A Systematic Approach To Calculate Molecular Properties of Organosulfur Compounds Containing the $C_{sp}2$–S Bond

James Kao,* Charles Eyermann, Everett Southwick, and Diane Leister

Contribution from the Phillip Morris, U.S.A., Research Center, Richmond, Virginia 23261. Received November 5, 1984

Abstract: Ab initio molecular orbital theory has been employed to investigate the structures, energies, and conformations of vinyl sulfide, methyl vinyl sulfide, divinyl sulfide, 1,4-dithiin, 1,3-dithiole, and 1,4-dithiafulvene. A force field has been developed, on the basis of available experimental and theoretical data, to permit molecular mechanics calculations on organosulfur compounds containing C_{sp^2}–S bonds. Force field calculations are presented for the above six compounds as well as benzo-1,4-dithiin, dibenzo-1,4-dithiin, and 2,2′-bi-1,3-dithiole. Also presented here are ionization potentials of these nine compounds calculated by the VEH method and optical transitions of 1,4-dithiin and dibenzo-1,4-dithiin obtained from the $X\alpha$–SCF method. Extensive comparison is made with experimental results while predictions are made for others.

Theoretical calculations have been widely applied to interpret and organize results and to resolve chemical mysteries. The most important role theoretical calculations may play for the future is probably to make correct predictions before any costly experimental work begins. Unfortunately, there is currently no single method which is adequate for all problems. In this paper, we explore a systematic way to study molecular and electronic structures of organosulfur comounds containing the C_{sp^2}–S bond by using several theoretical tools in a complementary manner.

Recently the ab initio molecular orbital (MO) theory has been proven to be useful in systematic studies of equilibrium geometries, electric dipole moments, charge distributions, relative energies, and conformational analysis of a variety of small compounds.[1-3] However, the computation time required for MO calculations is still, at present, a major practical problem to the application of this method to large molecules. Furthermore, there is a sizable error in the calculated total energy (which is directly related to the heat of formation), although it is occasionally possible to derive correct heats of formation from theoretical heats of reactions in conjunction with experimental enthalpies of formation.[4] On the other hand, the molecular mechanics (MM) or force field method has been shown to be a very reliable, fast, and efficient way of determining molecular structures, energies, and other properties for a wide variety of compounds.[5,6] A handicap of the molecular mechanics method lies in the fact that it is an empirical method and, hence, a great amount of accurate data must be available for a given class of compounds before an appropriate force field can be developed. A promising theoretical approach to study molecular geometries and properties of large molecules would therefore seem to be a combined utilization of the molecular orbital and molecular mechanics methods.[2]

The nature of chemical bonding and other electronic properties is described in the electronic structure, which can only be obtained from quantum mechanics. There has been considerable success in the combined use of spectroscopy and quantum mechanics in the investigation of the electronic structure of a molecule. Unfortunately, sophisticated ab initio methods, for medium-sized molecules are time consuming and become almost prohibitively expensive when applied to large molecules and polymers. The recent Valence Effective Hamiltonian (VEH) method appears to be a reasonable and practicable approach for these large systems since it yields ab initio (double ζ) quality results with negligible computer time.[7] The VEH method achieves its computation speed by evaluating only one-electron integrals and including no self-consistent-field (SCF) iterative cycles. Hence, a theoretical or experimental structure is a prerequisite to carry out VEH calculations. This may introduce a problem since the molecular

(1) For reviews see: (a) Pople, J. A.; Radom, L. *MTP Int. Rev. Sci.: Theor. Chem.* **1972**, *71*. (b) Pople, J. A. *Tetrahedron*, **1974**, *30*, 1605. (c) Pople, J. A. In "Modern Theoretical Chemistry"; Schaefer, H. F., Ed.; Plenum Press: New York, 1977. (d) Newton, M. D. in ref 1c.

(2) For example, see: Kao, J.; Huang, T. *J. Am. Chem. Soc.* **1979**, *101*, 5546.

