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Oxygen-by-Sulfur Substitution in CH₃OCH₂CH₂OH: An ab Initio Comparative Study of Conformational Effects and Intramolecular Interactions

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Conformational energies, structural parameters and vibrational frequencies for the tgg′, ggg′, ttg, and ttt conformers of CH₃XCH₂CH₂YH (X, Y = O, S) have been determined by MO ab initio calculations at the MP2/6-31G* level. The results show that the relative strength of the intramolecular X···HY interaction in tgg′ and ggg′ conformers diminishes gradually along the series of molecules (O,O) → (O,S) → (S,O) → (S,S), as the X···HY contact distance increases by ca. 2 × 10 pm for each of these substitutions. For the (O,O) and (O,S) molecules, the CX—CC trans form is favored over the gauche arrangement, whereas for the (S,O) and (S,S) molecules, the gauche conformation is more stable. In addition, the oxygen-by-sulfur substitution in the YH bond increases the relative stability of the CC—YH gauche form with respect to the trans arrangement. In turn, gauche,gauche′ arrangements for the XC—CY and CC—YH axes, respectively, lead to closing of intramolecular rings through X···HY attractive interactions, hence contributing to improve the stability of the conformations with those dihedral arrangements.

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1. Introduction

Among the most relevant conformers of 2-methoxyethanol (CH₃O—CH₂—CH₂—OH: tgg′, ggg′, ttg, and ttt), tgg′ and ggg′ are more stable than ttg and ttt, and tgg′ is 6—7 kJ mol⁻¹ more stable than ggg′[1] The relative stability of gauche and gauche′ arrangements in the second and third dihedral angles, COC⁻ᵍC⁻ᵍ′OH, with respect to their tg and tt counterparts results mainly from the formation of five membered intramolecular rings due to O···H—O hydrogen bonds in the tgg′ and ggg′ conformations. Competition between conformational effects and intramolecular hydrogen-bonding interactions gives rise to interesting structural and vibrational features. While a number of studies of these effects have been carried out in our laboratory,[2,3] further understanding of the interplay between conformational effects and intramolecular hydrogen-bonding interactions requires the possibility of varying those effects in a systematic way and simultaneously modulating the X···HY interactions. To this end, oxygen-by-sulfur substitutions in CH₃OCH₂CH₂OH were considered, and calculations at the MP2/6-31G* level were carried out using the *Gaussian 92* program system.[4] Fully optimized geometries of the four above-mentioned relevant conformations of CH₃XCH₂CH₂YH (X, Y = O, S) are identified by a letter acronym which specifies the dihedral arrangements from left to right in CX⁻ᵃC⁻ᵇC⁻ᶜYH (t, g, and g′ designate trans, gauche, and gauche′ conformations, respectively). The absolute errors in bond lengths and bond angles with respect to the equilibrium geometrical parameters are less than 1 pm and 0.1,° respectively, and the stopping criterion for the SCF iterative process required a density matrix convergence of less than 10⁻⁸. Conformational energy differences, structural parameters, normal modes of vibration, and vibrational frequencies (calculated with the ab initio derived force fields) are herein analyzed and discussed.

Figure 1. Conformational energy differences (×10⁻³Eₕ; 1 Eₕ = 2625.5 kJ mol⁻¹) between tgg′, ggg′, ttg, and ttt conformers of CH₃XCH₂-CH₂YH (X, Y = O, S). MP2 and HF-MP2 stand for the MP2/6-31G* energy and correlation correction with respect to the 6-31G* energy value, respectively.

