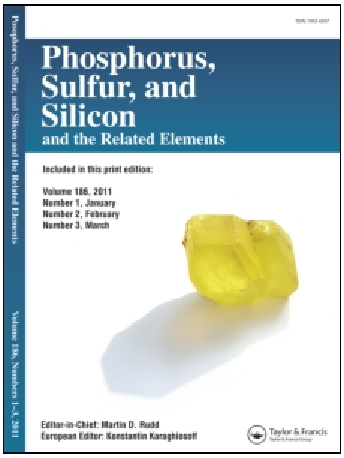

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Sulfur Versus Oxygen in Interaction with the Double Bond: AB Initio Study of Electronic Structure and Prototropic Rearrangement of 1-Methoxy-2-propene and 1-Methylthio-2-propene

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SULFUR VERSUS OXYGEN IN INTERACTION WITH THE DOUBLE BOND: AB INITIO STUDY OF ELECTRONIC STRUCTURE AND PROTOTROPIC REARRANGEMENT OF 1-METHOXY-2-PROPENE AND 1-METHYLTHIO-2-PROPENE

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*The ab initio calculations of 1-methoxy-2-propene (**1**), 1-methylthio-2-propene (**2**), and their anions are performed using the RHF/6-31+G* geometry optimization followed by MP2/6-31+G* energy calculations. Both **1** and **2** are found to rearrange toward 1-substituted 1-propenes with a comparable exothermic effect. However, the proton abstraction energies of **1** and **2** differ significantly. So, the acidity of propene is just slightly affected by the OCH$_3$ group while the SCH$_3$ group decreases its proton abstraction energy by 17.5 kcal/mol. Changes in charge distribution, bond lengths and bond orders suggest the negative hyperconjugation to stabilize anions of **2** but not that of **1**. This divergence is explained with a difference in sulfur and oxygen electronegativity. The* d*-functions of both sulfur and oxygen act in polarization. The* Z*-isomer of anion **1** is found to be by 2.9 kcal/mol more stable than its* E*-isomer, this could provide a predominant kinetic formation of the less stable* Z*-isomer of 1-methoxy-1-propene under base catalysis.*

Keywords: 1-Methoxy-2-propene; 1-methylthio-2-propene; ab initio calculations; anions; isomerism

INTRODUCTION

Reactions involving migration of a multiple bond and base-catalyzed isomeric transformations are known to be characteristic of unsaturated

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compounds, in particular, alkenes, alkynes, and their derivatives containing a heteroatom in addition to the multiple bond.[1–5] In this case the multiple bond usually migrates toward the heteroatom,[4,5] which is explained by a decrease in the energy due to conjugation between the lone electron pair of the heteroatom and the π-system.

Usually, prototropic isomerizations of unsaturated compounds accompanied by the multiple bond migrations are described[1–3] as two-stage transformations with intermediate formation of carbanions. The direction of the multiple bond migration depends on the relative stability of the anions, ease of their mutual transformations, and the electron distribution determining the reprotonation position.

The isomerization of 1-methoxy-2-propene (**1**) yielding 1-methoxy-1-propene and of the analogous conversion of 1-methylthio-2-propene (**2**) to 1-methylthio-1-propene

$$X\text{—}CH_2\text{—}CH\text{=}CH_2 \rightarrow X\text{—}CH\text{=}CH\text{—}CH_3, \quad X\text{=}OCH_3\,(\mathbf{1}), SCH_3\,(\mathbf{2}). \quad (1)$$

are convenient model reactions for the further elaboration of the neighboring heteroatom effect on the proton transfers. For both methylthiopropene and methoxypropene the 1-propenyl form dominates over the 2-propenyl form.[6–8] However, **2** reacts more readily then **1**, reflecting a higher stability of the corresponding thiocarbanion.[9]

Another aspect of the reaction (1) concerns the relative stability of *E*- and *Z*-isomers of the products. Although *E*-isomers of 1-substituted **1**-propenes are usually the most stable ones, the base catalyzed reactions of 1,3-hydrogen shift often lead to less stable *Z*-forms.[3] In particular, it takes place in the 1-methoxy-2-propene rearrangement to 1-methoxy-1-propene in *tert*-C_4H_9OK solution.[6] One can suppose a kinetically controlled formation of *Z*-1-methoxy-1-propene to be caused by the difference in the rates of the corresponding anions formation.

