December, 1984] © *1984 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 57, 3589—3590 (1984)* 3589

Ab Initio Gradient Calculation of the Molecular Structures of Dimethyl Ether and Dimethyl Sulfide

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(Received June 28, 1984)

Synopsis. The molecular structures and torsional potentials of $(CH_3)_2O$ and $(CH_3)_2S$ have been calculated by the *ab initio* gradient method using a MIDI-4 basis set augumented with polarization functions. The calculations have confirmed that the molecules take the staggered-staggered conformation with C_{2v} symmetry.

According to microwave spectroscopic studies, dimethyl ether[1)] and dimethyl sulfide[2)] molecules have C_{2v} symmetry in the equilibrium state and each methyl group is staggered against the opposite C–O or C–S bond. However, there remains a possibility of a near staggered-staggered conformation with C_2 symmetry. Actually, the torsional angle, τ, for dimethyl ether was calculated to be 4° from the r_s-structure (as for the definition of τ, see Fig. 1), although Blukis *et al.* ascribed it to the zero-point torsional effect because such a small separation of the two potential minima requires an unreasonably high and sharp potential hump between them.[1)] Recently Tamagawa *et al.*[3)] have studied the structure of dimethyl ether by a joint analysis of the electron-diffraction and microwave spectroscopic data and determined τ to be 2(11)°. The possibility of C_2 symmetry has thus not been excluded.

Lombardi *et al.* performed a conformational analysis of dimethyl ether based on a model where the barrier to internal rotation was assumed to arise only as a result of exchange interactions among electrons on nonbonded atoms and lone-pair electrons on the oxygen.[4)] According to their calculation, the torsional potential of dimethyl ether has two separate minima at $\tau=\pm17.5°$ and the height of the barrier between them is 0.52 kcal/mol.[†] It may be noted that their exchange perturbation theory was successfully applied to the calculation of the rotational barriers of more than thirty molecules.[5)]

A recent electron-diffraction study[6)] has revealed that the di-*t*-butyl sulfide molecule takes only one stable conformation of C_2 symmetry with the *t*-butyl groups rotated by 12(8)° from the staggered conformation. Although no question has so far been raised on the molecular symmetry of dimethyl sulfide, it is worthwhile to investigate it theoretically in connection with dimethyl ether and di-*t*-butyl sulfide.

A number of *ab initio* MO calculations have been reported for dimethyl ether and dimethyl sulfide. The barriers to internal rotation have been studied with the STO-3G basis set,[7,8)] but the possibility of a near staggered-staggered conformation has not been examined. The bond lengths and angles of dimethyl ether for the staggered model have been calculated by several authors,[9–11)] but no *ab initio* calculation has been reported for the structural parameters of dimethyl sulfide. The purpose of the present work is to study the torsional potentials and structures of these molecules by *ab initio* calculations using Pulay's gradient method.[12)] The JAMOL3 program[13)] and the MIDI-4 basis set,[14)] augumented with d polarization functions for the C, O, and S atoms, were used for the SCF-LCAO-MO calculations, while geometry optimizations were performed with the GRAMOL program[15)] by assuming C_2 symmetry. Optimizations were repeated until the largest atomic forces were of the order of 2×10^{-2} mdyn.[††]

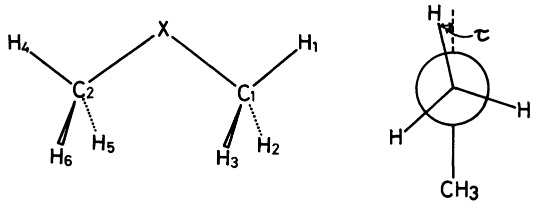

Fig. 1. Numbering of atoms and definition of the torsional angle, τ. X represents O or S.

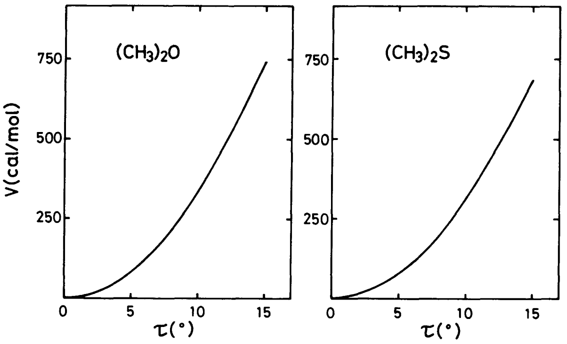

Fig. 2. Torsional potentials for dimethylether and dimethylsulfide.

The calculated torsional potentials are displayed in Fig. 2. The minima of the potentials are at $\tau=0$. The calculated potentials cover only a limited range of τ-values, but they fit well into a simple analytical expression for the torsional potentials with threefold symmetry, *i.e.*, $V_3(1-\cos3\tau)$. The values of the potential barrier, V_3, were thus estimated to be 2.5 and 2.3 kcal/mol for dimethyl ether and dimethyl sulfide respectively. The experimental values of V_3 are 2.72[1)] and 2.70 kcal/mol[16)] for dimethyl ether and 2.1 kcal/mol[2)] for dimethyl sulfide. The present calculations give potential barriers close to the experimental data.

The calculated geometrical parameters are compared with the observed ones in Table 1. The agreement between the calculated and experimental geometries is

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[†] 1 cal/mol=4.184 J/mol.

[††] 1 mdyn=10^{-8} N.

TABLE 1. STRUCTURAL PARAMETERS FOR DIMETHYL ETHER AND DIMETHYL SULFIDE[a)]

	$(CH_3)_2O$			$(CH_3)_2S$		
	r_e[b)]	r_s[c)]	r_{av}[d)]	r_e[b)]	r_s[e)]	r_{av}[f)]
$r(C\text{–}X)$/Å	1.389	1.410(3)	1.413(1)	1.817	1.802(2)	1.805(2)
$r(C\text{–}H_1)$Å	1.089	1.091(7)	1.108(2)[g)]	1.092	1.091(5)[g)]	1.104(3)[g)]
$r(C\text{–}H_2)$/Å	1.097	1.100(5)		1.093		
$\angle CXC$/°	114.1	111.7(3)	111.8(2)	99.5	98.9(2)	99.05(4)
$\angle XCH_1$/°	107.6	107.2(6)		107.3		
$\angle XCH_2$/°	111.5	110.8(3)		110.9		
$\angle H_1CH_2$/°	108.8	109.5(6)	109.2(2)[h)]	108.9	109.6(3)[h)]	109.3(5)[h)]
$\angle H_2CH_3$/°	108.5	108.7(5)		109.8		
θ[i)]/°	2.6	2.5(7)	3.6(17)	2.4	2.45(25)	2.35[j)]
E[k)]/a.u.[l)]	−153.8834			−475.8927		

a) The numbers in parentheses represent the limits of error attached to the last significant digits. See Fig. 1 for atomic numbering. b) Equilibrium structures calculated in the present study. c) r_s–structure from Ref. 1. d) Zero-point average structure from Ref. 3. e) r_s-structure from Ref. 2. f) Zero-point average structure from Ref. 17. g) Average C–H distance. h) Average HCH angle. i) θ is the tilt angle of the methyl groups, which is defined as the angle between the C–X bond and a line perpendicular to the H_3 plane. j) Assumed value. k) Total energy. l) 1 a.u.$=4.359814\times10^{-18}$ J.

reasonable. The present calculations demonstrate that both dimethyl ether and dimethyl sulfide molecules take the staggered conformation with C_{2v} symmetry in the equilibrium state. Computations were performed on a HITAC M-200H of the Institute for Molecular Science.

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