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Energetic Preferences for α,*β* versus *β*,*γ* Unsaturation

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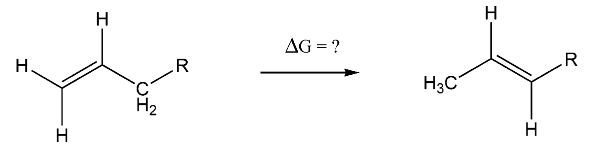
Density functional theory has been applied at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level to examine the energetics of α,*β*- versus *β*,*γ*-unsaturation for some common organic functional groups. Specifically, the relative stabilities of allyl-X ($H_2C{=}CHCH_2X$) and 1-propenyl-X ($H_3CCH{=}CHX$) isomers have been computed for X = methyl, vinyl, phenyl, formyl, acetyl, methoxy, methylthio, methylsulfinyl, methylsulfonyl, sulfamoyl, and methoxysulfonyl, and the results are compared to available experimental data. The intrinsic preference of 3 kcal/mol for the 1-propenyl isomer when X = CH_3 is exceeded by 2−4 kcal/mol for first-row conjugating groups, but it is not met for the sulfur-containing groups. In particular, α,*β*-unsaturation is favored by less than 1 kcal/mol for the sulfone and sulfonamide analogues, while it is preferred by 8 kcal/mol for the vinyl-substituted case. Detailed structural results and torsional energy profiles are also reported.

Introduction

It is generally assumed that bringing a double bond into conjugation with a functional group is energetically favorable. Thus, the stability of nonconjugated isomers is often in question and can affect decisions regarding their synthesis and use, for example, in drug design. Our own experiences in this area led us to seek quantitative knowledge of the energetic effects of conjugation, especially for sulfur-containing functional groups for which directly relevant experimental data is mostly lacking. Thus, the relative thermodynamic stabilities of α,*β*- and *β*,*γ*-unsaturated isomers, as illustrated in Scheme 1, have been investigated for R = methyl, vinyl, formyl, acetyl, phenyl, methoxy, methylthio, methylsulfinyl, methylsulfonyl, sulfamoyl, and methoxysulfonyl.

Experimentally determined thermochemical data for some of the compounds are available.[1−13] The heats of combustion for 1-butene and (*E*)-2-butene, as well as (*E*)-1,3-pentadiene and 1,4-pentadiene, were obtained by Prosen and co-workers in the 1950s.[5,6] Taskinen resolved the relative equilibrium concentrations for alkyl allyl and alkyl propenyl ethers[7] and along with Lindholm resolved the equilibrium concentrations for propenylbenzene isomers in DMSO.[2] Heats of combustion of various α,*β*- and *β*,*γ*-unsaturated sulfones were determined in the 1960s by Mackle and co-workers.[8−12]

SCHEME 1



Early computational investigations on conjugation involving sulfur compounds focused on α-thia carbanions in view of their importance in synthesis. An ab initio molecular orbital investigation by Bernardi and co-workers[14] determined conjugation between 2p and 3d orbitals of C and S, respectively, does not contribute to the stabilization of carbanions by adjacent sulfur. Lehn and Wipff reported results from ab initio calculations that reinforced this conclusion and the greater importance of polarization effects.[15] Similarly, Schade and Schleyer provided computational evidence on the lack of π-donation from phosphorus lone pairs to alkene π-systems.[16]

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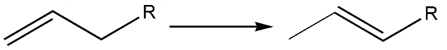
10.1021/jo049363y CCC: $27.50

TABLE 1. Changes in the Electronic Energy at 0 K and the Enthalpy and Free Energy at 298 K for the Isomerization (kcal/mol)[a]



	R	ΔE_{calc}	ΔH_{calc}	ΔG_{calc}	ΔH_{exp}
I	CH_3	−3.2	−3.3	−3.0	−2.7[b]
II	$CH{=}CH_2$	−7.9	−7.9	−8.0	−7.3 ± 0.3[c]
III	(C=O)H	−8.1	−7.8	−7.5	
IV	(C=O)CH_3	−5.9	−5.6	−5.3	
V	Ph	−5.8	−5.8	−5.9	−5.6[d]
VI	OCH_3	−6.6	−6.4	−6.1	−4.8[e]
VII	SCH_3	−2.8	−2.8	−2.7	<−2.7[f]
VIII	(S=O)CH_3	−2.0	−2.1	−2.1	−0.9 ± 0.1[f]
IX	SO_2CH_3	−0.6	−0.7	−0.8	−0.14 ± 0.1[f]
X	SO_2NH_2	−0.6	−0.7	−0.3	
XI	$(SO_2)OCH_3$	−1.2	−1.2	−1.2	

[a] Computed values are B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) results. [b] Ref 1. [c] Ref 5. [d] Ref 2. [e] Ref 7; enthalpy difference in DMSO. [f] Ref 3; free energy differences in 2-methyl-2-propanol.

