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Equilibria of simple thioenol/thiocarbonyl pairs. Comparison with the oxygen analogs and with the parent selenium and tellurium systems. A theoretical study † [1]

Stepan Sklenak,[a,b] **Yitzhak Apeloig** *[a,b] **and Zvi Rappoport** *[b,c]

[a] *Department of Chemistry, Technion - Israel Institute of Technology, Haifa 32000, Israel*
[b] *The Lise Meitner-Minerva Center for Computational Quantum Chemistry*
[c] *Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel*

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Thiocarbonyl–thioenol and carbonyl–enol equilibria ($CH_3C(=X)R \rightleftharpoons H_2C{=}C(XH)R$, X = S, O) were calculated by high level *ab initio* and density functional quantum mechanical methods for R = H, Me, Et, *i*-Pr, *i*-Bu, *t*-Bu, SiH_3, CN, Ph, CH_2Y (Y = Ph, CN, CF_3, $CH{=}CH_2$), cyclic $(CH_2)_nC{=}X$, $n = 4$–6, $(PhCH_2)_2C{=}S$, $PhCH_2C(=S)CHPh_2$ and *i*-$Bu_2C{=}S$. A detailed study when R = H, Me shows that B3LYP/6-31G(d,p) overestimates ΔH(thiocarbonyl–thioenol) by *ca.* 2 kcal mol^{-1}. Isodesmic equations are used to evaluate separately the effect of R on each of the four species. A good agreement exists between the theoretical and the available experimental values. The ΔH(thiocarbonyl–thioenol) values of *ca.* −5.5 to 8 kcal mol^{-1} are much smaller than the ΔH(carbonyl–enol) values of *ca.* 5–17 kcal mol^{-1}. A correlation exists between the ΔH terms of the two series. For R = H, Me the $\Delta H(CH_3C(=X)R - CH_2{=}C(XH)R)$ values at the B3LYP/6-31G(d,p) level decrease as X is changed to a heavier chalcogen; *e.g.*, when R = Me, $\Delta H = 14.9$ (X = O), 6.1 (X = S), 1.7 (X = Se), −0.2 (est., X = Te).

Introduction

The carbonyl $\rightleftharpoons$ enol equilibrium is one of the oldest and most studied topics in physical organic chemistry and is important to synthesis and to many biological processes.[2] For carbonyl compounds which do not carry strong electron-withdrawing groups or conjugating (*e.g.*, aryl) substituents, the carbonyl–enol equilibrium constants (K_{Enol}) are generally very low. Many K_{Enol} values (frequently given as $pK_{Enol} = -\log K_{Enol}$) have been accurately determined and recently summarized.[3] For example, for acetaldehyde and acetone pK_{Enol} (H_2O) = 6.23[4] and 8.33,[4,5] respectively. For enols with β-electron-withdrawing groups such as C=O, K_{Enol} values are much lower (*e.g.* $pK_{Enol} = 0.83$ for acetylacetone)[6] and the enol is frequently observable.[3] Many enols substituted with bulky aryl groups are also stable, observable and display low pK_{Enol} values.[7] Many carbonyl–enol energy differences were calculated by a variety of quantum-mechanical methods.[8]

The situation differs for the sulfur analogs. Due to the lower stability of the thiocarbonyl (C=S) compared with the C=O group,[9] thiocarbonyl derivatives having α-hydrogens have greater tendency to tautomerize.[9f] This influences the thiocarbonyl $\rightleftharpoons$ enethiol equilibria. From bond energies (BE, in kcal mol^{-1}) for H–C–C=O (C=O, 177; C–H, 97; C–C, 84; total BE 358), C=C–O–H (C=C 149; O–H, 110; C–O, 88; total BE 347), H–C–C=S (C=S, 115; C–H, 97; C–C, 84; total BE 296) and C=C–S–H (C=C, 149; S–H, 82; C–S, 41; total BE 292),[10] the carbonyl and the thiocarbonyl derivatives are 11 and 4 kcal mol^{-1} more stable than the enol and the enethiol, respectively. We conclude that $pK_{Thioenol}$ values should be lower than the corresponding pK_{Enol} values.

This conclusion is reflected by many qualitative observations. UV[11a] or X-ray[11b] irradiation of H_2S and alkynes generate several simple aliphatic enethiols, which do not isomerize to the thiocarbonyl analogs. Metal cleavage of vinyl thioethers in liquid NH_3 gives pure stable aliphatic thioenols.[11c] Cyclic thioenols obtained by this procedure tend to isomerize to the thiocarbonyl derivatives.[11c] Trimethylsilylated thioethers or silylvinyl sulfides react with MeOH to give the pure thioenols.[11d] Pyrolysis of cyclic spirotrithianes gave *c*-$(CH_2)_nC{=}S$–*c*-$[(CH_2)_{n-1}$-$CH{=}C]$–SH ($n = 4,6$) mixtures.[11e] However, the high reaction temperature, the low yield, the incomplete pyrolyses and the far from equilibrium reaction conditions make the observed thioenol : thioketone ratios (*e.g.*, $K_{Thioenol} = 34 : > 13$ ($n = 4$), 12 : >34 ($n = 6$)) non-reliable measures of the equilibrium ratios.

Thioaldehydes are less stable towards isomerization than thioketones. However, with bulky substituents both tautomers can be stable. For example, both $(t\text{-}Bu)_2CHCH{=}S$ and $(t\text{-}Bu)_2C{=}CHSH$ are formed by reacting zirconocene and $(t\text{-}Bu)_2C{=}C{=}O$. The thioenol does not isomerize with HCl and only heating to 150 °C produces traces of the thioaldehyde.[12a] Another enolizable thioaldehyde was recently prepared.[12b] A series of aliphatic and alicyclic α- and β-alkyl-substituted thiocarbonyl/thioenol pairs had been prepared.[13] The thioenol was observed when an α-H which does not belong to a Me group is present.[13a] The thiocarbonyl : thioenol ratios obtained by pyrolysis of the *gem*-dithiol[13b] are not necessarily the equilibrium values but they provide several interesting comparisons. Thus, for R = Me and *t*-Bu the thioketones MeC(=S)R are the exclusive products but for R = Me, *i*-Pr, the thioenol $Me_2C{=}C(SH)R$ is 60 and 80% of the product, respectively.[13b] For R′ = Me, *i*-Pr, R′CH=C(SH)Me is 35 and 65% of the product, respectively,[13b] and for cyclohexenyl and cyclopentenyl thiols only the thioenol was formed, in contrast with an earlier report.[14a] Other cyclic thioenols are also known.[9g,14b]

Conjugation increases the percentage of the thioenol. Attempted generation of 1,1,2-triphenylthioacetone gave exclusively $Ph_2C{=}C(SH)CH_2Ph$.[15a] Likewise, phenyl cyclo-

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† Tables S1–S7 are available as supplementary data. Tables S1–S6 include calculated absolute energies and zero point energies of all species calculated, and the activation barrier for the **3a** $\rightleftharpoons$ **4a** reaction. Table S7 includes the cartesian coordinates of all calculated species. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b004289g/

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propyl thioketone is completely enolized[13e] and $(PhCH_2)_2C{=}O$ with Lawsson's reagent gives only the thioenol $PhCH{=}C(SH)CH_2Ph$.[15b] β-Fluorines increase the thioenol stability: pentafluorocyclobutene-1-thiol is known,[16] whereas alkyl-substituted cyclobutene-1-thiols are unstable.[13g]

These results indicate that many enethiols are observable species, *i.e.*, their $K_{Thioenol}$ values should much exceed the K_{Enol} values for the oxygen analogs. However, *quantitative* $K_{Thioenol}$ values for simple thiocarbonyl/enethiol pairs are very limited. Mayer and co-workers[17] found thioenol : thioketone ratios of 69–66 : 31–34 for i-$Pr_2C{=}S$ by iodine titration, potentiometry and polarography in MeOH–NaOAc (*i.e.*, $K_{Thioenol} \sim 2$) and a 53 : 47 ratio by NMR,[17a] and ≥99.6% thioenol was found for $PhCH_2C({=}S)CHPh_2$ and $PhC({=}S)CH(CN)Ph$.[17a,c]

The equilibria for two **2/1** pairs (eqn. (1)) were determined

$$\begin{array}{ccc} [Me_2CH(CH_2)_n]_2C{=}S & \rightleftharpoons & Me_2(CH)_nC(H)_m{=}C(SH){-}(CH_2)_nCHMe_2 \\ \mathbf{1a} & m, n = 0 & \mathbf{2a} \\ \mathbf{1b} & m, n = 1 & \mathbf{2b} \end{array} \qquad (1)$$

by ^1H NMR in CCl_4 at 40 °C to be: [**2a**] : [**1a**] = 58 ± 3 : 42 ± 3 ($K_{Thioenol} = 1.38$) and [**2b**] : [**1b**] = 53 ± 3 : 47 ± 3 ($K_{Thioenol} = 1.13$).

It was recently shown[18] that $Ph_2C{=}C(SH)Ar$ (Ar = Ph, p-anisyl) are completely enolic ($K_{Thioenol} \geq 100$) in hexane and do not tautomerize to the thioketone under basic or acidic conditions. It was estimated that the corresponding $K_{Thioenol}$ values as well as those for $PhCH{=}C(SH)CH_2Ph$ are $>10^6$ times higher than the K_{Enol} values for the corresponding oxygen analogs. A similar value was estimated for i-$Pr_2C{=}S$ and i-$Pr_2C{=}O$ from the data above.[18] Kresge and co-workers[19] have recently measured for methyl fluorene-9-carbothioxylate $pK_{Thioenol}(H_2O) = 5.8$,[19a] while the estimated corresponding pK_{Enol} is 9.5. For 2,4,6-trimethylthioacetophenone,[19b] $pK_{Thioenol}(H_2O)$ is 0.94, *ca.* 6 pK units higher than for the oxygen analog.