In this work we have performed for the first time an ab initio comparative investigation of the fundamental features of the **1** and **2** prototropic isomerization focusing upon the relative stability and the structural preferences of the corresponding ions. The geometry optimization was carried out at the RHF/6-31+G* level followed by MP2/6-31+G* energy calculations using the standard GAMESS program.[10] The charge difference maps were plotted using the MOLDEN program.[11]

RESULTS AND DISCUSSION

The unsubstituted propene molecule has a cisoid conformation with respect to the rotation about the C(1)—C(2) bond corresponding to the minimal repulsion between the electrons of the C—H σ- and C(2)=C(3)

π-bonds. Hence, the XCH_3 group in **1** and **2** may take either *cis*- or *gauche*-positions relative to the vinyl fragment. Our computational results predict the *gauche*-conformers to be the most stable ones for the both molecules. The *cis*-conformer **1** is only by 0.10 kcal/mol less stable than the *gauche* one and rearranges into *gauche*-form with the activation barrier of 3.01 kcal/mol. The rotational barrier separating two *gauche*-structures in **1** amounts to 1.32 kcal/mol.

The *cis*-conformer **2** is by 1.87 kcal/mol higher in energy and rearranges into *gauche*-form with the activation barrier of 0.57 kcal/mol. The rotational barrier separating two *gauche*-structures in **2** amounts to 0.97 kcal/mol. The *gauche*-conformation of **2** was established in Raman[12] and microwave[13] experiments, while the *cis*-conformation is reported to be at least by 0.5 kcal/mol less stable.[13]

Since a mechanism of the reaction (1) assumes elimination of a proton from the *gauche*-position, *E*-anions should be derived from *gauche*-conformers of **1** and **2**, while *Z*-conformers are related to *cis*-structures. However, the internal rotation about the C(1)—C(2) bond in **1** and **2** proceeds sufficiently free and one can examine isomerization and anion formation in relation to the most stable conformers (Figure 1).

For both **1** and **2** the isomerization (1) leads to a comparable decreasing of the total energy. The MP2 energy change for the rearrangement of **1** to to *Z*-1-methoxy-1-propene–4.79 kcal/mol, agrees with the experimental reaction enthalpy—4.83 ± 0.05 kcal/mol, in DMSO solution.[14] The experimental enthalpy of the **2** isomerization to *E*-1-methylthio-1-propene in DMSO is -3.32 ± 0.12 kcal/mol,[15] and our calculated energy change in is -4.03 kcal/mol. Finally, MP2 calculated *E*-1-methoxy-1-propene was found to be more stable than *Z*-isomer by 1.08 kcal/mol, and the experimental value is -0.913 ± 0.57 kcal/mol.[16] So, the enthalpy changes could explain neither difference in **1** and **2** behavior nor preference of *Z*-1-methoxy-1-propene formation.

The ionization energies are summarized in Table I. The calculated values are overestimated with respect to observed ones. However, the relative energies reveal a good agreement of theoretical results and experimental data. Except for the *E*-$[CH_3OCH_2CHCH_2]^-$ anion, the absolute errors are less than 1 kcal/mol. In the former case the difference can be attributed to the uncertain structure of the anion under experimental conditions. As it will be discussed later, the *Z*-isomer of this anion is more stable than the *E*-isomer and should dominate in gas phase giving the principal contribution to the observed proton loss energy.