And, a recent atoms-in-molecules (AIM) study has focused on the nature of the SO bond in sulfoxides and sulfones.[17]

Methods

The energies and structures detailed here have been optimized using the B3LYP functional and the 6-31G(d) basis set with Gaussian 98.[18] All structures have been validated as minima via calculation of vibrational frequencies. Single-point calculations on these optimized geometries were then carried out with the 6-311+G(d,p) basis set and B3LYP functional to incorporate effects of basis set expansion including diffuse functions. Changes in enthalpy and free energy for the isomerization in Scheme 1 have been calculated using the electronic energies determined at the B3LYP/6-311+G(d,p) level with zero-point and thermal corrections determined from unscaled B3LYP/6-31G(d) vibrational frequencies. In addition, torsional energy profiles were explored at the B3LYP/6-31G(d) level for rotation about the (C,O,S)−C_α bonds with 30° dihedral increments.

Results and Discussion

The computed thermodynamic results are listed in Table 1, along with the available experimental data. For each molecule, the lowest-energy E/Z isomer and s-cis/s-trans conformer has been used. The allyl derivatives are given numbers **nA**, and the 1-propenyl isomers are designated **nB**.

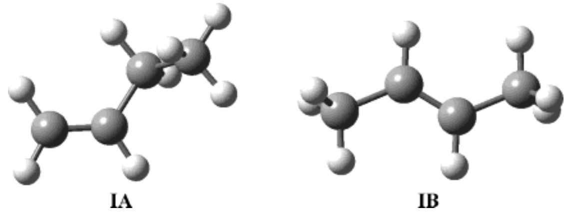


FIGURE 1. Lowest-energy conformers of 1-butene (**IA**) and (*E*)-2-butene (**IB**).

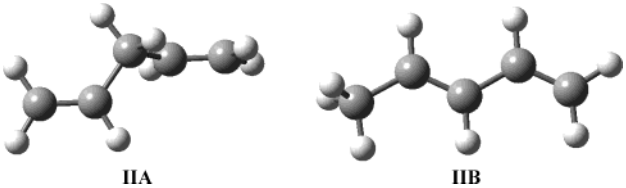


FIGURE 2. Lowest-energy conformers of 1,4-pentadiene (**IIA**) and (*E*)-1,3-pentadiene (**IIB**).

The calculated enthalpy difference between 1-butene (**IA**) and (*E*)-2-butene (**IB**), which are illustrated in Figure 1, is −3.3 kcal/mol; this is close to the experimental value of −2.7 kcal/mol, and it is consistent with the DFT results of Mole et al.[19] They compared six different DFT methods, namely, B3LYP, BLYP, B3PW91, BPW91, B3P86, and LSDA for 23 hydrocarbons and found that B3LYP provided the best performance for energies. The lower energy for **IB** than **IA** is normally attributed to an inductive stabilization associated with sp^{2}−sp^{3} C−C bonds, which increase in number with increased substitution of a C=C double bond.

The most stable conformer of (*E*)-1,3-pentadiene (**IIB**) is the s-trans structure in Figure 2. The calculated enthalpy difference between 1,4-pentadiene (**IIA**) and **IIB** is −7.9 kcal/mol, which is again close to the experimental result of −7.3 kcal/mol.[1] Approximately 3.3 kcal/mol of the 7.9 kcal/mol arises from the substitution effect, as found in **I**, and the remaining 4.6 kcal/mol can be attributed to stabilization from π-conjugation of the two double bonds. The resonance energy for 1,3-dienes is an old topic, and most values fall in the 4−6 kcal/mol range including the estimate from the experimental data for **I** and **II** in Table 1.[20−22] Incidentally, the ΔG values in Table 1 include the RTln 2 symmetry factor favoring **IIB** and disfavoring **IB**.