Thione–thiol equilibria of systems carrying β-carbonyl substituents also show higher $K_{Thioenol}$ than K_{Enol}; *e.g.*, for ethyl thiobenzoylacetate in EtOH the thioenol is 87% at equilibrium[20] compared with 29% of the enol for ethyl benzoylacetate. Enolization *vs.* thioenolization of thioesters and thioxoketones has also been studied, but we give only a few references.[9f,g,21]

We know of only three studies in which $K_{Thioenol}$ values for simple systems were calculated by quantum mechanical methods. Early STO-3G calculations for butane-2-thione and 2-methylbutane-3-thione (**3c** and **3d**), indicated that the thioketone is *ca.* 1 kcal mol^{-1} more stable than the thioenol.[22] A recent study reported high level *ab initio* CBS-4 (complete basis set, enolization enthalpies of nine thiocarbonyl/thioenol pairs and the analogous carbonyl/enol pairs.[23] The ΔH_{298} values are 8–11.3 kcal mol^{-1} lower for the thiocarbonyl than for the carbonyl derivatives. These values are compared below with our data. Ethenethiol was calculated recently by G1 and G2 methods to be 2.6 kcal mol^{-1} less stable than thioacetaldehyde.[24]

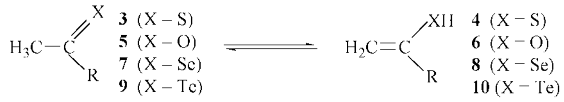
Selenoaldehydes and selenoketones (selones)[25a] are mostly unstable, except for highly hindered and non-enolizable ones.[25b] We know of no experimental or theoretical study on their equilibria with the selenoenols. Compounds with a C=Te bond are mostly unstable[25a,c] and likewise, no data are available on their equilibria with the telluroenol tautomer.

Consequently, although some fragmentary data are available on the thiocarbonyl–thioenol equilibria (and none for the Se and Te analogs), a systematic quantitative study is still missing. We report below systematic and highly reliable theoretical calculations on the energy differences of many thiocarbonyl–thioenol systems and compare them with those of the corresponding oxygen analogs, and with those of the parent selenium and tellurium analogs.

Results and discussion

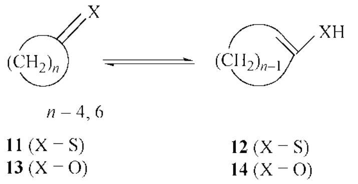
Systems studied

Quantum mechanical calculations using a variety of methods were carried out for thioacetaldehyde (**3a**), methyl thioketones **3b**–**k**, their isomeric thioenols **4a**–**k**, the corresponding oxygen analogs (aldehydes or ketones **5a**–**k** and enols **6a**–**k**), selenoaldehyde (**7a**) and selenoacetone (**7b**), their selenoenols **8a** and **8b**, as well as for their telluro-analogs **9a**, **9b** and **10a**, **10b** (eqn. (2)). Other systems, for which experimental data are available and which are mentioned in the Introduction above, were also calculated. These include the bis(isopropylthio) and bis(isobutylthio) systems **1a**,**1b** and **2a**,**2b**[13c] (eqn. (1)), the cyclic thio systems **11**/**12** and their oxygen analogs **13**/**14** (eqn. (3)),[11e] and the phenyl-substituted thio systems **15**/**16**, **17**/**18a**,**b** (eqns. (4) and (5), respectively).[15] In addition, the thioaldehyde **19** and aldehyde **21** and their conjugated enol isomers **20** and **22** (eqn. (6)), and the trifluoromethyl thioaldehyde (**23**) and aldehyde (**25**) and their thioenol (**24**) and enol (**26**) isomers (eqn. (7)), were calculated.



(2)

R	X = S	O	Se	Te	X = S	O	Se	Te
H	**3a**	**5a**	**7a**	**9a**	**4a**	**6a**	**8a**	**10a**
CH_3	**3b**	**5b**	**7b**	**9b**	**4b**	**6b**	**8b**	**10b**
CH_3CH_2	**3c**	**5c**			**4c**	**6c**		
$(CH_3)_2CH$	**3d**	**5d**			**4d**	**6d**		
$(CH_3)_2CHCH_2$	**3e**	**5e**			**4e**	**6e**		
$(CH_3)_3C$	**3f**	**5f**			**4f**	**6f**		
SiH_3	**3g**	**5g**			**4g**	**6g**		
CN	**3g**	**5h**			**4h**	**6h**		
CH_2CN	**3i**	**5i**			**4i**	**6i**		
Ph	**3j**	**5j**			**4j**	**6j**		
CH_2Ph	**3k**	**5k**			**4k**	**6k**		



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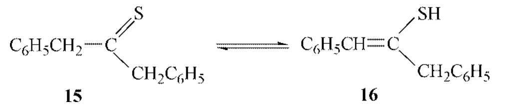

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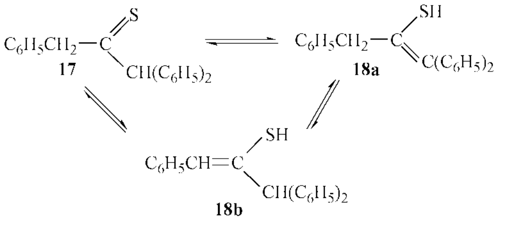

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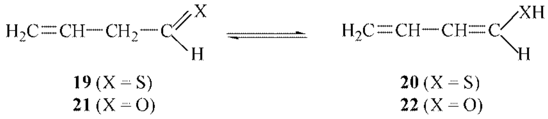

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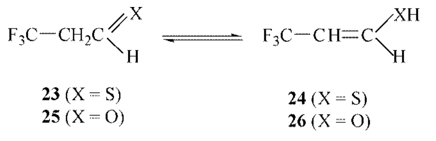


(7)

Theoretical methods

Quantum mechanical *ab initio* molecular orbital calculations were performed using both the *ab initio* Hartree–Fock (HF)[26a,b] and the MP2(full)[26c] methods as well as with hybrid Density Functional Theory (DFT) methods[27b] with the B3LYP[27b–d] functional. All calculations used the GAUSSIAN 94 series of programs.[28] The standard 6-31G(d,p)[29] (or 6-31G**) basis set was employed for X = O, S and Se. For Te, for which this basis set is not available, we used the Effective Core Potentials (ECP) of Wadt and Hay,[30] together with a valence basis set of double-zeta quality[30] augmented by a set of 5 d-type polarization functions (DZP) with exponents of 0.65 and 0.315 for S and Se, respectively (the same exponents as in 6-31G(d,p)), and 0.3 for Te.[31]

The geometries of all species were fully optimized either using all three methods (for most of the compounds with X = S), but for some of the larger systems, only at B3LYP/6-311G(d,p). All significant conformers (*i.e.*, with either *syn*, *gauche* or *anti* orientations of the C=C–X–H moiety) were calculated. Vibrational frequencies were computed for all species (at the levels in which their geometries were optimized), in order to determine whether they are minima, transition structures, or higher order saddle points on the potential energy surface (PES) and for evaluating zero-point vibrational energies (ZPEs). The enthalpies of the species at 0 K (Δ*H*) were calculated as the sum of the absolute energies and the ZPE. The calculated absolute energies and the zero point energies of all species are listed in Tables S1–S6 and the cartesian coordinates of all calculated species are given in Table S7 of the Electronic Supplementary Information.

In the discussion below the designations HF, MP2, B3LYP, *etc.* stand for single point HF/6-31G(d,p), MP2/6-31G(d,p) and B3LYP/6-31G(d,p) calculations, respectively, performed at the optimized geometries obtained at the same level of theory (*e.g.*, MP2 denotes a MP2(full)/(6-31G(d,p)//MP2(full)/(6-31G(d,p) calculations). The basis set is indicated generally only when it is different from 6-31G(d,p).

Thioketone–thioenol equilibria

To be able to make meaningful comparisons between the variety of systems studied, a uniform level of theory should be used. To determine which are the most suitable methods, combining a balance between reliability and computational time we have studied in detail the parent systems **3a**/**4a** and **5a**/**6a**.

(1) The parent sulfur (3a/4a) and oxygen (5a/6a) systems. For these systems, in addition to the HF, B3LYP and the MP2 methods, the more elaborate QCISD (full),[32] QCISD(T) (full)[32] and CCSD(T) (full)[33] methods (full ≡ treating all electrons) were also used. Also, in addition to the 6-31G (d,p) basis set, we have also used the larger 6-311G(2d, 2p)[34] and 6-311G(3d, 3p)[34] basis sets.

