51688	-660.68676	-1117.51618	-759.03746	-1.57	-2.08	-0.72	-0.18							
		Anti	-699.51437	-660.68345	-1117.51504	-759.03717											
	HF/6-31 + G**	Syn	-703.08772	-664.04104	-1122.94810	-762.92068	-1.86	-2.45	-1.24	-0.57							
		Anti	-703.08475	-664.03713	-1122.94612	-762.91976											
	HF/3-21G*	Syn	-699.51698	-660.68688	-1117.51632	-759.03261	-1.59	-2.10	-0.72	-0.19							
		Anti	-699.51443	-660.68353	-1117.51517	-759.03733											
78.54	HF/6-31 + G**	Syn	-703.08783	-664.04119	-1122.94824	-762.92084	-1.89	-2.49	-1.25	-0.58							
		Anti	-703.08481	-664.03722	-1122.94625	-762.91991											
MP2/6-31 + G**	Syn	-704.19877	-665.00555	-1124.04502	-764.05125	-1.52	-1.86	-0.87	-0.07								
	Anti	-704.19635	-665.00258	-1124.04363	-764.05114												

<sup>a</sup> Values in parentheses are dipole moments<sup>b</sup> Values in parentheses are Gibbs free energy differences

barriers to rotation are in good agreement with the experimental values of ca. 10 kcal mol<sup>-1</sup> [19] which is substantially greater than the barrier to free rotation within a saturated carbon compound like ethane (1–3 kcal mol<sup>-1</sup>) [20]. Thus, the interconversion between the two isomers will be a rather difficult process, even though the energy differences,  $\Delta E$ , between the two isomers are small. The dipole moments,  $\mu$ , were found to decrease as the syn-isomers are activated to the rotational TSs [3] so that the barriers tend to increase by a small amount in solution. Thus, the interconversion between the isomers is expected to become more difficult in solution than in the gas phase.

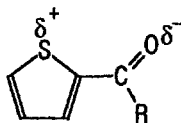
(ii) *Thiophene carbonyl derivatives.* The energy and Gibbs free energy differences,  $\Delta E (= E_{\text{syn}} - E_{\text{anti}})$  and  $\Delta G (= G_{\text{syn}} - G_{\text{anti}})$ , for thiophene carbonyl derivatives, **2a–d**, in gas phase and in solution are summarized in Table 5 together with the computed dipole moments,  $\mu$ .

The  $\Delta E$  and  $\Delta G$  values are all negative as experimentally found (**2a**), and the magnitude is seen to increase as we improve basis sets from 3–21 G\* to 6–31 + G\* but the effect of electron correlation at the MP2 level is again small [13]. This trend of more negative  $\Delta E$  at the 6–31 + G\*\* level of theory is similar to that found for the furan carbonyl derivatives for which the positive  $\Delta E$  values were found to decrease indicating that higher level calculation is in favor of syn stability for both carbonyl derivatives. The correlation ( $r = 0.92$ ) of  $\Delta E$  with Taft's  $\sigma^*$  is again fair but the slope is now positive ( $a = 0.34$ ) in contrast to the negative slope found for a similar correlation in furan carbonyl derivatives. In furan derivatives, the syn form is favored, i.e.,  $\Delta E$  and  $\Delta G$  decrease, by an electron withdrawing substituent,  $\sigma^* > 0$ , since electron withdrawal reduces the repulsive electrostatic interaction between the two oxygen atoms in the syn form. However, in the thiophene carbonyl derivatives, the S atom is positively charged (Table 6) so that there is an attractive electrostatic interaction between the S and O atoms in the syn form [2a]. This is why we obtained the negative  $\Delta E$  and  $\Delta G$  values in all cases, and also this is why we obtained a negative slope when  $\Delta E$  is correlated with  $\sigma^*$ ; in this case electron withdrawal by R reduces the attractive, stabilizing, interaction in the syn-isomer by decreasing the negative charge on the carbonyl oxygen atom, **III**. In the higher dielectric media,  $\Delta E$  is seen to become more negative indicating that the syn-isomer, which has a higher dipole moment than the corresponding anti form,

Table 6. Group charge densities ( $q$ )<sup>a</sup> for thiophene derivatives in electron unit

R		S <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>6</sup>	O <sup>7</sup>	R
CH <sub>3</sub>	Syn	0.499	-0.146	-0.052	0.039	-0.371	0.656	-0.633	0.006
	Anti	0.445	-0.146	-0.038	0.086	-0.378	0.662	-0.637	0.005
H	Syn	0.496	-0.137	-0.050	0.053	-0.393	0.498	-0.618	0.152
	Anti	0.459	-0.143	-0.037	0.087	-0.398	0.498	-0.618	0.153
Cl	Syn	0.512	-0.126	-0.050	0.101	-0.412	0.648	-0.593	-0.079
	Anti	0.503	-0.130	-0.044	0.113	-0.419	0.650	-0.596	-0.076
F	Syn	0.511	-0.129	-0.049	0.096	-0.437	1.053	-0.630	-0.414
	Anti	0.501	-0.131	-0.046	0.109	-0.441	1.057	-0.633	-0.415

<sup>a</sup> Group charge densities including the attached hydrogens by NBO calculations. See footnotes for Table 2



### III

**Table 7.** Calculated rotational barrier ( $\Delta E^\ddagger$ , kcal mol<sup>-1</sup>)<sup>a</sup> in gas and aqueous phase

		X = S	
R	$\epsilon$		
CH <sub>3</sub>		7.76	8.52
H		9.50	10.90
Cl		8.59	9.67
F		9.39	10.31

<sup>a</sup>  $\Delta E^\ddagger = E(\text{TS}) - E(\text{syn})$

becomes further stabilized by solvent [5b]. Albeit, the syn-isomer is favored compared to the anti-isomer, the energy difference between the two is again very small, as we found for the furan carbonyl derivatives. The barriers to internal rotation around the C<sup>5</sup>-C<sup>6</sup> bond are shown in Table 7.

The barrier heights are ca. 7–9 kcal mol<sup>-1</sup> which are quite similar to those for the furan carbonyl derivatives. We therefore think that the free rotation is not likely and internal rotations within the thiophene carbonyls are also restricted even though the energy differences between the two rotamers are very small. Dipole moments of the TSs become lower somewhat than the syn-isomer [3] so that the rotational barriers are expected to rise slightly and hence interconversion between isomers should become somewhat more difficult in solution. This trend is also similar to that found for the furan carbonyls.

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