2. Results and Discussion

Energies and Structures. Figure 1 presents conformational energy differences and correlation corrections obtained at the MP2/6-31G* level of calculation with respect to 6-31G* energy values, for the tgg′, ggg′, ttg, and ttt conformers of CH₃XCH₂-CH₂YH (X, Y = O, S). The following important conclusions can be drawn from this figure:

(i) Starting with the tgg′ and ggg′ conformers which are intramolecularly hydrogen bonded in 2-methoxyethanol,[1] it is found that, for ether molecules (X = O), tgg′ is more stable than ggg′, whereas ggg′ is more stable than tgg′ for thioether molecules (X = S). The absolute values of the ggg′—tgg′ energy differences are approximately equal for the molecules in each of these groups, in particular, ca. 6 kJ mol⁻¹ for X = O (CH₃OCH₂CH₂OH and CH₃OCH₂CH₂SH), and ca. 4 kJ mol⁻¹ for X = S (CH₃SCH₂CH₂OH and CH₃SCH₂CH₂SH). By comparing the energies of the tgg′ and ggg′ conformers, it can be concluded that the CO—CC skeleton stabilizes the trans form

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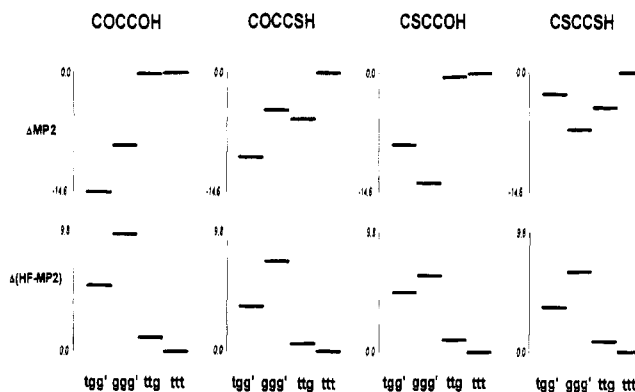⊗ Abstract published in *Advance ACS Abstracts*, October 15, 1995.

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O-by-S Substitution in CH$_3$OCH$_2$CH$_2$OH

J. Phys. Chem., Vol. 99, No. 45, 1995 **16587**

TABLE 1: Energy Differences and Changes in Geometrical Parameters for the tgg' and ggg' Conformers of CH$_3$XCH$_2$CH$_2$YH (X, Y = O, S) (MP2/6-31G* Calculations)

	COCCOH		COCCSH		CSCCOH		CSCCSH	
	tgg'	ggg'	tgg'	ggg'	tgg'	ggg'	tgg'	ggg'
CXCC,XCCY,CCYH	173, 60, −50	82, 54, −42	184, 65, −55	74, 59, −44	211, 67, −58	75, 61, −56	190, 73, −60	72, 67, −58
ΔE/kJ mol⁻¹	0.0	6.3	0.0	5.4	4.4	0.0	4.1	0.0
Δ angles/deg								
CXCC	0 (173)	0 (82)	11	−8	38	−7	17	−10
XCCY	0 (60)	0 (54)	5	5	7	7	13	13
CCYH	0 (−50)	0 (−42)	−5	−2	−8	−14	−10	−16
CXC	0 (112)	0 (113)	0	0	−12	−13	−13	−13
XCC	0 (106)	0 (110)	2	3	4	3	5	5
CCY	0 (110)	0 (110)	3	2	2	2	4	5
CYH	0 (105)	0 (105)	−10	−10	2	2	−8	−9
X···HY	0 (111)	0 (115)	−6	−5	1	−2	−3	−5
Δ bond lengths/pm								
CX	0 (142)	0 (142)	0	0	39	39	39	39
XC	0 (142)	0 (143)	0	−1	40	39	40	38
CC	0 (151)	0 (152)	0	0	1	0	2	1
CY	0 (142)	0 (142)	40	40	0	0	40	40
YH	0 (97)	0 (98)	37	36	0	0	38	36
X···H(Y)	0 (225)	0 (222)	26	22	43	43	60	64
Δ charges/e								
C	0.0 (−0.2)	0.0 (−0.2)	0.0	0.0	−0.4	−0.4	−0.4	−0.4
X	0.0 (−0.6)	0.0 (−0.6)	0.0	0.0	0.7	0.7	0.7	0.7
C	0.0 (0.0)	0.0 (0.0)	0.0	0.0	−0.5	−0.5	−0.5	−0.5
C	0.0 (0.0)	0.0 (0.0)	−0.5	−0.5	0.0	0.0	−0.5	−0.5
Y	0.0 (−0.8)	0.0 (−0.8)	0.7	0.7	0.0	0.0	0.7	0.7
H	0.0 (0.5)	0.0 (0.5)	−0.4	−0.4	0.0	0.0	−0.4	−0.4

with respect to the gauche form, whereas the CS−CC axis originates a gauche form more stable than the corresponding trans form.