The results (Table 1) show that Δ*H*(**3a**/**4a**) ranges between 2.2–5.7 kcal mol^{-1}, while Δ*H*(**5a**/**6a**) ranges between 11.2–14.8 kcal mol^{-1}. Δ*H* of the oxygen and the sulfur systems show similar behavior as a function of the computational method. For methods which include correlation energy (either *ab initio* or DFT), it appears that the most important factor in determining Δ*H* is the size of the basis set. Thus with the 6-31G(d,p) basis set, the Δ*H* values are by *ca.* 2.0–2.5 kcal mol^{-1} higher (*i.e.*, overestimating the stability of the carbonyl or thiocarbonyl) than with the larger basis sets. The most reliable theoretical results are probably those obtained at CCSD(T)/6-311G (3d,3p) (level I), where Δ*H*(**3a**/**4a**) is 2.9 kcal mol^{-1} and Δ*H* (**5a**/**6a**) is 11.5 kcal mol^{-1}. Similar values of 2.2 (2.6) and 11.6 (11.3) kcal mol^{-1} were obtained using the CBS-4 (G1) methods.[23,24] Unfortunately, no experimental data exists for **3a**/**4a**. For **5a**/**6a** a gas-phase Δ*H* value of 9.1 kcal mol^{-1} was calculated from data on enol ether hydrolysis in water.[35] The difference of 2.4–5.1 kcal mol^{-1} between this value and the best theoretical values (11.5–14.2 kcal mol^{-1}), may be due at least in part to the approximations used to convert the hydrolysis data to heats of formation.[35] Based on previous experience it is unlikely that at the high theoretical level used errors due to theoretical deficiencies will exceed 1–2 kcal mol^{-1}. Δ*H*(**5a**/**6a**) even increases by 0.3 kcal mol^{-1} when corrected to 298 K. Zero-point energies favor the thioenols relative to the thiocarbonyls (*e.g.*, by 1.5 kcal mol^{-1} for **4a**/**3a**). In contrast, ZPEs disfavor the enols relative to the carbonyls (*e.g.* by 0.8 kcal mol^{-1} for **6a**/**5a**).

Table 1 Enthalpy differences (Δ*H*/kcal mol^{-1}) between $CH_3C(=X)H$ and $CH_2=C(XH)H$, (X = O, S) isomers

Method[a]	**3a**/**4a**, X = S	**5a**/**6a**, X = O
A	4.36	
B	4.25	13.08
C	2.26	11.16
D	5.74	14.77
E	3.35[e]	11.78[e]
F	3.19[e]	12.45[e]
G	4.81[e]	14.21[e]
H	2.73[e]	11.55[e]
I	2.94[e]	11.46[e]
J	2.64[e]	11.87[e]
K	4.93[e]	13.94[e]
L	4.81[e]	14.22[e]
M[b]	2.2	11.6
N[c]	2.6	11.3[d]
O[d]		11.2

[a] A: B3LYP/ECP//B3LYP/ECP; B: B3LYP/6-31G(d,p)//B3LYP/6-31G-(d,p); C: B3LYP/6-311G(2d,2p)//B3LYP/6-311(2d,2p); D: MP2(full)/6-31G(d,p)//MP2(full)/6-31G(d,p); E: MP2(full)/6-311G(2d,2p)//MP2-(full)/6-311G(2d,2p); F: CCSD(T)(full)/6-311G (2d,p)//MP2(full)/6-31G(d,p); G: QCISD(full)/6-31G(d,p)//MP2(full)/6-31G(d,p); H: QCISD(T)(full)/6-311G(2d,2p)//MP2(full)/6-311G(2d,2p); I: CCSD-(T)(full)/6-311G(3d,3p)//QCISD(full)/6-31G(d,p); J: QCISD(full)/6-311G(2d,2p)//MP2(full)/6-311G(2d,2p); K: QCISD(T)(full)/6-31G-(d,p)//MP2(full)/6-31G(d,p); L: QCISD(full)/6-31G(d,p)//QCISD(full)/6-31G(d,p). [b] M: CBS-4 (data from ref. 23). [c] N: G1 (data from ref. 24). [d] O: G2 (data from ref. 24). [e] ΔZPE taken from the MP2(full)/6-31G(d,p)//MP2(full)/6-31G(d,p) level.

(2) Methyl-substituted systems. Δ*H* for **3b**/**4b** at CCSD(T)-(full)/6-311G(2d,p)//MP2(full)/6-31G(d,p) is 4.2 kcal mol^{-1}, by 3.0 and 1.9 kcal mol^{-1} lower than at MP2(full)/6-31G(d,p) and B3LYP/6-31G(d,p), respectively. In the corresponding oxygen systems, acetone (**5b**) is more stable than the enol (**6b**) by 16.2, 15.0 and 13.7 kcal mol^{-1} at MP2(full)/6-31G(d,p), B3LYP/6-31G(d,p) and CCSD(T)(full)/6-311G(2d,p)//MP2-(full)/6-31G(d,p), respectively.

(3) The $CH_3C(=X)R$ (3) and $H_2C=C(XH)R$ (4) systems. As many of the systems studied are large, the 6-31G(d,p) basis set was used. On the basis of the higher level calculations mentioned above, we apply a correction, reducing the calculated *ab initio* or DFT 6-31G(d,p) Δ*H* values by *ca.* 2.0 kcal mol^{-1}.

The calculated HF, MP2 and B3LYP (all with the 6-31G(d,p) basis set) reaction enthalpies Δ*H*, for eqn. (2) (Table 2) show that for all substituents R the thiocarbonyl, **3a**–**k** are more stable than the corresponding thioenols, **4a**–**k**. All three theoretical methods reveal similar qualitative results. However, there are quantitative differences of 1–2 kcal mol^{-1} between the methods: the HF Δ*H* values being smaller and the MP2 values being higher than the B3LYP values. The discussion below refers primarily to the B3LYP results, which can be applied to larger systems, unless stated otherwise.

The Δ*H* (eqn. (2)) values for X = S (Table 2) range over a relatively narrow span, between 2.1–7.1 kcal mol^{-1} (B3LYP).

Table 2 Calculated reaction enthalpies ΔH (kcal mol^{-1}) for the thioenol–thiocarbonyl energy differences of systems **3** (eqn. (2)) and the effect of substituents on the thioenol–thioketone equilibrium (eqn. (8))[a]

		ΔH(2, X = S)/kcal mol^{-1}			ΔH(8, X = S)/kcal mol^{-1}		
Isomers	R	HF	MP2	B3LYP	HF	MP2	B3LYP
3a/4a	H	3.08	5.74	4.25	0.0	0.0	0.0
3b/4b[b]	Me	5.03	7.16	6.14	1.94	1.42	1.89
3c/4c	Et	5.13	7.47	6.71	2.05	1.73	2.46
3d/4d	*i*-Pr	4.76	6.98	6.09	1.67	1.24	1.84
3e/4e	*i*-Bu	4.17	6.40	5.39	1.08	0.66	1.14
3f/4f	*t*-Bu	4.45	6.80	5.70	1.36	1.06	1.45
3g/4g	SiH_3	0.11	3.32	2.14	−2.97	−2.42	−2.11
3h/4h	CN	0.07	5.82	3.56	−3.01	0.07	−0.69
3i/4i	CH_2CN	3.04	6.53	5.22	−0.04	0.79	0.97
3j/4j	Ph			7.15			2.91
3k/4k	CH_2Ph			5.52			1.28

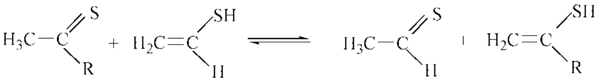
[a] Values include ZPE energies. The calculated total energies and ZPEs of all species are reported in Table S1 of the Electronic Supplementary Information. [b] 4.2 kcal mol^{-1} at CCSD(T)(full)/6-311G(2d,p)//MP2(full)/6-31G(d,p).

Table 3 Calculated reaction enthalpies ΔH (kcal mol^{-1}) for eqns. (9)–(12)[a]

Species	R	ΔH(9)	ΔH(11)	ΔH(10)	ΔH(12)
3b/4b	Me	6.80 (8.90) [7.48]	2.03 (3.04) [1.70]	4.86 (7.48) [5.59]	0.09 (1.62) [−0.19]
3c/4c	Et	6.24 (9.49) [7.32]	1.68 (3.61) [1.80]	4.19 (7.76) [4.86]	−0.37 (1.88) [−0.66]
3d/4d	*i*-Pr	4.59 (9.12) [5.82]	0.14 (3.05) [0.45]	2.92 (7.88) [3.98]	−1.53 (1.82) [−1.39]
3e/4e	*i*-Bu	6.11 (10.25) [6.92]	1.38 (3.93) [1.28]	5.02 (9.60) [5.78]	0.29 (3.27) [0.14]
3f/4f	*t*-Bu	1.11 (7.28) [3.02]	−1.90 (2.03) [−1.29]	−0.26 (6.22) [1.57]	−3.26 (0.97) [−2.74]
3g/4g	SiH_3	−1.21 (1.98) [−0.22]	−3.33 (−1.38) [−2.86]	1.76 (4.40) [1.89]	−0.36 (1.04) [−0.75]
3h/4h	CN	−3.56 (3.84) [0.82]	−6.54 (−1.37) [−4.18]	−0.55 (3.76) [1.51]	−3.53 (−1.44) [−3.49]
3i/4i	CH_2CN	1.77 (6.81) [3.58]	−1.30 (1.86) [−0.71]	1.81 (6.03) [2.61]	−1.26 (1.08) [−1.68]
3j/4j	Ph	[8.93]	[0.77]	[6.02]	[−2.14]
3k/4k	CH_2Ph	[6.76]	[1.16]	[5.49]	[−0.12]

[a] Values at HF (no parentheses), MP2 (parentheses) and B3LYP [brackets].

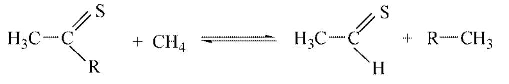
The effect of the α-R groups on the thiocarbonyl–thioenol equilibrium is better evaluated by calculating ΔH for the isodesmic eqn. (8) (Table 2), which are obtained by the subtraction of eqn. (2) for R = H from eqn. (2) for R ≠ H. Isodesmic equations are generally more reliable[26a] than direct calculations of equilibria as in eqn. (2). The less positive (or more negative) ΔH of eqn. (8) is, the higher the thermodynamic stability of the R-substituted thioenol species relative to the corresponding R-substituted thioketone (compared with **3a/4a**); *i.e.*, the smaller is ΔH(8), the more R favors the thioenol over the thioketone.