(*E*)-2-Butenal (**IIIB**) and (*E*)-3-penten-2-one (**IVB**) have a double bond conjugated with a formyl and an acetyl group, respectively, and are illustrated in Figure 3. The lowest-energy DFT-optimized structure of crotonaldehyde, **IIIB**, is the s-trans form, which has also been observed in electric dipole moment experiments.[23] Prior DFT and ab initio calculations further support the s-trans conformer of **IIIB** as being the lowest in energy.[24,25]

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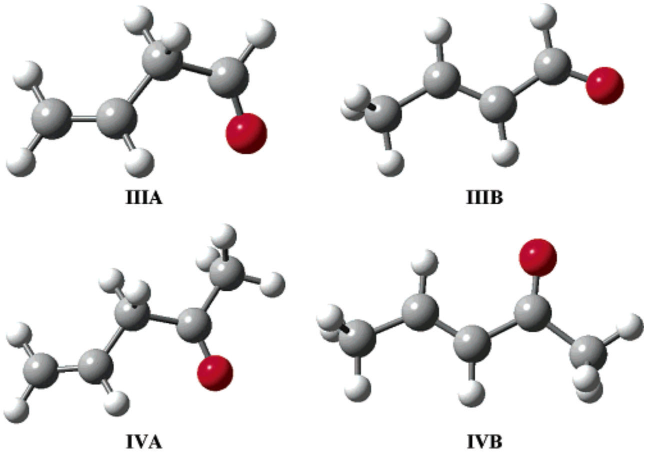

FIGURE 3. Lowest-energy conformers of 3-butenal (**IIIA**), (*E*)-2-butenal (**IIIB**), 1-penten-4-one (**IVA**), and (*E*)-3-penten-2-one (**IVB**).

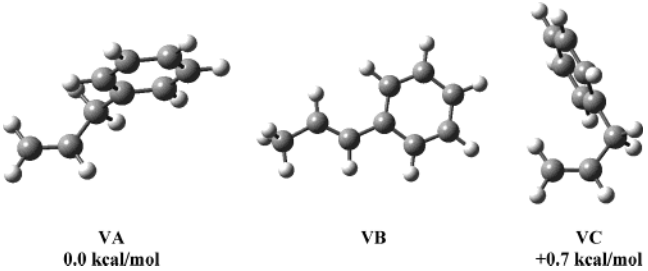

FIGURE 4. Optimized gauche (**VA**) and eclipsed (**VC**) conformers of 3-phenylpropene with their relative energies (B3LYP/6-31G(d)) and (*E*)-1-phenylpropene (**VB**).

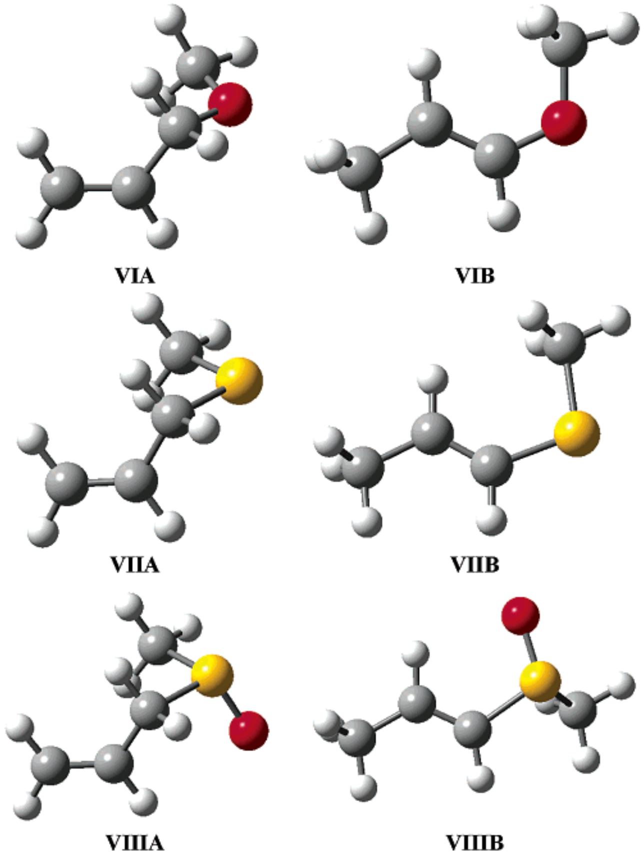

FIGURE 5. Lowest-energy conformers for allyl methyl ether (**VIA**), methyl (*E*)-1-propenyl ether (**VIB**), allyl methyl sulfide (**VIIA**), methyl (*E*)-1-propenyl sulfide (**VIIB**), allyl methyl sulfoxide (**VIIIA**), and methyl (*E*)-1-propenyl sulfoxide (**VIIIB**).