The results obtained characterize the feature of the allyl system. The effective delocalization of negative charge over π-MO stabilizes the allyl anion and decreases ionization energy of propene by 27.7 kcal/mol as compared to the propane molecule. Further substitution of methyl

TABLE I Proton Affinities (kcal/mol)

			Relative to propane		
Anion	Calc	Exp	Calc	Exp	Diff
$CH_3CH_2CH_2^-$	425.9	419.4 ± 2.0[17]	0.0	0.0	0.0
$CH_2CHCH_2^-$	398.2	390.7 ± 2.1[18]	−27.7	−28.7	1.0
Z-$[CH_3OCH_2CHCH_2]^-$	394.5	388.7 ± 4.1[19]	−31.4	−30.7	−0.7
E-$[CH_3OCH_2CHCH_2]^-$	397.4		−28.5		2.2
Z-$[CH_3SCH_2CHCH_2]^-$	380.6	373.4 ± 4.1[19]	−45.3	−46.0	0.7
E-$[CH_3SCH_2CHCH_2]^-$	380.8		−45.1		0.9

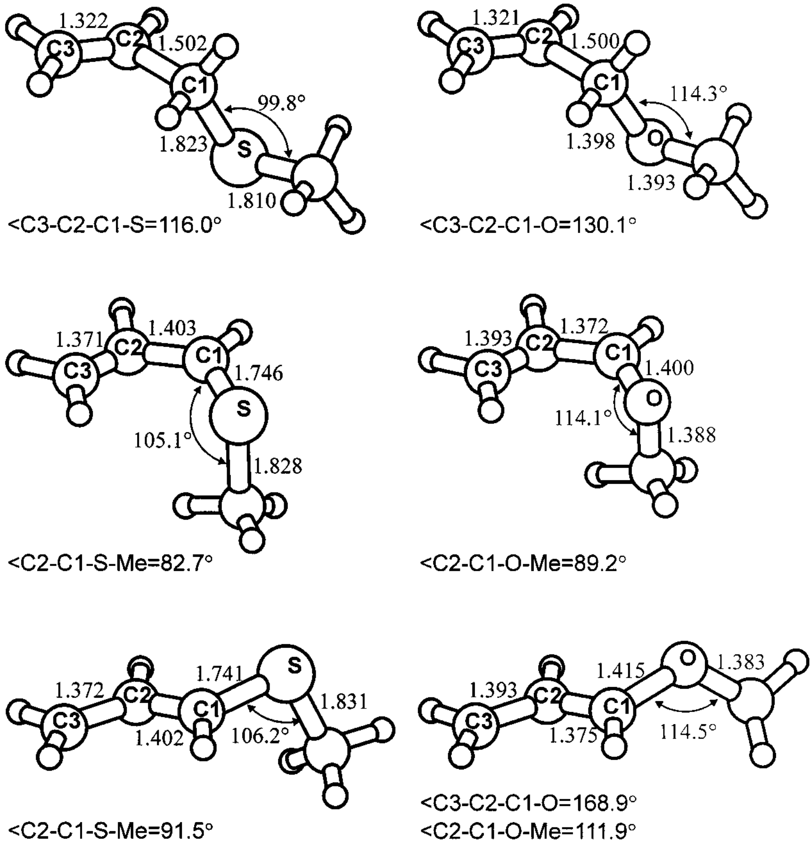


FIGURE 1 RHF/6-31+G calculated structures of 1-methylthio-2-propene (**1**), 1-methoxy-2-propene (**1**), and their anions. Bond lengths in Å.

hydrogen in propene with the OCH_3 group reduces deprotonation energy only by 0.8–3.7 kcal/mol in contrast to the effect of oxygen electronegativity in dimethyl ether that lowers the energy by 10–12 kcal/mol relative to methane and propane. On the contrary, the presence of the SCH_3 group in **2** leads to further decrease of the proton abstraction energy by 17.5 kcal/mol.