(8)

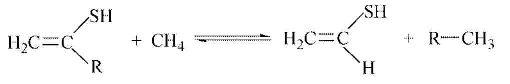
3 **4a** **3a** **4**

The substitution of H with an α-alkyl group (eqn. (8)), increases the thiocarbonyl–thioenol energy gap. The largest increase of 1.4–1.9 kcal mol^{-1}, (depending on the theoretical level) is for the change R = H→Me and ΔH increases further (by 0.1–0.6 kcal mol^{-1}) for the change R = Me→Et, where ΔH (**3**/**4**) reaches a maximum of 5.1–7.5 kcal mol^{-1}. ΔH decreases by 0.4–0.6 kcal mol^{-1} for the change R = Et→*i*-Pr, by an additional 0.6–0.7 kcal mol^{-1} for R = *i*-Pr→*i*-Bu and by 0.3–0.4 kcal mol^{-1} for R = *i*-Pr→*t*-Bu. In contrast, the substitution R = H→SiH_3 decreases the thiocarbonyl–thioenol energy gap by 2.1–3 kcal mol^{-1} to 0.1–3.3 kcal mol^{-1}. Substitution of H by the electron-withdrawing cyano group reduces ΔH by 0.7 kcal mol^{-1} at B3LYP (by 3.0 kcal mol^{-1} at HF), but it leaves ΔH unchanged at MP2. The change R = H→CH_2CN increases ΔH by 0.8 and 1.0 kcal mol^{-1} by the MP2 and B3LYP methods, respectively (but ΔH remains unchanged at HF). A phenyl group increases the thiocarbonyl–thioenol gap by 2.9 kcal mol^{-1} (B3LYP). With R = CH_2Ph, where the phenyl group is separated from the functional groups by a CH_2 group, the effect is reduced by 1.3 kcal mol^{-1}.

The effect of substituents on the energy gap between the isomers can be separated into contributions from its effect on the thiocarbonyls and the thioenols by using isodesmic eqns. (9) and (10), respectively. A more positive ΔH value


(9)

3 **3a**


(10)

4 **4a**

reveals a higher thermodynamic stability of the substituted derivative compared with the parent compound (relative to the corresponding RCH_3). Note that subtraction of eqn. (10) from eqn. (9) yields eqn. (8).

The computational results for eqns. (9) and (10) (Table 3) show that α-alkyl substituents stabilize significantly both the thiocarbonyls and the thioenols, but the stabilization is larger by 1–2 kcal mol^{-1} for the thioketones. The α-substituent effect for the substituents studied covers a range from –3.6 to 10.3 kcal mol^{-1}. For α-alkyl substitution the effect ranges from −0.3 to 10.3 kcal mol^{-1}. Whereas the HF and B3LYP results are in general close to each other, the MP2 values are generally higher by several kcal mol^{-1} and they also show a somewhat different qualitative behavior. Thus, the maximal stabilization for the thioketones (eqn. (9)) is reached for R = Me by HF and B3LYP methods (ΔH(9) of 6.8 and 7.5 kcal mol^{-1}, respectively) while

Table 4 Reaction enthalpies ΔH (kcal mol^{-1}) at B3LYP/6-31G(d,p) for eqn. (2) (X = O) and eqns. (13)–(17)

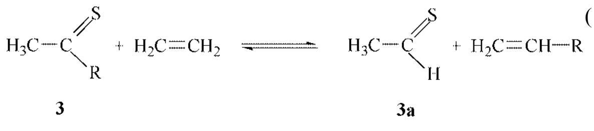
Compounds	R	ΔH(2)	ΔH(13)	ΔH(14)	ΔH(15)	ΔH(16)	ΔH(17)
5a/6a	H	13.08	0.0				
5b/6b	Me	14.93[a]	1.86	9.75	7.89	3.97	2.11
5c/6c	Et	15.86	2.78	10.38	7.60	4.86	2.08
5d/6d	*i*-Pr	14.76	1.68	8.84	7.16	3.47	1.79
5e/6e	*i*-Bu	15.41	2.33	10.81	8.48	5.17	2.84
5f/6f	*t*-Bu	14.76	1.68	7.48	5.80	3.18	1.50
5g/6g	SiH_3	10.23	−2.85	−1.44	1.41	−4.08	−1.23
5h/6h	CN	11.34	−1.74	−0.04	1.70	−5.05	−3.31
5i/6i	CH_2CN	14.35	1.27	6.96	5.68	2.66	1.39
5j/6j	Ph	16.15	3.07	11.39	8.32	3.23	0.16
5k/6k	CH_2Ph	15.28	2.20	9.34	7.14	3.74	1.54

[a] 16.2 and 13.7 kcal mol^{-1} at MP2 and CCSD(T)(full)/6-31G(2d,p)//MP2(full)/6-31G(d,p), respectively.

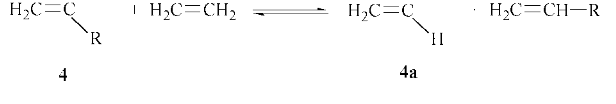
at MP2 it is reached for R = *i*-Bu (10.3 kcal mol^{-1}), but the stabilization for R = Me is only slightly lower (8.9 kcal mol^{-1}). In the thioenols (eqn. (10)) the highest stabilization is calculated for R = *i*-Bu at all three levels with stabilization energies ranging from 5.0–9.6 kcal mol^{-1}. The smallest stabilization effect among the alkyl groups is calculated (at all levels) for R = *t*-Bu for both the thioketones (stabilization range 1.1–7.3 kcal mol^{-1}) and the thioenols (−0.3 to 6.2 kcal mol^{-1}); this may be due to the steric effect of the *t*-Bu moiety. The second least stabilizing substituent is R = *i*-Pr. The other substituents have at least two hydrogens on C_α and this seems to increase their stabilizing effect. Thus, R = *i*-Bu (two α-hydrogens) is more stabilizing than R = *t*-Bu (no α-hydrogens) by 3–5 kcal mol^{-1} (eqn. (9)) and 3.4–5.3 kcal mol^{-1} (eqn. (10)).

The change R = H→SiH_3 destabilizes the thiocarbonyl slightly at HF and B3LYP (by −1.2 and −0.2 kcal mol^{-1}, respectively), at MP2 it shows a small stabilization by 2.0 kcal mol^{-1}. In contrast, the thioenol is stabilized by the R = H→ SiH_3 change at all levels (by 1.8–4.4 kcal mol^{-1}). A cyano group stabilizes both the substituted thiocarbonyl and thioenol at MP2 and B3LYP (but destabilizes it at HF). The substitution R = CN→CH_2CN causes a higher stabilization of both tautomeric forms. A phenyl substituent stabilizes the parent thiocarbonyl by 8.9 kcal mol^{-1}, 2.9 kcal mol^{-1} more than it stabilizes the parent thioenol. When the phenyl group is separated from the thiocarbonyl group by one CH_2 group (R = Ph→ R = CH_2Ph) the stabilization decreases by *ca.* 2.2 kcal mol^{-1} for the thioketone (eqn. (9)) and by 0.5 kcal mol^{-1} for the thioenol (eqn. (10)). The relatively small effect of the intervening CH_2 group strongly indicates that conjugation between the phenyl ring and the C=S or the C=C bonds is not the major effect of the phenyl substituent, an effect which is rather inductive or steric.

Since a major factor in eqns. (9) and (10) is the transfer of R from a sp^2 hybridized carbon in $H_3CC(=S)R$ or $H_2C=C(SH)R$ to a sp^3 hybridized carbon in H_3CR, we also calculated the energies of the isodesmic eqns. (11) and (12), where R is transferred between two sp^2 carbon atoms (Table 3). Subtraction of eqns. (11) and (12) also gives eqn. (8).



(11)



(12)

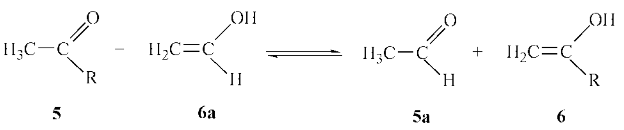
Isodesmic reactions (11) and (12) indeed reveal a substantially smaller (by *ca.* 3–6 kcal mol^{-1}) stabilization (or even destabilization) of the substituted thioketones and thioenols with respect to isodesmic eqns. (9) and (10), respectively. The calculated reaction energies range from −6.5 to 3.9 kcal mol^{-1}. For the alkyl substituents, the bond separation energies for the thioketones (eqns. (9) and (11)) show very similar trends, with Me, Et and *i*-Bu being the most stabilizing substituents for both reactions at the HF, B3LYP and at MP2 levels, respectively. The least stabilizing alkyl substituent (at all levels) is *t*-Bu. Thioenols are less stabilized by alkyl substitution (eqns. (10) and (12)) than the corresponding thioketones and in some cases they are even destabilized (relative to $H_2C=CHSH$). The most stabilizing alkyl substituent is *i*-Bu and the least stabilizing is *t*-Bu (at all levels), but the differences are only 2–4 kcal mol^{-1}. For the non-alkyl substituents the cyano is the least stabilizing substituent (actually destabilizing) at most levels for both the thioketones and the thioenols. According to eqns. (9) and (10) a Ph group highly stabilizes the keto/thioketone, but compared with $H_2C=CHR$ (eqns. (11) and (12)) Ph stabilizes the thioketone by 0.8 kcal mol^{-1}, while it destabilizes the thioenol by 2.1 kcal mol^{-1}.

Carbonyl–enol tautomerism in the oxygen analogs

To compare thiocarbonyl–thioenol with carbonyl–enol tautomerism, we also performed B3LYP/6-31G(d,p) calculations for the oxygen analogs, *i.e.*, **5a**–**5k** and **6a**–**6k**. The calculated ΔH values for the carbonyl–enol equilibrium (eqn. (2)) given in Table 4 show that with all the substituents studied the carbonyl isomer is significantly more stable than the corresponding enol. Furthermore, the keto–enol energy gaps are much larger, by *ca.* 9 kcal mol^{-1}, than those for the corresponding thiocarbonyl/thioenol pairs.