(3) For example, see: (a) Kao, J.; Seeman, J. *J. Comput. Chem.* **1984**, *5*, 200. (b) Kao, J.; Katz, T. *THEOCHEM.* **1984**, *108*, 229.

(4) For example, see: Kao, J.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 760 and references cited therein.

(5) For review see: (a) Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, D.C., 1982. (b) Osawa, E.; Musso, H. *Top. Sterochem.* **1982**, *13*, 117. (c) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. (d) Ermer, O. *Struct. Bonding (Berlin)* **1976**, *27*, 161.

(6) For example, see: Houminer, Y.; Kao, J.; Seeman, J. I. *Chem. Commun.* **1984**, 1608.

(7) (a) Brédas, J. L.; Chance, R. R.; Silbey, R.; Nicolas, G.; Durand, Ph. *J. Chem. Phys.* **1981**, *75*, 225. (b) Brédas, J. L.; Chance, R. R.; Baughman, R. H.; Silbey, R. *J. Chem. Phys.* **1982**, *76*, 3673. (c) Brédas, J. L.; Chance, R. R.; Silbey, R.; Nicolas, G.; Durand, Ph. *J. Chem. Phys.* **1982**, *77*, 371. (d) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci. Polym. Lett. Ed.* **1980**, *18*, 9. Lin, J. W. P.; Dudek, L. P., *Ibid.* **1980**, *18*, 2869. (e) Shacklette, L. W.; Elsenbaumer, R.L.; Chance, R. R.; Eckhardt, H.; Frommer, J. E.; Baughman, R. H. *J. Chem. Phys.* **1981**, *75*, 1919. (f) Nicolas, G.; Durand, Ph. *J. Chem. Phys.* **1979**, *70*, 2020; **1980**, *72*, 453. (g) Andre, J. M.; Burke, L. A.; Delhalle, J.; Nicolas, G.; Durand, Ph. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1979**, *13*, 283. (h) Andre, J. M.; Gouverneur, L.; Leroy, G. *Int. J. Quantum Chem.* **1967**, *1*, 451. (i) Brédas, J. L.; Themans, B.; Andre, J. M. *J. Chem. Phys.* **1983**, *78*, 6137.

structures of interest may not be readily available experimentally or theoretically.

Additional information on the electronic structure of a molecule can be obtained from studying the energy of transition from the ground state (E_g) to an excited state (E_e). Consider in this case the excitation of only one electron, namely transitions normally associated with electronic absorption spectra. The usual approach in the self-consistent-field (SCF) linear combination of atomic orbitals (LCAO) molecular obital (MO) model is to approximate E_e by a state resulting from the removal of an electron from an occupied MO to an unoccupied MO (virtual orbital).[8] No separate SCF calculation is performed for the excited state. Since the virtual orbitals, in this context, are byproducts of a variational procedure designed for the ground state, they are physically undefined and should not be treated as excited-state orbitals in describing electronic transitions.[8,9]

In the Xα treatment, on the other hand, energies of electronic transitions are predicted by the transition-state concept to be the difference between the energy of the ground-state orbital from which one-half unit of electronic charge has been removed and that of the virtual orbital with an electron population of one-half.[9] For this transition state a separate SCF calculation is carried out, using initially the ground-state potential. Application of this method has been tremendously successful in the interpretation of the electronic spectra of a variety of compounds.[10]