The origin of the difference in the acidity between sulfides and their oxygen analogs is commonly explained by the sulfur *d*-orbital participation in stabilization of the anions.[9] Indeed, the inclusion of *d*-functions in the basis set leads to dramatic changes in geometry and energies of molecules containing the second row atoms. On the other hand, these changes turn out to be similar for both neutral molecules and their anions. The energy of proton abstraction in dimethylsulfide changes only by 1.0–1.6 kcal/mol when polarization *d*-functions are added,[20] and the effect of diffuse *s*- and *p*-functions resulting in the energy difference change of 11.9 kcal/mol is more significant.

Actually, the meaning of the basis *d*-functions to be the atomic orbitals is not a correct one. Properly, the only role of basis functions in calculations is to provide the total electron distribution to be described as accurately as possible. Since the properties of a molecule ultimately depend only on this distribution, it would seem more appropriate to examine the changes in total electron density under the increase of the basis set flexibility. These changes may be seen from charge density difference maps.

Figure 2 shows density difference plots between wave functions of **1**, **2**, and their anions calculated using the 6-31+G* basis set and the same except *d*-functions of sulfur and oxygen. The change in charge density distribution is seen to be similar to that for a neutral molecule and its anion and thus should lead to similar changes in energy. In **2**, the inclusion of sulfur *d*-functions leads to an increase in the C—S bonds charge density, which is taken from the region of the sulfur lone pairs. The same effect occurs in the anion. However, in **1** and its anion, the oxygen *d*-functions affect a charge distribution in a similar manner. The inclusion of these functions results in the shifting of charge density from the oxygen lone pair to the C—O bonds. Moreover, the effect of *d*-function is of a comparable extent in **1** and **2**. Thus, the *d*-functions of both sulfur and oxygen improve the description of the binding area and should be characterized as polarization functions.

The useful information of the divergence between **1** and **2** can be obtained by examining the structural parameters and their changes in the process of anion formation (see Figure 1).

Neither *E*- nor *Z*-isomer of the anion of **2** should be suggested as the preferable one. The Hartree-Fock level calculations predict both

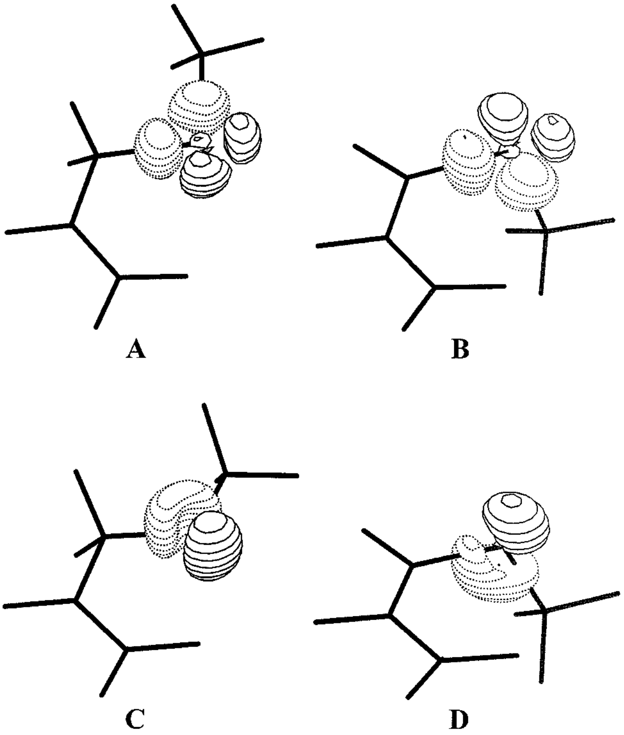
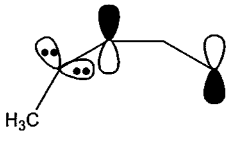
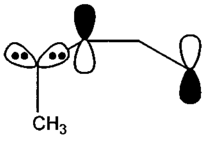