The effect of α-alkyl groups on the carbonyl–enol equilibria was also evaluated by using eqn. (13) (*cf.* Table 4), which are analogous to eqn. (8) for the sulfur derivatives.

(13)



For all substituents, ΔH(13) resemble those of ΔH(8). Thus, the effect of the α-alkyl groups is relatively small ranging between 1.7 (R = *i*-Pr, *t*-Bu) and 2.8 kcal mol^{-1} (R = Et). The changes R = H→Me and R = Me→Et, increase the stabilization of the carbonyl relative to the enol by 1.9 and 0.9 kcal mol^{-1}, respectively. The ethyl group is the most stabilizing α-alkyl substituent (stabilizing effect of 2.8 kcal mol^{-1}). ΔH decreases by 1.1 kcal mol^{-1} for the change R = Et→*i*-Pr; it remains unchanged for R = *i*-Pr→*t*-Bu and increases by 0.6 kcal mol^{-1} for R = *i*-Pr→*i*-Bu. The change R = H→SiH_3 decreases the keto/enol gap by 2.85 kcal mol^{-1}. The CH_2CN, Ph and CH_2Ph substituents stabilize (by 1.3–3.1 kcal mol^{-1})

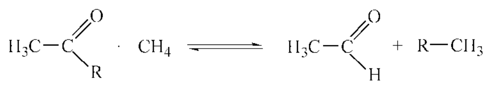
Table 5 Calculated (B3LYP/6-31G(d,p) (MP2(full)/6-31G(d,p) values are given in parentheses) enthalpy differences $\Delta H((g) - (s))$ or $\Delta H((a) - (s))$ (kcal mol^{-1}) between the *syn* (*s*) and *gauche* (*g*) or *anti* (*a*) conformers of the thioenols (**4a**–**4k**) and the enols (**6a**–**6k**) and values of the C=C–X–H dihedral angles (°)[a]

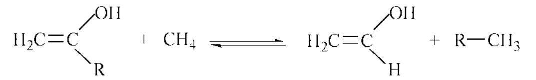
		X = S		X = O	
Compounds	R	ΔH[b]	Dihedral angle[c]	ΔH[b]	Dihedral angle[d]
4a/6a	H	0.49 (0.41)	154.8 (146.4)	1.76	180.0[e]
4b/6b	Me	0.19 (0.14)	147.9 (144.1)	1.93	180.0[e]
4c/6c	Et	0.00 (0.47)	147.1 (142.2)	2.04	171.0[e]
4d/6d	*i*-Pr	0.28 (0.41)	142.5 (135.1)	2.10	180.0[e]
4e/6e	*i*-Bu	0.07 (0.09)	147.9 (145.1)	1.87	172.0[e]
4f/6f	*t*-Bu	0.63 (0.50)	124.4 (137.7)	2.30	124.4
4g/6g	SiH_3	−0.19 (−0.18)	150.1 (146.2)	2.38	161.7
4h/6h	CN	−0.73 (−0.53)	147.3 (141.0)	−0.38	180.0[e]
4i/6i	CH_2CN	−1.01 (−1.06)	142.4 (137.8)	3.36	159.4
4j/6j	Ph	−0.39	144.6	1.03	175.3[e]
4k/6k	CH_2Ph	0.86	−149.4	0.30	17.3

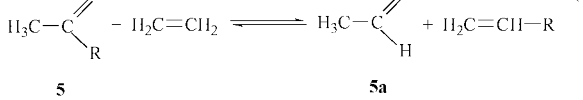
[a] A positive value indicates that the *syn* conformer is the more stable. [b] The energy of the *syn*-conformer is taken as zero. [c] For the *syn* conformer, the C=C–X–H dihedral angles are: R = Et(−0.9), CH_2CN (0.7), Ph (−11.1), CH_2Ph (5.4). [d] For the *syn*-conformer, the C=C–X–H dihedral angles are: R = Et (−1.1), *i*-Bu (−1.3), Ph (156.6), CH_2Ph (−2.1). [e] *anti* Conformer.

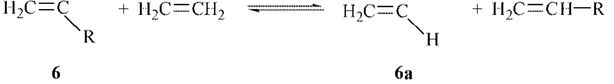
and a CN substituent destabilizes (by 1.7 kcal mol^{-1}) the substituted keto forms, relative to the enols; the trends and values being similar to those for the thioketone/thioenol pairs.

The substituent effect can again be separated into the contributions from the carbonyl (eqn. (14)) and the enol (eqn. (15)) species. The results (Table 4) show, as found previously,[8] that α-alkyl substitution stabilizes significantly both isomers, the range of values being 5.8–10.8 kcal mol^{-1}. However, the stabilizing effect is always larger for the ketones, thus increasing the carbonyl–enol equilibrium constant. The maximal stabilization for both the keto and enol forms, by 10.8 and 8.5 kcal mol^{-1}, respectively, is reached for R = *i*-Bu while a *t*-Bu substituent shows the smallest stabilization of 7.5 and 5.8 kcal mol^{-1}, respectively. The change R = H→SiH_3 destabilizes the carbonyl species by 1.4 kcal mol^{-1} but stabilizes the substituted enol by 1.4 kcal mol^{-1}. A CN substituent does not change the stability of the carbonyl isomer but it stabilizes the enol species by 1.7 kcal mol^{-1}. CH_2CN, Ph and CH_2Ph stabilize significantly both isomers (by 1.0–3.1 kcal mol^{-1} more for the keto) and the trends are similar to those found for the thiocarbonyl/thioenol pairs.


5 **5a** (14)


6 **6a** (15)

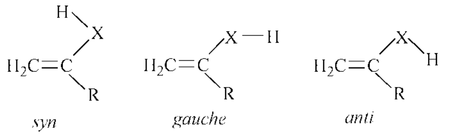

5 **5a** (16)


6 **6a** (17)

Eqns. (16) and (17), where R is transferred between two sp^2 carbons, show much smaller stabilization of **5** and **6** in comparison with eqns. (14) and (15) (Table 4) for reasons discussed above for eqns. (9)–(12). All four isodesmic eqns. (14)–(17) reveal similar trends for the alkyl substituents: the most stabilizing substituent is *i*-Bu, the least stabilizing being *t*-Bu. Among the non-alkyl substituents Ph is the most stabilizing and SiH_3 is the least stabilizing according to eqns. (14) and (15) but eqns. (16) and (17) reveal CH_2Ph as the most stabilizing and CN as the least stabilizing substituent. Similarly to the thiocarbonyl–thioenol tautomerism Ph is disfavored by eqns. (16) and (17) relative to eqns. (14) and (15).

Conformation of the C=C–X–H moiety

Enols and thioenols of the type $H_2C{=}C(R)XH$ may exist in at least three distinct conformers with regard to the C=C–X–H dihedral angle *θ*; *i.e.*, *syn* (*θ ca.* 0°), *gauche* (*θ ca.* 120°) or *anti* (*θ ca.* 180°) (Scheme 1). Experimental microwave spectra and previous *ab initio* calculations on simple thioenols show that the conformation of the C=C–SH moiety depends on R.[36] For example, for $H_2C{=}CHSH$ the most stable conformation is *syn* (in agreement with early calculations[37b]), whereas it is *gauche* for (*E*)-MeCH=CHSH.[37a] Analysis of the experimental spectra of propene-1-thiol[37c] indicates a nearly *anti* conformation, while *ab initio* calculations suggest the existence of both *syn* and *gauche* (*θ* = 110°) conformations, the latter being more stable by 0.3 kcal mol^{-1}.[37a]



X = O, S, Se, Te

Scheme 1

The calculated enthalpy differences between the *syn* and *gauche* (or *anti*) conformers and the C=C–X–H dihedral angle (*θ*) as calculated at the HF, MP2 and B3LYP levels for all relevant species (X = O, S, Se, Te) are listed in Tables 5 and 6. In the parent thioenol the *syn* conformer **4a** is slightly more stable (by 0.4 kcal mol^{-1}) than the *gauche* (*θ* = 138–154°) at the MP2 and B3LYP levels. The parent enol, **6a**, prefers the *syn* conformation more strongly, *i.e.*, by 1.1–1.9 kcal mol^{-1} relative to the *anti* conformer. For $H_2C{=}CHSeH$, the C_s *syn* conformer is slightly preferred, but in $H_2C{=}CHTeH$ the *gauche* conformation is slightly more stable. Methyl substitution decreases the energy gap between the *syn* and *gauche* conformers to *ca.* 0.15 kcal mol^{-1} for the parent thio system, it has a minor effect for X = O, and it slightly increases this gap for X = Se and Te. For the other substituted thioenols the most stable conformer is *syn* in half of

Table 6 Enthalpy differences $\Delta H((g) - (s))$ (kcal mol^{-1}) between the *syn* (*s*) and *gauche* (*g*) conformers of several thioenols, enols, selenols and telluroenols, at various levels of theory. The value for the (*s*) conformer is taken as zero