However, the lowest-energy conformer of **IVB** has the s-cis conformation. The s-trans rotamer is computed to be approximately 0.8 kcal/mol higher in energy, which may reflect a small steric differential between the methyl group and oxygen. The aldehyde **III** has the same enthalpic preference for the α,β-unsaturated form as the vinyl analogue **II**. The preference is diminished by 2.2 to −5.6 kcal/mol for the ketone **IV**. The difference can be attributed to the unavoidable steric interactions with the acetyl methyl group in the s-cis and s-trans forms for **IVB**.

The computed enthalpy difference for the phenyl derivatives **VA** and **VB** (−5.8 kcal/mol) is similar to the experimental value of −5.6 kcal/mol and to the difference for the ketones **IV**. Again, the unavoidable steric interactions, when there is no hydrogen at the attachment point for the R group, diminish the preference for the planar conjugated structures (e.g., **VB**). Interestingly, MP2/6-311+G(d,p) results of Panja and Chakraborty found the most stable form of 3-phenylpropene to be the eclipsed structure, **VC**, in Figure 4, where the allyl group is oriented perpendicular to the plane of the benzene ring, and the terminal hydrogen atom is directed toward the π-system.[26] However, they also reported that the preference for the eclipsed conformer decreases at the B3LYP/6-31G(d) level and actually becomes unfavorable by approximately 0.6 kcal/mol relative to the gauche conformer **VA**. The energy difference between **VA** and **VC** calculated here at that level is 0.7 kcal/mol.

The preferred conformer for the conjugated ether **VIB** is s-cis according to the B3LYP/6-31G(d) calculations (Figure 5), which is in agreement with prior HF/3-21G calculations[27] and experiments in the gas phase and solution.[28] The s-cis conformer is also observed in simpler systems such as vinyl alcohols, as exemplified by the 1.4 kcal/mol difference between the s-cis and the s-trans forms for vinyl alcohol at the B3LYP/6-311++G(d,p) level.[29] For allyl methyl ether, **VIA**, the preferred conformer maintains the roughly H-eclipsing C=C geometry found in propene and the staggered preference for the ether fragment, although the energy difference for the C−C−O−C dihedral being gauche or anti is slight. The enthalpic preference for the conjugated isomer **VIB** over the β,γ-isomer **VIA** is −6.4 kcal/mol, while experiments provide an energy difference of −4.8 kcal/mol in DMSO, which places methoxy between vinyl and phenyl for conjugating ability.

Similarly, the most stable conformer of the conjugated sulfide **VIIB** is s-cis, and again the conformer with a

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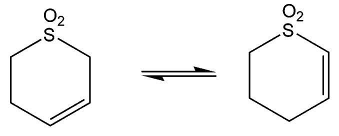
SCHEME 2



XIIA **XIIB**

gauche C−C−S−C dihedral angle is found for allyl methyl sulfide, **VIIA**. The latter preference is also consistent with conformational results for methyl 1-phenylethyl sulfide at the MP2/6-31G(d) level.[30] The enthalpy difference between the two unsaturated isomers for **VII** in Table 1 is similar to that for **I** and does not reveal the benefits of conjugation found for the ether **VIB**. The lessened stabilization with sulfur arises from the longer C−S than C−O bond length, poorer $C_{2p}-S_{3p}$ than $C_{2p}-O_{2p}$ overlap, and the greater mismatch in π-orbital energies; the ionization potentials for dimethyl sulfide, dimethyl ether, and ethene are 8.65, 10.04, and 10.51 eV, respectively.