FIGURE 2 Charge density difference maps showing the effect of *d*-functions for *cis*-conformers of **1** (A), **2** (C) and their *Z*-anions (B and D). The contour level is 4×10^{-3} e/au.^{3}

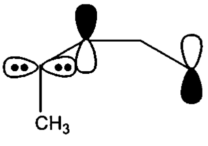
isomers to have the same energy, and the *Z*-isomer is found to be only by 0.17 kcal/mol more stable when calculated using the MP2/6-31+G* approach. The SC(1)C(2)C(3) chain in these anions has a planar structure with S—Me bonds approximately perpendicular to this plane (see Figure 1). This conformation preference could be discussed using a hybrid lone pair model. The X—Me bond should be oriented to minimize a repulsion between the C(1) p_π-AO and two lone pairs of sulfur or oxygen. Two different conformations **a** and **b** look to be appropriate for the pure sp^3-hybrid.



a



b



c

In the *gauche*-conformation **a**, the in-plane lone pair does not interact with the allyl p_π-AOs, while the latter repulsion with the other pair and the X—Me bond is relatively strong. In the perpendicular conformation **b**, the p_π-system repulsion with the X—Me bond is the strongest, and the interaction with any of lone pairs is less so. As a contribution of s-AO into the lone pair hybrid increases, the relative stability of the perpendicular conformation grows, and this structure should be the most stable when the s-AO contribution reaches a value of 50% (**c**).

The C(1)SMe bond angle in the E-isomer of anion **2** is calculated to be 106.2° and the torsion angle C(2)C(1)SMe is 91.5°. The energy localized lone pairs of sulfur contain approximately a 40% contribution of s-AO. In the Z-isomer, the same character of the lone pairs is obtained. However, the perpendicular conformation of this anion is sufficiently distorted and indicates shifting of the methyl group toward the C(3) atom. The HOMO analysis suggests a weak interaction of the S—Me bond with the C(3) p_π-AO in a binding manner.

In contrast to **2**, the E-anion of **1** has the C(1)OMe bond angle of 114.5° and the C(2)C(1)OMe torsion angle of 111.3° that corresponds to the *gauche*-conformation **a**. The localized oxygen lone pairs consist of ~30% s-contribution. The perpendicular structure is only 0.2 kcal/mol higher in energy, but this conformation is a nonstationary point on the potential energy surface. Additionally, the C(1)—O bond in the E-anion of **1** is sufficiently distorted from the allyl plane. One can suppose that there is no satisfactory balance of repulsive interactions when the E-isomer of anion **1** is formed.

Finally, the Z-anion of **1** has again a perpendicular structure. This isomer is by 2.9 kcal/mol more stable than the E-isomer, and it should lead to predominate kinetic formation of Z-1-methoxy-1-propene in the reaction (1). However, a relatively large p-contribution to the lone pairs in the anions of **1** makes these anions less stable than those derived from **2**.

The conversion of parent molecules to the corresponding anions leads to different changes in structures (see Table II). The S—C(1) bond in **2** shortens significantly when anions are formed, and the S—Me bond length increases. The RHF/6-31G* S—C(1) bond order grows from 0.956 in **2** to 1.060 in its Z-anion and the S—Me bond order decreases from 0.958 to 0.891. This indicates the strengthening of the S—C(1) bond and weakening of the S—Me one.

The opposite occurs in **1**. The anion formation is accompanied by some lengthening of the O—C(1) bond and shortening of the O—Me bond with corresponding changes in bond orders from 0.844 to 0.802 for the O—C(1) and from 0.866 to 0.922 for the O—Me bonds.