In view of the current status of theoretical calculations, systematic studies should be encouraged. Such studies may be necessary for useful predictions because they increase the effectiveness of "cancellation of errors" and make systematic corrections possible. In this paper, we report our systematic studies of organosulfur compounds. First, we select a set of model compounds for deriving a force field. Extensive ab initio calculations, using various basis sets, are then carried out for those model compunds whenever experimental data are not available or are questionable. Secondly, an appropriate force field to calculate accurate structures and energies is developed on the basis of Allinger's force field. Calculations are then performed for large molecules. Finally, Xα–SCF and VEH methods are employed to calculate ionization potentials and spectral properties. In this paper, we report our results for organosulfur compounds containing the C_{sp^2}–S linkage. This series of compounds is of great interest to organic, inorganic, and biological chemistry. In addition, we are particularly interested in the structural and electronic properties of organosulfur compounds because of their potential applications in organic polymers and conductors. We shall also point out that our main focus here is on nonthiophenic organosulfur compounds. Thiophenic compounds have to be specially treated within the existing force field framework.[5] It is expected that this work will provide the starting point for developing a thiophenic force field. Extensive comparison is made with experimental results while predictions are made for others. Several striking features are revealed by this study.

Computational Aspects

Ab Initio Calculations. Ab initio molecular orbital calculations were carried out by using GAUSSIAN 80[11] or GAUSSIAN 76[12] systems

Chart I

of programs. Both STO-3G[13] and 3-21G[14] basis sets were employed for geometry optimizations to derive structural features and potential functions while the larger basis set,[15] 6-21G, was utilized occasionally to assess the reliability of conformational energies. Structural parameters and conformational energies obtained from ab initio calculations are depicted in Tables I and II, respectively. In addition, the calculated lowest total energies for various basis sets are listed in Table III.
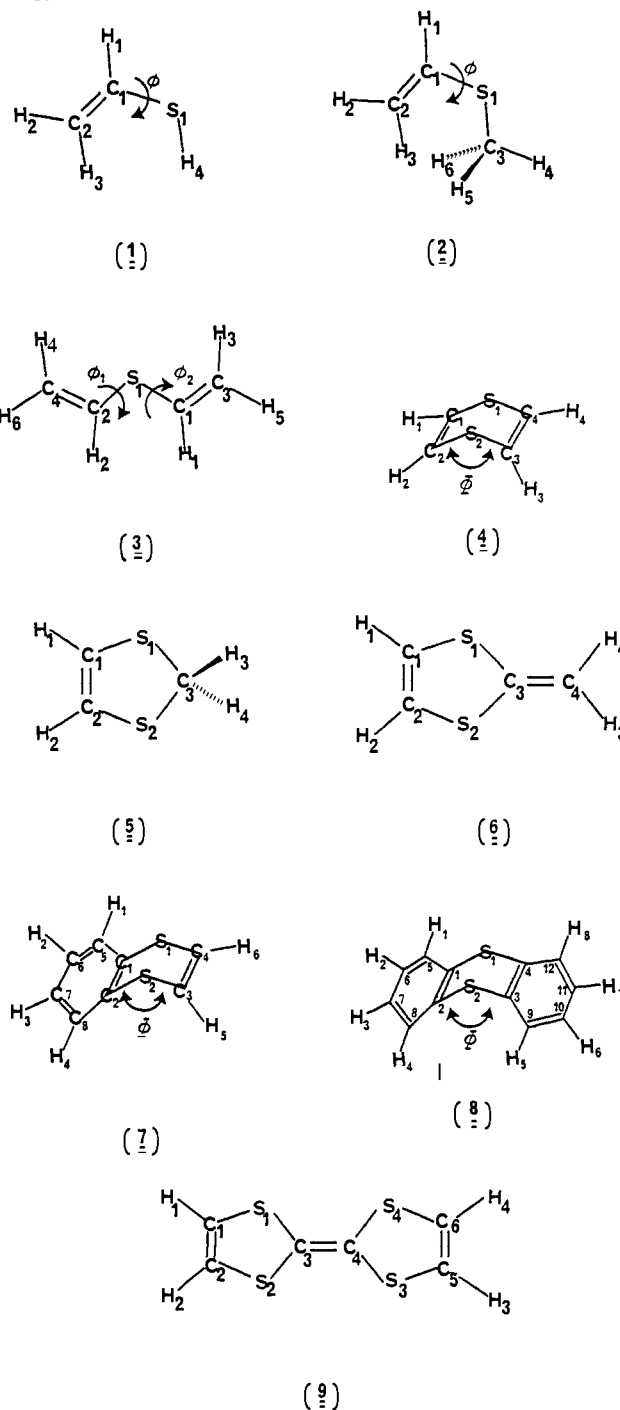
(8) (a) For example: Schaefer, H. G., III, Ed. "Methods of Electronic Structure Theory"; Plenum Press: New York, 1977; p 357. (b) For example: Segal, G. A., Ed. "Semiempirical Methods of Electronic Structure Calculation"; Plenum Press: New York, 1977; Part A, Technique, p 105. (c) For a recent review on the applications of MO methods to organometallics see, for example: Mingos, D. M. P. *Adv. Organomet Chem.* **1977**, *15*, 1.