The computed enthalpic results for the sulfoxide and sulfone analogues (**VIII** and **IX**) show further weakening of the benefits of conjugation (Table 1). The conventional view would be that the greater electron-withdrawing nature of these functional groups as compared to a sulfide is inductively unfavorable for attachment to an sp^2 hybridized carbon; the positive charge on sulfur does increase significantly in progressing from sulfoxides to sulfones.[17] Consistently, the computed enthalpic preferences for conjugation are now 1.2 (sulfoxide) and 2.6 (sulfone) kcal/mol less than that for a methyl group (**I**). Results of experimental studies[3] of base-catalyzed isomerizations for unsaturated sulfides, sulfoxides, and sulfones are in good agreement with the calculated findings, as summarized in Table 1. For cases in which the substitution of the double bond is constant (e.g., $CH_3CH{=}CHCH_2SO_nCH_3 \rightarrow CH_3CH_2CH{=}CHSO_nCH_3$), the β,γ-unsaturated sulfoxides and sulfones are predicted here and observed to be favored, while with sulfides there is little preference, and ethers, amines, carboxylic acids, esters, and nitriles strongly favor the conjugated isomers.[3]

A strong preference for the nonconjugated isomer has also been observed for the six-membered cyclic sulfone in Scheme 2.[31] In fact, base-catalyzed isomerizations starting from either compound only yield **XIIA** with no evidence for the presence of any **XIIB**.[31] The present calculations were extended to these molecules, and the resultant ΔE at 0 K and ΔH and ΔG at 298 K from the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations are 2.5, 2.6, and 2.6 kcal/mol for the reaction in Scheme 2.

The pattern with sulfur in Table 1 extends to the sulfonamide and sulfonate ester analogues, **X** and **XI**. Thus, conjugation with a C=C double bond for sulfur-containing functional groups is uniformly less favorable than substitution by a methyl group. An equilibrium in which we were particularly interested from a synthetic standpoint involved competition between phenyl and sulfonamide groups, $PhCH{=}CHCH_2SO_2NHR \rightarrow PhCH_2CH{=}CHSO_2NHR$; it can now be estimated from Table 1 that the phenyl-conjugated isomer is favored by 5−6 kcal/mol.

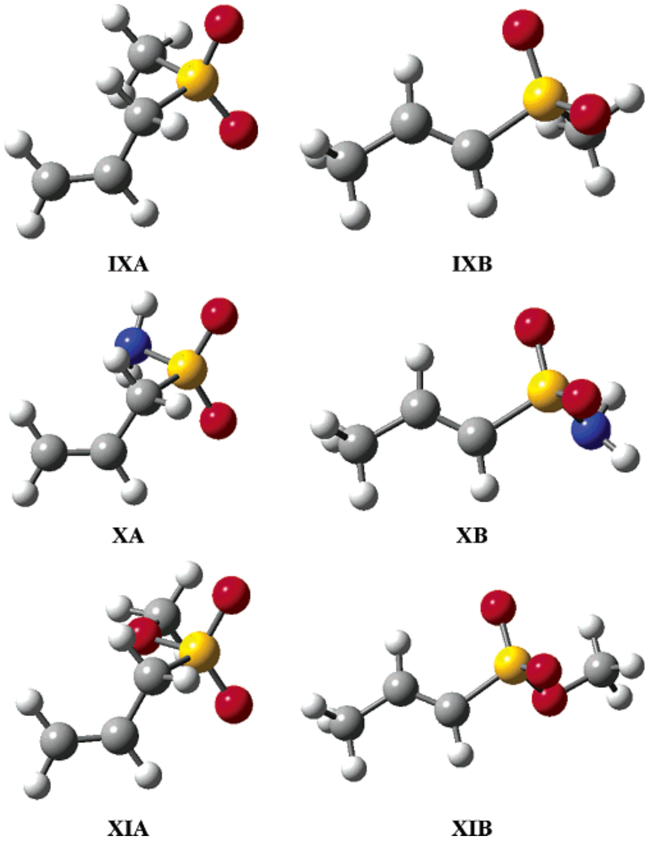

IXA **IXB**
XA **XB**
XIA **XIB**

FIGURE 6. Lowest-energy conformers of allyl methyl sulfone (**IXA**), methyl (*E*)-1-propenyl sulfone (**IXB**), 3-propenesulfonamide (**XA**), (*E*)-1-propenesulfonamide (**XB**), methyl 3-propenesulfonate (**XIA**), and methyl (*E*)-1-propenesulfonate (**XIB**).