(ii) Passing now to the ttg and ttt forms, ttg is more stable than ttt for all the studied molecules. However, for YH = OH, the ttt−ttg energy differences are smaller than 0.4 kJ mol⁻¹, whereas for YH = SH, these differences are 5.3 and 4.0 kJ mol⁻¹, for X = O and X = S, respectively. The increased relative stability of the ttg conformer in the latter molecules makes this conformer the second more stable among the four considered conformers. The ttg vs ttt energy comparisons lead to the general conclusion that the CC−OH axis stabilizes only slightly the gauche form with respect to the trans form, whereas the CC−SH axis gives rise to a gauche form far more stable than the corresponding trans conformation.

(iii) The stabilizing effect of correlation as measured by Δ(HF-MP2) increases along the ttt < ttg < tgg' < ggg' series of conformers, i.e., with the number of gauche arrangements. Intuitively, this suggests that the effect of electrons avoiding each other is less important for trans arrangements than for gauche arrangements, i.e., is larger for folded conformations than stretched ones.[5]

(iv) If the oxygen-by-sulfur substitution effect is considered for the tgg' and ggg' conformers, then it is concluded that the stabilizing effect of correlation is less important for thioethers (X = S) than for their ether counterparts (X = O).

(v) On the whole, correlation corrections are of the same magnitude or in some cases even larger than conformational energy differences and change appreciably with conformation.

Tables 1 and 2 present changes in dihedral angles, bond angles, bond lengths, contact distances, and angles, and Mulliken charges, for the (tgg', ggg') and (ttg, ttt) pairs of conformers, respectively. The latter pair (ttg, ttt) is not herein discussed in detail, since it follows similar patterns of variation for oxygen-by-sulfur substitutions.

In general, larger changes are found for structural parameters involving a substituted atom. For instance, a decrease of 12°−13° in the CXC angle is observed for oxygen-by-sulfur substitution in the X atomic position, whereas the CYH angle

closes by 8°−10° when O is replaced by S in the YH bond. In turn, the XCC and CCY angles tend to open by 3°−5°, while for the tgg' and ggg' conformers, the XCC and CCY changes lead to an opening of the intramolecular ring, the closing of the CYH angle compensates for that, thus reducing the contact angle of the X···HY interaction.

The CX, XC, CY and YH bond lengths increase by 36−40 pm and the X···H(Y) contact distances increase by ca. 2 × 10 pm for each oxygen-by-sulfur substitution along the series of molecules (O,O) → (O,S) → (S,O) → (S,S). In addition, both X and Y Mulliken charges increase by ca. 0.7e, becoming less negative when the O atom is replaced by the less electronegative S atom. In turn, the H(Y) atom becomes less positive by ca. 0.4e when Y = O is substituted by Y = S, and C atoms become negative or more negative by (0.4−0.5)e when O is replaced by S in one X or Y adjacent position.

Vibrational Frequencies. Table 3 presents νYH, τCCYH, and τCXCC for the tgg', ggg', ttg, and ttt conformers of CH$_3$-XCH$_2$CH$_2$YH (X, Y = O, S). Besides having the dominant contribution of a single vibrational coordinate, these vibrations are sensitive to both conformational changes and oxygen-by-sulfur substitutions. While the first of these vibrational frequencies (νYH) probes the X···HY interaction, the other two (τCXCC and τCCYH) probe important dihedral angles, namely, CX−CC and CC−YH.