(9) (a) Johnson, K. H. *J. Chem. Phys.* **1966**, *45*, 3085. (b) Johnson, K. H.; Smith, F. C. *Phys. Rev. B: Solid State* **1972**, *5*, 831. (c) Slater, J. C.; Johnson, K. H. *Ibid.* **1972**, *5*, 844. (d) Slater, J. C. "The Self-Consistent Field for Molecules and Solids"; McGraw-Hill: New York, 1974.

(10) (a) Ozin, G. A.; Huber, H.; McIntosh, D.; Mitchell, S.; Norman, J. G., Jr.; Noodleman, L. *J. Am. Chem. Soc.* **1979**, *101*, 3504. (b) Norman, J. G., Jr.; Kolari, H. J.; Gray, H. B.; Trogler, W. C. *Inorg. Chem.* **1977**, *16*, 987. (c) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1975**, *97*, 33. (d) Jolly, W. L.; Eyermann, C. J. *J. Phys. Chem.* **1982**, *86*, 4834. (e) Eyermann, C. J.; Chung-Phillips, A. *Inorg. Chem.* **1984**, *238* 2025.

(11) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A.; QCPE, University of Indiana, Bloomington, Indiana, Program No. 406.

(12) Binkley, J. S.; Whitehead, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A., QCPE, University of Indiana, Bloomington, Indiana, Program No. 368. Marsh, P.; Williams, D. E. *Ibid.*, Program No. 421.

(13) Hehre, W. J.; Stewart, R.F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(14) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(15) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

Molecular Properties of Organosulfur Compounds

J. Am. Chem. Soc., Vol. 107, No. 19, 1985 5325

In this paper, we have to deal with conformations resulting from rotation about the C_{sp^2}–S bond. For convenience, we shall use letters to approximately represent rotamers resulting from the torsional C_{sp^2}–C_{sp^2}–S–R angles (ϕ) in order to facilitate our discussion. The letters used to represent torsional angles are C ($\phi \sim 0°$), G ($\phi \sim 60°$), E ($\phi \sim 120°$), T ($\phi \sim 180°$), E' ($\phi \sim 240°$), and G' ($\phi \sim 300°$). The torsional angle is always measured by looking down the C_{sp^2}–S bond and rotating the C=C bond against the C_{sp^2} bond. We also arbitrarily define a clockwise rotation to be positive.

The theoretical STO-3G structure of vinyl sulfide (**1**) was reported previously;[16] we report here our 3-21G results. Full structural optimizations, with the exception of assuming a planar double bond system, were used to study the potential function about the C_{sp^2}–S bond from $\phi = 0°$ (C) to $\phi = 180°$ (T). Similarly, with the exception of assuming a planar double bond system, structural features of several conformations of methyl vinyl sulfide (**2**) were fully optimized by using the 3-21G basis set to examine the C_{sp^2}–S rotational function (see Chart I).