On the structural side, the lowest-energy conformers for the sulfoxides, sulfones, sulfonamides, and sulfonate esters in Figures 5 and 6 are analogous; alkyl groups prefer staggered geometries with adjacent sulfonyl groups, and there appears to be an electrostatically attractive 1,5-interaction between an oxygen and an alkenyl hydrogen in every case. The sulfonamides, **XA** and **XB**, also feature the electrostatically favorable eclipsing of the amino hydrogens with the oxygens, which also allows anomeric-like mixing of the nitrogen lone pair with the σ^* orbitals of the S−O bonds. At the B3LYP/6-31G(d) level, rotation of the amino group by 180° costs 2.1 kcal/mol. Prior G2MP2 calculations on model sulfonamides,[32] as well as RHF/6-31+G(d) results,[33] support the preference for conformers of sulfonamides with the amino hydrogens eclipsing the oxygens. Another computational study that should be noted is that of Jenks et al.[34] From MP2/6-31G(d,p)//RHF/6-31G(d,p) calculations, they found that S=O bond strengths and lengths in simple sulfoxides are not affected by introduction of adjacent C=C double bonds.[34] This is consistent with the energetic results and

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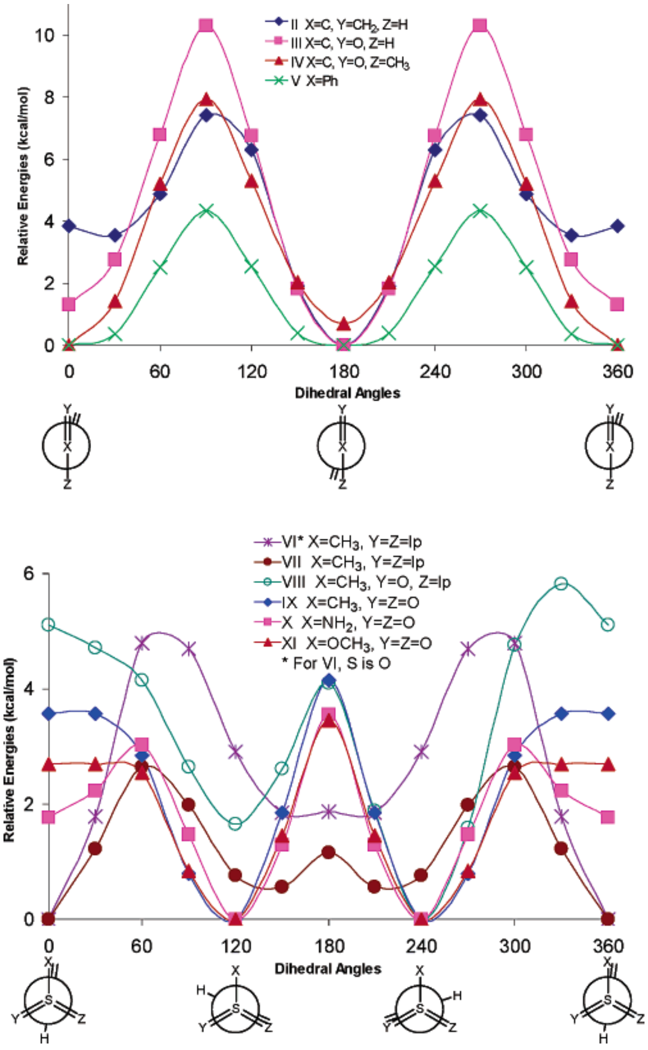

FIGURE 7. B3LYP/6-31G(d) torsional energy profiles for **IIB**−**VB** (top) and **VIB**−**XIB** (bottom).

the minimal S═O bond length change (<0.001 Å) observed in this study between the α,*β*- and the *β*,*γ*-unsaturated compounds **VIII**−**XI** at the B3LYP/6-31G(d) level.

Torsional Energy Profiles. In the process of establishing the lowest-energy conformers, torsional energy profiles were computed at the B3LYP/6-31G(d) level for rotations about the C_α−C, O, S bonds in the compounds. The results using 30° increments for the C═C−(C,O,S)−X dihedral angle for the α,*β*-unsaturated compounds, **IIB**−**XIB**, are illustrated in Figure 7 and reflect any *π*-conjugative effects. The analogous results for the *β*,*γ*-unsaturated isomers mostly show the expected roughly 3-fold symmetry for rotation about an RCH_2−XY bond with barrier heights of 2−4 kcal/mol, and they are not illustrated here. For some of the α,*β*-unsaturated compounds, results of similar torsional profile calculations have been reported by other groups.[14,30,35,36] The present B3LYP/6-31G(d) results provide a uniform treatment.