Comp.	$\Delta H°$/kcal mol^{-1}	Dihedral angle[a]/° g(*s*)/°
4a[b]	0.23[b,e]; 0.28[c,d,e,g]; 0.34[e,f]; 0.08[e,g]; 0.16[e,k]; 0.12[i]; 0.48[n]	145.7 (0.0)[b]; 145.4 (0.0)[c]; 157.1 (0.0)[i]; 156.3 (0.0)[u]
4b	−0.25[e,h]; 0.17[n]	148.4 (0.0)[n]
6a[c]	1.93[c,e]; 1.10[e,j]	180.0[q] (0.0)[c]
6b[l]	2.22[l]; 2.02[k]	180.0[q] (0.0)[l]
8a	0.11[m]; 0.05[n]	145.8 (0.0)[m]; 149.9 (0.0)[n]
8b	−0.35[m]; −0.29[n]	136.0 (0.0)[m]; 145.1 (0.0)[n]
10a	−0.23[n]	138.1 (0.0)
10b	−0.61[n]	138.0 (0.0)
2a	0.09[l]; −0.32[m]; −0.17[o]	131.7 (−38.1)[l]; 143.9 (−39.6)[m]; 118.5 (−50.3)[o]
2b	−1.07[l]; −0.96[m]; −1.22[o]	152.3 (−12.5)[l]; 151.3 (−7.4)[m]; 143.9 (−27.8)[o]
12 (*n* = 4), (*n* = 6)	−0.13[m]; 0.45[m]	148.1 (−2.1)[m]; 139.2 (0.9)
14 (*n* = 4), (*n* = 6)	1.39[m]; 2.23[m]	171.7 (−0.7)[m]; −170.0 (1.3)[m]
16	−0.94 [m]	−161.4 (14.5)
18a	−0.28[e,m]	−165.5 (12.8)
18b	−1.19 [m]	147.4 (−17.6)
20	0.40 [m]	−156.7 (0.0)
22	1.42 [m]	180.0[o] (0.0)
24	0.24 [m]	180.0[o] (0.0)
26	5.30 [m]	−179.6(?) (0.0)

[a] Angle (C=C–X–H) (degree). [b] MP2(full)/6-311G(2d,2p)//MP2(full)/6-311G(2d,2p). [c] QCISD(full)/6-31G(d,p)//QCISD(full)/6-31G(d,p). [d] QCISD(full)/6-31G(d,p)//MP2 (full)/6-31G(d,p). [e] ΔH does not include ZPE. [f] QCISD(T)(full)/6-31G(d,p)//MP2(full)/6-31G(d,p). [g] QCISD(full)/6-311G(2d,2p)//MP2(full)/6-311G(2d,2p). [h] QCISD(T)(full)/6-311G(2d,2p)//MP2(full)/6-311G(2d,2p). [i] B3LYP/6-311G(2d,2p). [j] CCSD(T)(full)/6-311G(3d,3p)//QCISD(full)/6-31G(d,p). [k] CCSD(T)(full)/6-311G(2d,p)//MP2(full)/6-31G(d,p). [l] MP2(full)/6-31G(d,p)//MP2(full)/6-31G(d,p). [m] B3LYP/6-31G(d,p). [n] B3LYP/ECP. [o] HF/6-31G(d,p)//HF/6-31G(d,p). [p] The (*s*) conformer contains a H · · · F bond. [q] *anti* Conformer.

Table 7 Selected calculated optimized geometrical parameters for several species (bond lengths in pm, bond angles in degrees)

Compound	Level[a]	Sym.	*r*(CC)	*r*(CX)	*r*(XH)	<(CCX)	<(CXH)	θ (CCXH)
3a	A	C_s	149.6	160.6		126.6		
3a	B	C_s	149.0	161.8		125.9		
3a	C	C_s	148.9	162.0		126.4		
3a	D	C_s	149.8	162.5		126.1		
4a-(*s*)[b]	A	C_s	131.7	176.8	132.7	127.8	98.2	0.0
4a-(*s*)[b]	B	C_s	133.2	176.4	133.2	127.6	96.1	0.0
4a-(*s*)[b]	C	C_s	132.6	177.1	134.2	128.4	97.3	0.0
4a-(*s*)[b]	D	C_s	133.6	176.8	133.4	127.6	96.4	0.0
4a-(*g*)	A	C_1	131.7	177.6	132.7	122.8	97.8	138.1
4a-(*g*)	B	C_1	133.2	177.2	133.1	122.4	96.3	145.7
4a-(*g*)	C	C_1	132.5	177.9	134.1	123.2	96.8	157.1
4a-(*g*)	D	C_1	133.6	177.5	133.4	122.8	96.3	145.4
5a	D	C_s	150.6	121.7		124.3		
6a-(*s*)[b]	D	C_s	133.5[c]	136.8[c]	96.4[c]	126.7[c]	108.4[c]	0.0[c]
6a-(*a*)	D	C_s	133.2	137.4	96.0	121.7	108.8	180.0
7a	E	C_s	149.2	177.2		126.7		
8a-(*s*)[b]	E	C_s	133.3	192.0	147.8	127.9	95.2	0.0
8a-(*g*)	E	C_1	133.2	192.7	147.8	122.9	95.1	149.9
9a	E	C_s	149.0	196.8		127.6		
10a-(*s*)	E	C_s	133.3	211.1	165.9	127.6	93.7	0.0
10a-(*g*)[b]	E	C_1	133.3	211.7	166.1	123.3	93.9	138.1

[a] Level: A - HF/6-31G(d,p)//HF/6-31G(d,p); B - MP2(full)/6-311G(2d,2p)//MP2(full)/6-311G(2d,2p); C - B3LYP/6-311G(2d,2p); D - QCISD(full)/6-31G(d,p)//QCISD(full)/6-31G(d,p); E - B3LYP/ECP. [b] The more stable conformer. Energy differences between the conformers are given in Tables 5 and 6. [c] The experimental data (ref. 38) are as follows: 132.6, 137.2, 96.0 pm, 126.2, 108.3, 0.0°.

the cases and in the other half the energy differences between the conformers are small, not exceeding 1.0 kcal mol^{-1} (except for R = CH_2CN). For the carbonyl/enol pairs a *syn* conformer is strongly preferred for most derivatives (except for R = CN) by up to 3.4 kcal mol^{-1} (for R = CH_2CN).

Selected optimized geometrical parameters of the calculated parent species (R = H) at all employed levels are given in Table 7. The enol and chalcogenoenol species are minima in both the *syn* and *gauche* (θ = 138–157°) conformations for **4a**, **8a** and **10a**. For **6a** the minima are at the *syn* and *anti* conformations. The most stable conformer is the *syn* except for **10a** which is slightly more stable as the *gauche* conformer (Table 7). Experimental structural data for comparison are available only for acetone and vinyl alcohol (**6a**). For **6a** (*syn*) the calculated and experimental[38] geometrical data are in very good agreement (Table 7).

Activation barriers for the unimolecular gas phase transformation of the parent thiocarbonyl/thioenol

The calculated activation barriers for the unimolecular tautomerization in the gas phase for the parent thiocarbonyl (**3a**)/thioenol (**4a**) were calculated to be very high in both directions, from 72.4–75.5 kcal mol^{-1} at HF *via* 58.0–63.8 kcal mol^{-1} at MP2 to 53.6–57.8 kcal mol^{-1} at the B3LYP level (Table 8). The B3LYP values are close to the recently calculated G1 and G2 values.[24] Consequently, a high kinetic stability is predicted for the isolated individual tautomeric forms. Calculations employing the SCIPCM-SCRF solvation model[31] using CCl_4 as the solvent, show only a very minor solvent effect (0.0–0.3 kcal mol^{-1}) on the activation barriers (see Electronic Supplementary Information). As the thioenol $\longrightarrow$ thiocarbonyl isomerization is quite facile in solution, the high calculated barrier for the gas-phase tautomerism serves as an indirect indication for the existence of effective specific solvent–solute interactions in solutions[39] which facilitate the tautomeric interconversion. The calculated transition structure for the tautomerism is shown in Fig. 1.

The corresponding activation barriers for the acetone/propen-2-ol (**5a**/**6a**) system (Table 8) resemble the **3a**/**4a** ones in the enol ⟶ aldehyde direction, but are higher in the aldehyde ⟶ enol direction. This simply reflects the larger energy gap between the oxygen species than between the sulfur species.

Other sulfur-substituted systems. Comparison of calculated *vs.* measured equilibrium data

Calculations for sulfur-substituted systems other than **3**/**4** are given in Table 9.

The only reliable kinetic/equilibrium data known to us[13c] are for the diisopropyl **1a**/**2a** and diisobutyl **1b**/**2b** systems (eqn. (1)) for which we have calculated from the literature data K_{Thioenol} values of 1.4 and 1.1, respectively (at 40 °C in CCl_4) which give ΔH of −0.2 and −0.06 kcal mol^{-1}, respectively, the thioenol forms being slightly more stable. According to the calculations (Table 9) the thioketone isomers are preferred for both systems and the calculated enthalpy differences are higher than the measured ones by 0.1–2.6 kcal mol^{-1} for **1b**/**2b** and by 3.2–6.0 kcal mol^{-1} for **1a**/**2a**, depending on the theoretical method used (Table 9). However, as pointed above, the ΔH(**1**/**2**) values in Table 9 calculated using the 6-31G(d,p) basis set, have to be corrected downwards by *ca.* 2 kcal mol^{-1}. Such correction brings the calculated ΔH for the **1b**/**2b** pair into excellent agreement with experiment, while for the **1a**/**2a** pair the calculated ΔH still remains by 1–3.7 kcal mol^{-1} higher than determined experimentally.

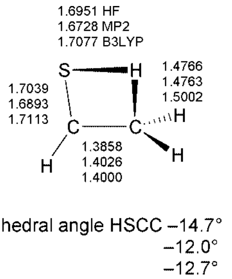


Fig. 1 Calculated transition state (at B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) for the **3a** $\rightleftharpoons$ **4a** interconversion.