Divinyl sulfide (**3**) has two possible rotational axes. The conformations of divinyl sulfide are denoted as (ϕ_1, ϕ_2), where ϕ_1, ϕ_2 are the CC–SC torsional angles in degrees, measuring deviations from the corresponding syn CCSC angles. They may also be approximately represented by a combination of two letters, where the first letter refers to ϕ_1 and the second one to ϕ_2. For example, TT is approximately equivalent to (180°, 180°). Several conformations of divinyl sulfide have been studied by both STO-3G and 3-21G methods. All structural parameters, with the exception of assuming planar C=C bond systems, were fully optimized at both levels of theory.

The butterfly-flapping potential function of 1,4-dithiin (**4**) has been studied by optimizing all structural parameters with STO-3G, 3-21G, and 6-21G basis sets. Finally, structures of 1,3-dithiole (**5**) and 1,4-dithiafulvene (2-methylene-1,3-dithiole) (**6**) have been studied by using the STO-3G method with full structural optimization.

The Molecular Mechanics Method. The Allinger MMI[17a,17b] and MMPI76[17c] force field described previously was used as a starting point to extend these force field calculations to a study of organosulfur compounds.[18] The Allinger force field is one of the force fields for which extensive usage and development have been reported.[5] The force field parameters developed previously[17] for hydrocarbons are carried over here. Some additional parameters, which pertain to bond lengths, bond angles, dihedral angles, and dipoles involving the C_{sp^2}–S functional group, are needed to deal with organosulfur compounds appearing in this paper and their values settled upon are given in Table IV.

Although the available experimental structural and energetic data are scarce, we are able to obtain the numerical values for the rest of the necessary parameters by augmenting the ab initio results. These parameters were initially given the values from the appropriate analogous structures and were varied several times, through trial and error, until a reasonable overall agreement was reached. Comparison of structural parameters between experimental data and theoretical (ab initio and molecular mechanics) calculations is made in Table I, and comparison for the conformational energies is shown in Table II.

The Valence Effective Hamiltonian Method (VEH). The complete methodology for obtaining molecular one-electron valence effective Hamiltonians from first principles has recently been developed for molecular and polymer systems.[7] The atomic potentials are now available for carbon,[7a] hydrogen,[7a] sulfur,[7c] and nitrogen.[7i]

The VEH program of Bredas' et al was kindly provided to us and has been installed in our DEC-2060 systems. In addition, we have made certain modifications so that it can read in coordinates of the molecular mechanics format. The equilibrium geometries obtained by the molecular mechanics method were used for VEH calculations.

The Xα–SW Method. Standard and well-defined procedures[19] were followed to perform Xα–SCF calculations. The theoretical equilibrium geometries obtained by MM calculations were used for Xα–SCF calculations on 1,4-dithiin and dibenzo-1,4-dithiin for which experimental data are known. The coordinates for the outer sphere were chosen to make it tangent to the atomic spheres. Schwarz's values[20] were used for the atoms. For the inter- and outer-sphere regions a valence-electron weighted average of all the atomic α's was employed. Atomic sphere radii were obtained vis Norman's method and the absolute values were taken as 88% of the atomic number sphere radii.[20] Spherical harmonics up to $l = 2$ for sulfur, $l = 1$ for carbon, $l = 0$ for hydrogen, and up to $l = 3$ for the outer region were included in the partial wave expansion. Ionization potentials and optical transition energies were calculated via Slater's transition-state method.[9,19]

Results and Discussion

Geometrical Structures. (A) Comparison between Experimental and ab Initio Structures. The difference between experimental and ab initio structural data requires comment here (Table I). There are only four molecules in Table I, methyl vinyl sulfide, 1,4-dithiin, dibenzo-1,4-dithiin, and 2,2'-bi-1,3-dithiole (tetra-thiafulvalene, TTF), for which experimental structures[21–27] are available. Methyl vinyl sulfide and 1,4-dithiin have been selected for ab initio calculations because of molecular size considerations. The experimental data for methyl vinyl sulfide appears to be more accurate than the data for 1,4-dithiin, thus we shall put more weight on the former for comparison.