The favored conformations for the α,*β*-unsaturated vinyl and formyl derivatives (**II** and **III**) have a (C,O)−C−C_α═C_β dihedral of 180°, while the acetyl analogue **IV** prefers the s-cis (0°) structure, as illustrated in Figures 2, 3, and 7. The maximal rotational barrier heights are >7.5 kcal/mol for **II**−**IV** and occur near 90°. Wiberg and co-workers have performed calculations on 1,3-butadiene through the G2 level and have found a rotational barrier of approximately 6 kcal/mol, which is somewhat less than the ca. 7.5 kcal/mol obtained here for (*E*)-1,3-pentadiene.[35,36] For crotonaldehyde (**IIIB**), the rotational barrier is about 7.5 kcal/mol from experiments[37,38] but is calculated to be higher in this study, 10.5 kcal/mol. For (*E*)-1-phenylpropene, **VB**, the 0 and 180° rotamers are identical, and the rotational barrier is approximately 4.0 kcal/mol. This is qualitatively consistent with the results for **IIB**. Specifically, the s-cis/s-trans energy difference of 4 kcal/mol in that case gives an estimate of the steric strain energy for an s-cis diene. The barrier height of ca. 7.5 kcal/mol for the s-trans to s-cis conversion for **IIB** includes the loss of *π*-conjugation and a significant part of this strain increase. So, when the s-cis and s-trans forms are identical as for **VB**, it is reasonable that the barrier height is lowered by several kcal/mol.

Rotational barrier heights have been calculated at the MP2/6-31G(d)//RHF/6-31G(d) level by Schade and Schleyer for vinyl alcohol and vinyl thiol; the results are 5.6 and 2.0 kcal/mol for rotation about the C−O and C−S bonds, respectively.[16] These values are similar to those obtained here for methyl vinyl ether (**VIB**) and methyl vinyl sulfide (**VIIB**), ca. 5.0 and 2.5 kcal/mol, respectively (Figure 7, bottom). The lower barriers for the sulfur derivatives are consistent with the lack of *π*-conjugation in these molecules. Continuing in the bottom part of Figure 7, the torsional profiles for α,*β*-unsaturated sulfur-containing molecules, **VIIB**−**XIB**, are all symmetrical about 180° except for the sulfoxide since it is chiral. The R enantiomer of **VIIIB** is illustrated in Figure 5, and it prefers a C═CSC dihedral angle near 240° (Figures 5 and 7). As noted previously, the sulfone, sulfonamide, and sulfonate ester, **IXB**−**XIB**, prefer similar conformers with the C═C−SC, C═C−SN, and C═C−SOR dihedral angles near ±120° (Figure 7), which aligns an oxygen with the hydrogen on C_β. The barrier maximum for these molecules occurs at 180° with magnitudes near 4 kcal/mol. Overall, the smaller rotational barriers for **VIIB**−**XIB** as compared to **IIB**−**IVB** reflect the weaker conjugative interactions for the sulfur-containing molecules, which stems from the longer C−S bonds than C−C bonds and poorer 2p−3p overlap than 2p−2p.

Conclusion

The present DFT results have provided quantitative assessment for the energetic effects of *π*-conjugation between a C═C double bond and a variety of functional groups. Vinyl, phenyl, carbonyl, and alkoxy groups are all found to be significantly more stabilizing than a methyl substituent, while sulfur-based functional groups provide less conjugative stabilization than a methyl

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group. Notably, for equilibria involving sulfinyl and sulfonyl derivatives in which the degree of substitution of the double bond is constant (e.g., $CH_3CH{=}CHCH_2SO_nX \rightarrow CH_3CH_2CH{=}CHSO_nX$), the nonconjugated isomer is favored by 1−3 kcal/mol. Accord between the computed thermodynamic results and available experimental data is uniformly high. Detailed structures have also been provided to illustrate the lowest-energy conformers for allyl-X ($H_2C{=}CHCH_2X$) and 1-propenyl-X ($H_3CCH{=}CHX$) compounds. In addition, torsional energy profiles have been provided for the latter isomers to provide further characterization of the π-conjugative interactions.

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Supporting Information Available: Cartesian coordinates and energetics for all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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