TABLE II Calculated Bond Length Changes (Å). The Conformations of the Parent Molecules Are Marked in *c* (*cis*) and *g* (*gauche*), *E* and *Z* Mark the Isomers of the Resulting Anions

	1			**2**		
Bond	$g \to Z$	$c \to Z$	$g \to E$	$g \to Z$	$c \to Z$	$g \to E$
C(2)—C(3)	0.072	0.073	0.072	0.049	0.050	0.050
C(1)—C(2)	−0.128	−0.129	−0.125	−0.099	−0.107	−0.100
X—C(1)	0.007	0.009	0.021	−0.077	−0.067	−0.082
Me—X	−0.005	−0.005	−0.009	0.018	0.018	0.021

The structure of the allyl fragment in the anions derived from **1** also differs from the structure in the anions of **2**. In the *Z*-anion **2**, the terminal C(2)—C(3) bond is still shorter than the C(1)—C(3) one (1.371 and 1.403 Å respectively) and the bond orders are 1.654 and 1.337 respectively. In the analogous anion **1** the bond length and bond order changes are more dramatic. The C(1)—C(2) bond shortens from 1.501 Å in the neutral **1** to 1.372 Å in the anion, and its order increases from 1.040 up to 1.525, while the C(2)—C(3) bond length increases from 1.320 Å to 1.393 Å. The structural differences conform to the divergence in the negative charge distribution. So, the terminal CH_2 group in the anions of **2** is charged by −0.375 a.u., while the negative charge located on this group in **1** is ~0.10 a.u. higher.

The data of Table III indicate a significant difference in the participation of SCH_3 and OCH_3 in the overall negative charge distribution. The formation of the anion of **1** does not lead to much change at oxygen, and most of the charge remains at the allyl system. In contrast to OCH_3 in **1**, the SCH_3 group in **2** receives approximately 15% of extra

TABLE III Löwdin Charge Shifts (a.u.). The Conformations of the Initial Molecules are Marked in *c* (*cis*) and *g* (*gauche*), *E* and *Z* Mark the Isomers of the Resulting Anions

	1			**2**		
Group	$g \to Z$	$c \to Z$	$g \to E$	$g \to Z$	$c \to Z$	$g \to E$
$C(3)H_2$	−0.525	−0.494	−0.512	−0.393	−0.394	−0.392
C(2)H	0.012	−0.021	0.040	0.033	0.041	0.046
C(1)H	−0.428	−0.430	−0.412	−0.495	−0.492	−0.470
X	0.007	0.003	−0.018	−0.055	−0.051	−0.069
Me	−0.067	−0.059	−0.098	−0.090	−0.104	−0.114
Allyl	−0.941	−0.945	−0.884	−0.855	−0.845	−0.816
XCH_3	−0.060	−0.056	−0.116	−0.145	−0.155	−0.183

negative charge when the anion is formed, and the largest share of this is accepted by a methyl group. The changes in the charge distribution, the bond lengths, and bond orders suggest the stabilization of anions of **2** to be described in terms of the negative hyperconjugation mechanism involving double bond—no bond resonance structures such as

$$H_3C{-}S{-}CH{=}CH{-}CH_2^- \leftrightarrow H_3C{-}S{-}CH^-{-}CH{=}CH_2$$
$$\leftrightarrow H_3C^-\ S{=}CH{-}CH{=}CH_2.$$

Due to the comparable electronegativity of carbon and sulfur, this mechanism is available in **2** and can not be realized in **1** because of the large electronegativity difference between carbon and oxygen that prevents the negative charge shift towards a methyl group. That corresponds to the only two resonance structures:

$$H_3C{-}O{-}CH{=}CH{-}CH_2^- \leftrightarrow H_3C{-}O{-}CH^-{-}CH{=}CH_2$$

in agreement with anion structure and charge distribution discussed above.