A superficial inspection of Table I shows that STO-3G and 3-21G structures are rather similar to each other, with the exception that C–S and S–H bonds obtained by 3-21G are consistently longer than those obtained by STO-3G. STO-3G results appear to be more in line with experimental values. The 3-21G structures are very similar to 44-31G results[16] but the former (3-21G) requires less in CPU time. The results presented here are consistent with previous observations[28] in that the addition of a full set of valence orbitals to a minimal basis set tends to increase bond lengths and that although the absolute errors for bond lengths are generally large, the calculated bond lengths are expected to be consistently too long.

Comparison between experimental and STO-3G results of this and previous work[16] seems to suggest that (a) the C=C bond is consistently and characteristically[29] underestimated by about 0.03 Å; (b) the STO-3G CCS bond angle is about 2° larger than the experimental value; and (c) the STO-3G CSC bond angle is probably about 1° smaller than the experimental counterpart. Moreover, comparison between experimental and 3-21G results

(16) Kao, J. *J. Am. Chem. Soc.* **1978**, *100*, 4685.

(17) (a) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579. (b) Allinger, N. L.; Sprague, J. T. *Ibid.* **1975**, *31*, 21. (c) Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975.

(18) Alternatively, we may use the Allinger's new force field as our starting point for this study. However, part of the complete system (MM2P) is not accessible to us. Furthermore, we are not sure whether the force field parameters pertaining to this study have been fully examined within the new force field.

(19) (a) Slater, J. C. *Adv. Quantum Chem.* **1972**, *6*, 1. (b) Johnson, K. H. *Adv. Quantum Chem.* **1973**, *7*, 143. (c) Norman, J. G. *J. Chem. Phys.* **1974**, *61*, 4630. (d) Norman, J. G. *Mol. Phys.* **1976**, *31*, 1191.

(20) Schwarz, K. *Phys. Rev. B: Solid State* **1972**, *5*, 2466.

(21) (a) Samdal, S.; Seip, H. M. *J. Mol. Struct.* **1975**, *28*, 193. (b) *Acta Chem. Scand.* **1971**, *25*, 1903. (c) Almond, V.; Charles, S. W.; Macdonald, J. N.; Owen, N. L. *J. Chem. Soc., Chem. Commun.* **1977**, 483.

(22) Derissen, J. L.; Bijen, J. M. *J. Mol. Struct.* **1973**, *16*, 289.

(23) (a) Parham, W. E.; Wynberg, H.; Hasek, W. R.; Howell, P. A.; Curtis, R. M.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1954**, *76*, 4957. (b) Howell, P. A.; Curtis, R. M.; Lipscomb, W. N. *Acta Crystallogr.* **1954**, *7*, 498.

(24) Gallaher, K. L.; Bauer, S. H. *J. Chem. Soc., Faraday Trans. 2*, **1975**, *71*, 1173.

(25) Lynton, H.; Cox, E. G. *J. Chem. Soc.* **1956**, 4887.

(26) Rowe, I.; Post, B. *Acta Crystallogr.* **1958**, *11*, 372.

(27) (a) Cooper, W. F.; Kenny, N. C.; Edmonds, J. W.; Nagel, A.; Wudl, F.; Coppens, P. *Chem. Commun.* **1971**, 889. (b) Cooper, W. F.; Edmonds, J. W.; Wudl, F.; Coppens, P. *Cryst. Struct. Commun.* **1974**, *3*, 23.

(28) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. B.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

(29) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808. Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *Ibid.* **1971**, *93*, 5339. Kao, J.; Random, L. *Ibid.* **1978**, *100*, 379.