Table 8 Calculated activation barriers, $\Delta H^{\ddagger}$ (kcal mol^{-1}), for the tautomerization in the gas phase of **3a** $\rightleftharpoons$ **4a** and of **5a** $\rightleftharpoons$ **6a**

	$\Delta H^{\ddagger}$/kcal mol^{-1}		
Reaction	HF[a]	MP2[b]	B3LYP[c]
Thioaldehyde (**3a**)→thioenol (**4a**)	75.5	63.8	57.8[d]
Thioenol (**4a**)→thioaldehyde (**3a**)	72.4	58.0	53.6[e]
Aldehyde (**5a**)→enol (**6a**)	84.1	70.5	66.6
Enol (**6a**)→keto (**5a**)	69.6	55.7	53.5

[a] HF/6-31G(d,p)//HF/6-31G(d,p). [b] MP2(full)/6-31G(d,p)//MP2(full)/6-31G(d,p). [c] B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p). [d] 57.7 at G1 and 58.2 at G2 (ref. 24). [e] 55.1 at G1 and 55.6 at G2 (ref. 24).

For **11**–**24**, only B3LYP/6-31G(d,p) calculations are available and a correction for ΔH of −2 kcal mol^{-1} will be applied (*i.e.*, corrected values). The calculated ΔH for the cyclic **11**/**12** pair (eqn. (3)) are 4.0 ($n = 4$) and 3.0 ($n = 6$) kcal mol^{-1}, respectively (Table 9), leading to corrected values of 2.0 and 1.0 kcal mol^{-1}, respectively. These results are somewhat higher than the experimental product distributions showing a *ca.* 2.5-fold excess for the thioenol with $n = 4$ and a *ca.* 3-fold excess of the thioketone with $n = 6$.[11e] The product distributions however are unreliable measures of the equilibrium constants. The corresponding theoretical ΔH values for the analogous oxygen systems **13**/**14** are much higher, 14.5 ($n = 4$) and 12.9 ($n = 6$) kcal mol^{-1}. The experimental values[40a] are 10.4 ($n = 4$) and 9.4 ($n = 6$).[40] The increase in the tautomerization enthalpies with decrease in ring size can be understood in terms of increasing difficulty of introducing a double bond into a smaller ring.

The corrected B3LYP/6-31G(d,p) calculations suggest that thioenol **16** is more stable than thioketone **15** by *ca.* 1.8 kcal mol^{-1} (eqn. (4)), in good agreement with the isolation of only the thioenol.[15a]

Of the three isomers of the triphenyl substituted system—**17**, **18a** and **18b** (eqn. (5))—the only isomer experimentally observed is the thioenol **18a**.[15b] In full agreement, **18a** is calculated to be the most stable isomer with the isomeric thioenol **18b** and thioketone **17** lying higher in energy by 3.4 and 5.3 kcal mol^{-1} (corrected values), respectively.

The vinyl-substituted thioenol isomer **20** (eqn. (6)) is substantially more stable (corrected value, −7.6 kcal mol^{-1}) than the corresponding thioaldehyde **19**. This is consistent with the fact that buta-1,3-diene-1,4-dithiol is known,[41] while **19** and **20** are unknown. The corresponding aldehyde (**21**)–enol (**22**) equilibrium (eqn. (6)) is calculated to lie towards the aldehyde side (corrected value at B3LYP/6-31G(d,p) 2.6 kcal mol^{-1}, 3.0 kcal mol^{-1} at B3LYP/6-311G(3d,3p)//B3LYP/6-31G(3d,3p)). From heats of formation differences, but-3-enal **21** is less stable by *ca.* 2 kcal mol^{-1} than buta-1,3-dien-1-ol **22**.[42] This contrasts with the theoretical value, and the *ca.* 5 kcal mol^{-1} experimental–theoretical difference (Table 9) may be due to an experimental error (we favor this possibility), or to a theoretical error or to specific solvation effects (*e.g.*, aggregation *via* hydrogen bonding) which stabilize the enol relative to the aldehyde.[8b]

For the CF_3-substituted **23**/**24** (eqn. (7)) the experiment[11b] which shows the presence of only the thioenol **24** in the addition of H_2S to 3,3,3-trifluoropropyne agrees with the calcu-

Table 9 Calculated reaction enthalpies ΔH (B3LYP, kcal mol^{-1})[a] for (thioenol–thioketone) and (enol–ketone) energy differences (eqns. (1), (3)–(7))

Isomers	Eqn.	ΔH/kcal mol^{-1}	Isomers	Eqn.	ΔH/kcal mol^{-1}
(Thioenol/Thioketone)					
1a/**2a**	1	2.95[b]	**17**/**18a**	5	−5.31
1b/**2b**	1	0.89[c]	**17**/**18b**	5	−1.90
11/**12** ($n = 4$)	3	3.96[d]	**18a**/**18b**	5	−3.41
11/**12** ($n = 6$)	3	2.95	**19**/**20**	6	−5.58
15/**16**	4	0.23	**23**/**24**	7	0.48
(Enol/Ketone)					
13/**14** ($n = 4$)	3	14.49	**21**/**22**	6	4.63
13/**14** ($n = 6$)	3	12.89	**25**/**26**	7	7.46

[a] Values include ZPE energies. The calculated total energies and ZPEs of all species are reported in Table S1 of the Electronic Supplementary Information. [b] 3.71 (HF) and 5.76 (MP2). [c] 0.00 (HF) and 2.56 (MP2). [d] CBS-4 value: 2.7 (ref. 23).

Table 10 Enthalpy differences, ΔH (kcal mol^{-1}), between cation-radicals of keto/enol and thiocarbonyl/thioenol species

Compounds	MP2[a]	PMP2[a]	QCISD[b]	CCSD(T)
3a/4a	3.00	1.68	3.52	1.56[c]
3b/4b	6.66	5.47		4.86[d]
5a/6a	−19.61	−18.40	−12.03	
5b/6b	−15.20	−14.06		−7.18[d]

[a] MP2(full)/6-31G(d,p)//MP2(full)/6-31G(d,p). [b] QCISD(full)/6-31G-(d,p)//QCISD(full)/6-31G(d,p). [c] CCSD(T)(full)/6-311G(3d,3p)//QCISD(full)/6-31G(d,p). [d] CCSD(T)(full)/6-311G(2d,p)//MP2(full)/6-31G(d,p).

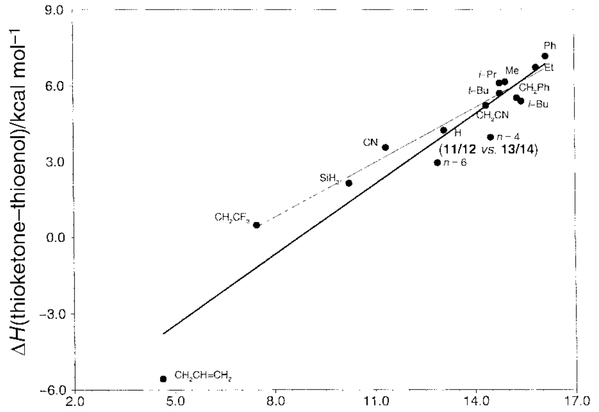


Fig. 2 Plot showing (ΔH(carbonyl–enol) *vs.* ΔH(thiocarbonyl–thioenol) at B3LYP/6-31G(d,p) for systems **3**–**6**, **11**–**14** and **19**–**26**. The points for CH_2CF_3 and $CH_2=CHCH_2$ are for systems **11**–**14** and **19**–**26**, respectively.

lations which reveal a preference by 1.5 kcal mol^{-1} (corrected value) for **24**. Substitution of S by O increases the stability of the carbonyl species **25**, which is more stable by 5.5 kcal mol^{-1} (corrected value) than the corresponding enol **26**. In agreement, only **25** is known in this system.[43]

In conclusion, for the experimentally available thiocarbonyl–thioenol equilibria we find in general a good agreement with the corrected B3LYP(d,p) calculated values. This is encouraging for future predictions of such equilibrium constants.

Cation-radicals

For the carbonyl/enol systems **5a/6a** and **5b/6b**, a dramatic stability change occurs on ionization. The enol cation-radicals are significantly more stable than the carbonyl cation-radicals (Table 10). The energy difference for $\mathbf{5a}^{+\bullet}/\mathbf{6a}^{+\bullet}$ is −19.6 (−18.4) kcal mol^{-1} at MP2/6-31G(d,p) (PMP2) and drops to −12.0 kcal mol^{-1} at QCISD/6-31G(d,p). The gap for $\mathbf{5b}^{+\bullet}/\mathbf{6b}^{+\bullet}$ is −15.2 (−14.1) kcal mol^{-1} at MP2/6-31G(d,p) (PMP2) but only −7.2 kcal mol^{-1} at CCSD(T)/6-311G(2d,p). In contrast, the cation-radicals of the corresponding thiocarbonyl species are more stable than those of the thioenol, although the energy gaps between the tautomers are reduced, relatively to those for the neutral system (by −1.3 to −4.1 kcal mol^{-1}, depending on the computational level, for **3a/4a**) and the gap changes less (by −1.7 to +0.7 kcal mol^{-1}) than for **3b/4b** (*cf.* Tables 1 and 10).

Comparison between the thiocarbonyl–thioenol and the carbonyl–enol tautomerism

Fig. 2 displays the relationships for all the studied systems between thioketone–thioenol and the carbonyl–enol energy gaps as calculated by the B3LYP/6-31G(d,p) method. The ΔH(carbonyl–enol) values are in the range of 5–17 kcal mol^{-1}, substantially larger than the ΔH(thiocarbonyl–thioenol) values which are in the range of −5.5 to 8 kcal mol^{-1}. We find a reasonably good correlation (correlation coefficient, $r = 0.957$) between ΔH(thiocarbonyl–thioenol) and ΔH(carbonyl–enol) with a slope of 0.97 (solid line in Fig. 2), corresponding to an almost 1 : 1 correspondence between the effect of the substituent on the thiocarbonyl–thioenol and the carbonyl–enol equilibria. This correlation is remarkable as it includes a variety of substituents and different acyclic and cyclic systems. The largest deviation from the correlation in Fig. 2 is for systems **19**–**22** having the strongly conjugating vinyl group. If this point is omitted, the correlation is significantly improved ($r = 0.979$) and the slope is 0.72 (dashed line in Fig. 2), indicating a 33% larger substituent effect on the oxygen compounds than on the sulfur compounds.