CONCLUSIONS

The MP2/6-31+G* calculations predict a comparable energy decreasing for the 1-methoxy-2-propene isomerization to 1-methoxy-1-propene and the 1-methylthio-2-propene isomerization to 1-methylthio-1-propene. However, the intermediate carbanion of 1-methylthio-2-propene can be formed sufficiently more easy than the corresponding anion of 1-methoxy-2-propene. The acidity of propene is slightly affected by the OCH_3 group while the SCH_3 group decreases its proton abstraction energy by 17.5 kcal/mol. This divergence could not be described with the participation of the sulfur *d*-AOs in the stabilization of the anion of 1-methylthio-2-propene. The *d*-functions of both sulfur and oxygen do act as polarization functions. Changes in charge distribution, bond lengths and bond orders under anions formation suggest the negative hyperconjugation to stabilize anions of 1-methylthio-2-propene but not of 1-methoxy-2-propene by reason of the relatively high electronegativity of oxygen. The larger *s*-contribution to the sulfur lone pairs decreases the repulsion with the p_π of adjacent carbon in the anions of 1-methylthio-2-propene as compared to the anions of 1-methoxy-2-propene. This difference could cause an extra stability of thiocarbanions.

The *Z*-isomer of the anion of 1-methoxy-2-propene is found to be by 2.9 kcal/mol more stable than the *E*-isomer. This could provide a predominant kinetic formation of the less stable *E*-isomer of 1-methoxy-1-propene in base media. The anions of 1-methylthio-2-propene do not show any preference.

REFERENCES

[1] J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure* (Wiley, New York, 1985).
[2] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* (Cornell University Press, Ithaca, New York, 1953).
[3] D. J. Cram, *Fundamentals of Carbanion Chemistry* (Academic Press, New York and London, 1965).
[4] D. J. Pasto and J. E. Brohby, *J. Org. Chem.*, **56,** 4554 (1991).
[5] A. S. Atavin, V. I. Lavrov, O. N. Sidorova, and B. A. Trofimov, *Zh. Org. Khim.*, **7,** 235 (1971) [*J. Org. Chem. USSR*, 1971, 7 (Engl. Transl.)].
[6] C. C. Price and W. H. Snyder, *J. Am. Chem. Soc.*, **82,** 1773 (1961).
[7] D. E. O'Connor and W. I. Lyness, *J. Am. Chem. Soc.*, **85,** 3044 (1963).
[8] D. E. O'Connor and W. I. Lyness, *J. Am. Chem. Soc.*, **86,** 3840 (1964).
[9] K. F. Reid, *Properties and Reactions of Bonds in Organic Molecules* (Longmans, London, 1968).
[10] M. W. Schmidt, K. K. Baldridge, J. A. Boatz et al., *J. Comput. Chem.*, **14,** 1347 (1993) [www http://www.msg.ameslab.gov/GAMESS/GAMESS.html].
[11] G. Schaftenaar and J. H. Noordik, *J. Comput.-Aided Mol. Design*, **14,** 123 (2000) [www http://www.caos.kun.nl/ schaft/molden/molden.html].
[12] M. T. Devlin, G. Barany, and I. W. Levin, *J. Mol. Struct.*, **238,** 119 (1990).
[13] A. C. Fantoni, *J. Mol. Struct.*, **243,** 131 (1991).
[14] E. Taskinen, *Tetrahedron*, **49,** 11389 (1993).
[15] R. Kimmelma, *Acta Chem. Scand.*, **42,** 550 (1988).
[16] T. Okuyama, T. Fueno, and J. Furukawa, *Tetrahedron*, **25,** 5409 (1969).
[17] C. H. DePuy, S. Gronert, S. E. Barlow, V. M. Bierbaum, and R. Damrauer, *J. Am. Chem. Soc.*, **111,** 1968 (1989).
[18] J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **101,** 6047 (1979).
[19] G. D. Dahlke and S. R. Kass, *J. Am. Chem. Soc.*, **113,** 5566 (1991).
[20] K. B. Wiberg and H. Castejon, *J. Am. Chem. Soc.*, **116,** 10489 (1994).