Table I. Theoretical and Experimental Equilibrium Geometries (Å or deg)

structural parameter	exptl[a]	MM	ab initio[b] STO-3G	3-21G
Vinyl Mercaptan (1)				
C_1-S_1		1.772	1.759[c]	1.828
C_1-C_2		1.338	1.310	1.310
C_1-H_1		1.093	1.084	1.070
C_2-H_2		1.092	1.080	1.073
C_2-H_3		1.091	1.081	1.073
H_4-S_1		1.346	1.331	1.351
$H_1C_1S_1$		113.0	112.9	110.8
$C_2C_1S_1$		125.1	127.3	126.4
$C_1C_2H_2$		120.0	121.4	120.6
$C_1C_2H_3$		122.2	122.8	122.8
$C_1S_1H_4$		98.6	95.9	98.3
$C_2C_1S_1H_4$		0.0	0.0	0.0
Methyl Vinyl Sulfide (2)				
C_1-S_1	1.752 (12),[d] 1.747 (3)[e]	1.768	1.760[c,g]	1.822[g]
C_1-C_2	1.342 (7), 1.341 (3)	1.338	1.311	1.312
C_3-S_1	1.794 (12), 1.807 (3)	1.813	1.797	1.881
C_1-H_1		1.093	1.085	1.071
C_2-H_2	1.082 (7), 1.086 (26)	1.093	1.079	1.071
C_2-H_3		1.089	1.080	1.073
C_3-H_4	1.105 (9), 1.101 (26)	1.095	1.086	1.078
$C_1S_1C_3$	102.5 (2.0), 104.6 (0.8)	103.3	101.6	102.3
$C_2C_1S_1$	127.0 (1.5), 127.5 (0.4)	128.0	129.6	127.7
$C_1C_2H_2$		119.7	120.9	120.3
$C_1C_2H_3$		123.9	123.7	123.3
$H_1C_1S_1$	112.1 (1.9)	111.7	111.4	110.6
$H_4C_3S_1$		109.7	107.6	105.5
$H_5C_3S_1$		109.7	112.3	109.7
$H_6C_3S_1$		109.7	112.3	109.7
$H_5C_3S_1C_1$		62.8	61.1	60.8
$H_6C_3S_1C_1$		62.8	61.1	60.8
$C_2C_1S_1C_3$		0.0	0.0	0.0
Divinyl Sulfide (3), C_1				
C_1-S_1		1.768	1.764[f]	1.833
C_2-S_1		1.768	1.765	1.833
C_1-C_3		1.338	1.310	1.311
C_2-C_4		1.338	1.310	1.311
C_1-H_1		1.092	1.085	1.071
C_2-H_2		1.093	1.085	1.071
C_3-H_3		1.092	1.080	1.072
C_3-H_5		1.091	1.079	1.074
C_4-H_4		1.092	1.080	1.072
C_4-H_6		1.091	1.079	1.073
$C_1S_1C_2$		100.1	103.9	101.1
$C_3C_1S_1$		124.2	131.5	126.2
$H_1C_1S_1$		113.5	110.0	111.2
$C_4C_2S_1$		122.4	122.8	122.0
$H_2C_2S_1$		114.6	117.5	115.1
$C_1C_3H_3$		121.8	124.4	122.5
$C_1C_3H_5$		120.1	120.4	120.5
$C_2C_4H_4$		121.0	122.7	121.9
$C_2C_4H_6$		120.3	121.4	121.0
$C_4C_2S_1C_1(\phi_1)$		123.8	180.0	115.8
$C_3C_1S_1C_2(\phi_2)$		38.0	0.0	18.3
Divinyl Sulfide (3), C_2				
C_1-S_1		1.769	1.765[f]	1.839
C_1-C_3		1.338	1.310	1.311
C_1-H_1		1.093	1.085	1.071
C_3-H_3		1.092	1.080	1.070
C_3-H_5		1.092	1.079	1.074
$C_1S_1C_2$		99.0	100.3	98.5
$C_3C_1S_1$		122.4	123.7	122.0
$H_1C_1S_1$		114.6	116.2	115.0
$C_1C_3H_3$		121.0	122.6	122.0
$C_1C_3H_5$		120.3	121.4	121.0
$C_3C_1S_1C_2(\phi_2)$		122.1	180.0	122.2