Starting with an oxygen-by-sulfur substitution for a particular conformation, larger changes are generally observed for vibrational coordinates involving a substituted atom. For instance, an oxygen-by-sulfur substitution in the YH oscillator leads to a large frequency decrease of νYH for the same conformer (940 to 1000 cm⁻¹).[6,7] Besides being associated with a mass effect, this substitution is accompanied by a big increase in the YH bond length (see Table 1) and by a force constant reduction. In turn, the same substitution on the ether O atom has little effect on νYH, as it yields a frequency decrease of a few wavenumbers.

A typical hydrogen bond is associated with a νYH frequency decrease. This effect is clearly observed for OH···O, if one compares νOH for hydrogen bonded and non-hydrogen bonded

TABLE 2: Energy Differences and Changes in Geometrical Parameters for the ttg and ttt Conformers of CH₃XCH₂CH₂YH (X, Y = O, S) (MP2/6-31G* Calculations)

	COCCOH		COCCSH		CSCCOH		CSCCSH	
	ttg	ttt	ttg	ttt	ttg	ttt	ttg	ttt
CXCC, XCCY, CCYH	182, 180, 72	180, 180, 180	181, 179, 68	180, 180, 180	181, 178, 70	180, 180, 180	179, 178, 66	180, 180, 180
ΔE/kJ mol⁻¹[a]	14.5	14.6	4.4	9.7	12.2	12.6	2.5	6.5
Δ angles/deg								
CXCC	0 (182)	0 (180)	−1	0	−1	0	−3	0
XCCY	0 (180)	0 (180)	−1	0	−2	0	−2	0
CCYH	0 (72)	0 (180)	−4	0	−2	0	−6	0
CXC	0 (112)	0 (112)	−1	0	−13	−14	−14	−14
XCC	0 (107)	0 (107)	0	0	3	3	3	2
CCY	0 (111)	0 (106)	2	3	0	0	2	2
CYH	0 (107)	0 (108)	−10	−12	0	0	−11	−11
Δ bond lengths/pm								
CX	0 (142)	0 (142)	0	0	39	39	39	39
XC	0 (142)	0 (142)	0	0	39	39	40	40
CC	0 (152)	0 (151)	0	1	0	1	0	1
CY	0 (143)	0 (143)	41	39	0	0	39	40
YH	0 (97)	0 (97)	37	37	0	0	37	37
Δ charges/e								
C	0.0 (−0.2)	0.0 (−0.2)	−0.4	−0.4	0.0	0.0	−0.4	−0.4
X	0.0 (−0.6)	0.0 (−0.6)	0.7	0.7	0.0	0.0	0.7	0.7
C	0.0 (0.0)	0.0 (0.0)	−0.5	−0.5	0.0	0.0	−0.5	−0.5
′C	0.0 (0.0)	0.0 (0.0)	0.0	0.0	−0.5	−0.5	−0.5	−0.5
Y	0.0 (−0.7)	0.0 (−0.8)	0.0	0.0	0.6	0.7	0.7	0.7
H	0.0 (0.4)	0.0 (0.4)	0.0	0.0	−0.3	−0.3	−0.3	−0.3

[a] $\Delta E = E$(conformer) − E(tgg′).

TABLE 3: νYH, τCCYH and τCXCC (cm⁻¹) for *tgg′*, *ggg′*, *ttg*, and *ttt* Conformers of CH₃XCH₂CH₂YH (X, Y = O, S)

	tgg′	ggg′	ttg	ttt
νYH				
O, O	3749	3728	3775	3789
O, S	2800	2789	2783	2789
S, O	3736	3723	3773	3777
S, S	2792	2779	2782	2781
τCCYH				
O, O	470	490	325	266
O, S	300	297	230	143
S, O	427	443	329	271
S, S	234	267	235	161
τCXCC				
O, O	95	67	102	102
O, S	85	62	99	101
S, O	39	71	55	52
S, S	39	54	61	60

conformers (for example, νOH(tgg′)−νOH(ttt) ≈ −40 cm⁻¹). However, this kind of comparison should not be valid for very weak interactions, as for SH···O and SH···S interactions, for then different YH···X geometries make the comparison misleading. Moreover, the anarmonicity corrections should be taken into consideration.