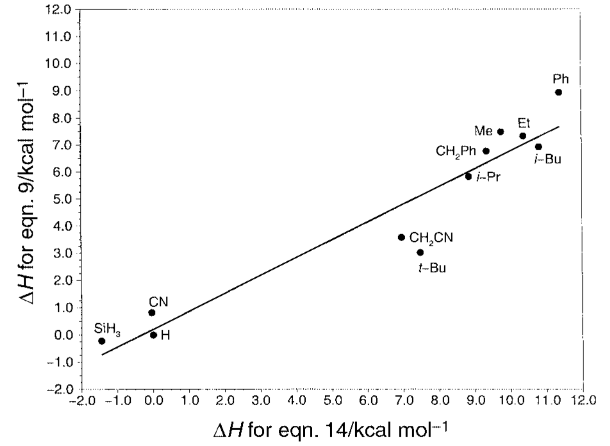


Fig. 3 Plot showing the dependence of the reaction enthalpies (at B3LYP/6-31G(d,p)) of eqn. (9) ($H_3C–C(=S)R + CH_4 \rightleftharpoons H_3C–C(=S)H + R–CH_3$) *vs.* those of eqn. (14) ($H_3C–C(=O)R + CH_4 \rightleftharpoons H_3C–C(=O)H + R–CH_3$).

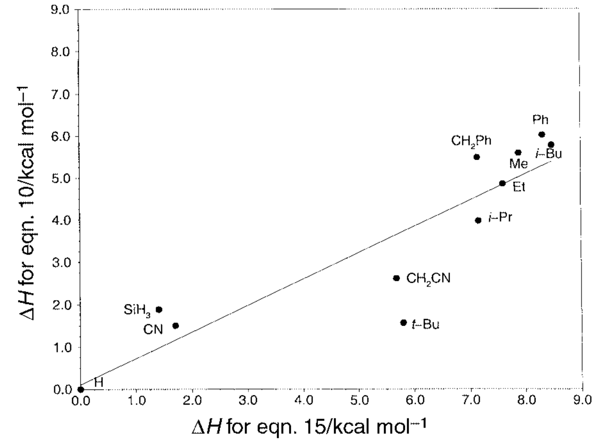


Fig. 4 Plot showing the dependence of the reaction enthalpies (at B3LYP/6-31G(d,p)) of eqn. (10) ($H_2C=C(SH)R + CH_4 \rightleftharpoons H_2C=C(SH)H + R–CH_3$) *vs.* those of eqn. (15) ($H_2C=C(OH)R + CH_4 \rightleftharpoons H_2C=C(OH)H + R–CH_3$).

Figs. 3 and 4 depict the relationship for compounds **3**–**6** between the calculated energies of the isodesmic eqn. (9) *vs.* eqn. (14), which denote the effect of the substituents on the stability of the carbonyl compared with the thiocarbonyl and of eqn. (10) *vs.* eqn. (15) which denote the effect of the substituents on the stability of the thioenol compared with the enol, respectively. Fig. 3 shows a reasonable linear correlation ($r = 0.956$) with a slope of 0.65, somewhat lower than the slope of 0.72 found for the same compounds in Fig. 2. The analogous correlation for the thioenols *vs.* enols (Fig. 4) exhibits a much larger scatter ($r = 0.896$) with a slope of 0.62, indicating a much more complex relationship. The scatter in Fig. 4 is reflected in the significant deviations from the correlation line in Fig. 2 displayed by some of the substituents.

Table 11 Enthalpy differences (ΔH, kcal mol^{-1}) between $CH_3C(=X)H$ and $CH_2=C(XH)H$ (X = O, S, Se, Te) isomers

	ΔH/kcal mol^{-1}							
Method[a]	**5a/6a** X = O	**3a/4a** X = S	**7a/8a** X = Se	**9a/10a** X = Te	**5b/6b** X = O	**3b/4b** X = S	**7b/8b** X = Se	**9b/10b** X = Te
A		9.36	2.84	1.27		6.29	4.36	2.49
B	13.08	4.25	0.27		14.93	6.14	1.68	
C					16.17	7.16		
D					13.70	4.21[b]		

[a] Method: A - B3LYP/ECP; B - B3LYP/6-31G(d,p); C - MP2(full)/6-31G(d,p)//MP2(full)/6-31G(d,p); D - CCSD(T)(full)/6-311G (2d,p)//MP2(full)/6-31G(d,p). [b] ΔZPE taken from the MP2(full)/6-31G(d,p)//MP2(full)/6-31G(d,p) level.

Comparison with literature calculations

For the thio derivatives the only available previous calculations are the CBS-4 calculations of Zhang and co-workers[23] and the G1 and G2 calculations for **3a**/**4a**.[24] The CBS-4 values calculated for nine thione/thioenol pairs are 8–11 kcal mol^{-1} lower than for the corresponding carbonyl/enol pairs.[23] At the B3LYP level we find similar differences (7.8–10.5 kcal mol^{-1}). Three systems are common to the CBS-4 and to our calculations, *i.e.*, **3a**/**4a**, **3b**/**4b** and **11**/**12** ($n = 4$). The order of the ΔH values for the three pairs is identical with all methods, but the CBS-4 tautomerization enthalpies are consistently lower by 0.9–4.0 kcal mol^{-1} than those calculated at our three standard levels. However, we note that ΔH(**3a**/**4a**) of 2.2 kcal mol^{-1} calculated at the CBS-4 level is lower than values calculated using nine other levels and is close only to the B3LYP/6-311G(2d,2p) and G1 values[24] (Tables 1 and 7). The G1, G2 and the CBS-4 ΔH values for **3b**/**4b** are lower than our calculated values at the three standard levels (Tables 1 and 7). For cyclic systems *e.g.*, *c*-$(CH_2)_nC=X$ (X = O, S), $n = 2$–5, both we and Zhang *et al.*[23] find a similar trend with ΔH increasing as n decreases.

Selenocarbonyl–selenoenol and tellurocarbonyl–telluroenol tautomerism

B3LYP/6-31G(d,p) calculations show that the parent selenoaldehyde **7a** is more stable by only 0.3 kcal mol^{-1} than the selenoenol **8a** (Table 11) and the difference increases to 1.7 kcal mol^{-1} for the methyl-substituted systems **7b**/**8b**. However, based on our experience with the corresponding oxygen and sulfur systems the above ΔH values are *ca.* 2 kcal mol^{-1} too high and we conclude that the selenoenol **8a** is actually more stable by *ca.* 1.5 kcal mol^{-1} than the selenoaldehyde **7a**, and the **7b**/**8b** pair have comparable stabilities. The substituent effect of the methyl group of 1.4 kcal mol^{-1} is close to those found in the thiocarbonyl/thioenol and carbonyl/enol systems (both 1.9 kcal mol^{-1}). According to calculations employing effective core potentials (ECPs)[33] the selenocarbonyls **7a** and **7b** are preferred by 2.8 and 4.4 kcal mol^{-1}, (*i.e.*, by *ca.* 2.6–2.7 kcal mol^{-1} more than by the B3LYP/6-31G(d,p)) method, respectively (Table 11), but the methyl group effect (1.5 kcal mol^{-1}) is almost identical to that calculated by B3LYP/6-31G(d,p).

Since a standard 6-31G(d,p) basis set for Te is not available, only B3LYP/ECP (together with a DZP basis set for the valence-electrons) calculations were performed for the tellurocarbonyl (**9a** and **9b**)/telluroenol (**10a** and **10b**) systems.[44] Both telluroketones **9a** and **9b** are calculated to be more stable, by 1.3 and 2.4 kcal mol^{-1}, than the corresponding telluroenol isomers **10a** and **10b,** respectively (Table 11). The calculated effect of the methyl group is 1.2 kcal mol^{-1}, somewhat smaller than in the O, S and Se systems. Based on calibration from the Se systems we conclude that the telluroenols **10a** and **10b** are actually 3 and 2 kcal mol^{-1} more stable than the tellurocarbonyls **9a** and **9b**, respectively.

Our calculations show clearly that upon moving down the series O, S, Se, Te, the energy difference between the tautomeric forms is reduced. Consequently, unsubstituted and alkyl-substituted selenoenols and telluroenols could be viable candidates for synthesis. The largest increase in the equilibrium constant of eqn. (2) occurs for the change X = O→X = S (*ca.* 9 kcal mol^{-1}). The effect of the change X = S→X = Se is smaller (*ca.* 2–4 kcal mol^{-1}) and that of X = Se→X = Te is the smallest (*ca.* 1.5 kcal mol^{-1}). This trend parallels the calculated C=X π-bond energies ($\Delta E(\pi)$),which decrease on going down the Periodic Table, *i.e.*, $\Delta E(\pi/\text{kcal mol}^{-1}) = 95.3$ (X = O), 54.6 (X = S), 43.2 (X = Se), 32.0 (X = Te).[45]

Acknowledgements

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Notes and references

1 Presented in part at the 7th Kyushu International Symposium on Physical Organic Chemistry, Kyushu University, Fukuoka, Japan, December 2–5, 1997, Abstract O57, p. 193.

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