Passing now to τCCYH (Table 3), it is found that for the (O,O), (O,S), and (S,O) compounds, these vibrational frequencies point out to three groups of conformers which are, by decreasing order of frequencies, (i) the pair of hydrogen bonded conformers, ggg′ and tgg′, (ii) the non-hydrogen bonded conformer gauche in the CCYH axis, ttg, and (iii) the non-hydrogen bonded conformer whose CCYH axis is trans, i.e., the ttt form. However, for the (S,S) compound, the distinction is rather between a CC−SH gauche arrangement (tgg′, ggg′, ttg conformers) and a CC−SH trans axis (ttt form). In addition, for a particular (X, Y) molecule, the difference between the highest and the lowest frequencies of the conformers takes the values 224, 157, 172, and 106 cm⁻¹, for the (O,O), (O,S), (S,O), and (S,S) molecules, respectively.

Considering now tgg′ and ggg′ with the same X atom, an oxygen-by-sulfur substitution in the Y position yields negative frequency shifts between −170 and −193 cm⁻¹. Instead, the

same vertical comparisons in Table 3, now for the ttg and ttt conformers, yield frequency shifts between −94 and −123 cm⁻¹. In addition, for the tgg′ and ggg′ forms with the same Y atom, an oxygen-by-sulfur substitution in the ether group yields frequency shifts between −30 and −66 cm⁻¹. In turn, for ttg and ttt, positive frequency shifts of a few wavenumbers are observed for the same oxygen-by-sulfur substitutions. Hence, it can be generally concluded that an oxygen-by-sulfur substitution causes a larger negative shift when it occurs in the YH oscillator, for the intramolecularly bonded conformers, tgg′ and ggg′.

Finally, considering τCXCC (Table 3) and oxygen-by-sulfur substitutions, then it is found that these frequencies are relatively close to each other for the same X atom. In turn, they show larger changes whenever X is replaced. In addition, with the single exception of the ggg′ form, an oxygen-by-sulfur substitution in the ether group leads to a frequency decrease of ca. 40 to 50 cm⁻¹. For ggg′, τCXCC frequency values occur in the short range 54−71 cm⁻¹.

Comparisons of different conformers for the same compound (i.e., horizontal comparisons in Table 3), lead to the conclusion that, for the (O, O) and (O, S) molecules, the frequencies tend to group according to the type of conformational arrangement around the CX−CC axis, i.e., one group includes frequency values for tgg′, ttg and ttt, the other includes τCXCC for the ggg′ form. When X = S, i.e., for the (S, O) and (S, S) molecules, τCXCC values do not show a clear pattern of variation.

3. Conclusions

In general, the above mentioned trends of conformational energy differences, structural parameters and vibrational frequencies can be classified in two types: one is made of gradual changes which modulate the strength of the X···HY intramolecular interaction along the (O,O) → (O,S) → (S,O) → (S,S) series of molecules; the other includes abrupt changes, namely those which invert the relative stability of conformers upon oxygen-by-sulfur substitution.

Energy changes associated with the strength of the X···HY intramolecular interaction and contact distances easily emerge

O-by-S Substitution in CH$_3$OCH$_2$CH$_2$OH

J. Phys. Chem., Vol. 99, No. 45, 1995 **16589**

from a comparison of tgg' and all-trans conformers. In particular, along the above series of molecules, the ttt−tgg' energy difference diminishes gradually and, for the tgg' and ggg' conformers, the X···H(Y) contact distance increases monotonically, suggesting a less stabilizing effect of the intramolecular interaction along that series of molecules.

Changes of the second kind are found, for example, when the relative stability of tgg' and ggg' conformers upon oxygen-by-sulfur substitution is considered. In fact, for X = O, tgg' is more stable than ggg', whereas for X = S, ggg' is more stable than tgg'. In addition, while ttg is more stable than ttt for all the studied molecules, these differences are small and negligible when Y = O, and appreciable and almost equal when Y = S. On the whole, oxygen-by-sulfur substitutions in the central bonds of the dihedral angles CX−CC and CC−YH favor gauche over trans conformations.

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