structural parameter	exptl[a]	MM	ab initio[b] STO-3G	3-21G
Dithiin (4)				
S_1-C_1	1.78 (5)[h]	1.762	1.768[f]	1.831
C_1-C_2	1.29 (5)	1.336	1.310	1.306
C_1-H_1		1.092	1.083	1.070
$S_1C_1C_2$	124.5 (2.0)	126.3	128.8	123.5
$C_2C_1H_1$		121.0	118.8	122.3
$C_1S_1C_4$	100.2 (2.0)	102.3	100.6	99.7
$S_1C_1H_1$		112.6	112.4	114.1
Φ	137 (2.0)	150.3	161.9	132.9
1,3-Dithole (5)				
C_1-C_2		1.335	1.309	
C_1-S_1		1.764	1.762	
C_3-S_2		1.815	1.814	
C_1-H_1		1.091	1.081	
C_3-H_3		1.095	1.090	
$C_1S_1C_3$		94.2	94.9	
$H_1C_1S_1$		116.2	117.3	
$C_2C_1H_1$		124.9	123.8	
$C_2C_1S_1$		118.9	118.9	
$S_1C_3S_2$		113.8	112.3	
$H_3C_3H_4$		112.1	106.3	
$C_1S_1C_3H_3$		119.4	121.9	
1,4-Dithiafulvene (6)				
C_1-C_2		1.336	1.315	
C_1-S_1		1.767	1.760	
C_3-S_1		1.769	1.776	
C_1-H_1		1.091	1.081	
$C_2C_1S_1$		117.4	118.4	
$C_1S_1C_3$		95.7	94.3	
$S_1C_3S_2$		113.8	114.4	
$C_4C_3S_1$		123.1	122.8	
$C_3C_4H_3$		120.7	122.0	
$C_2C_1H_1$		125.7	123.9	
$H_3C_4H_4$		118.7	116.0	
$H_1C_1S_1$		116.9	117.6	
Benzo-1,4-dithiin (7)				
C_1-S_1		1.772		
C_4-S_1		1.763		
C_1-C_2		1.401		
C_3-C_4		1.335		
C_1-C_5		1.399		
C_5-C_6		1.397		
C_6-C_7		1.396		
C_3-H_5		1.092		
C_5-H_1		1.094		
C_6-H_2		1.094		
$C_1S_1C_4$		100.7		
$C_3C_4S_1$		124.1		
$H_6C_4S_1$		113.7		
$C_3C_4H_6$		122.1		
$C_2C_1S_1$		122.6		
$C_5C_1S_1$		117.9		
$C_2C_1S_5$		119.5		
$C_1C_5H_1$		120.4		
$C_6C_5H_1$		118.7		
$C_1C_5C_6$		120.9		
$C_5C_6C_7$		119.7		
$C_5C_6C_2$		120.3		
$C_7C_6H_2$		120.0		
Φ		134.5		

Table I (Continued)

structural parameter	exptl[a]	MM	ab initio[b]		structural parameter	exptl[a]	MM	ab initio[b]	
			STO-3G	3-21G				STO-3G	3-21G
Dibenzo-1,4-dithiin (8)					2,2'-Bi-1,3-dithiole (9)				
C₁–S₁	1.770 (3),ⁱ 1.759 (15),ʲ 1.773 (7)ᵏ	1.772			C₁–C₂	1.314 (3)ⁱ	1.336		
C₁–C₂		1.400			C₁–S₁	1.731 (2)	1.766		
C₁–C₅		1.398			C₃–S₁	1.757 (2)	1.772		
C₅–C₆	1.400 (2), 1.393 (25), 1.379 (15)	1.397			C₃–C₄	1.349 (3)	1.343		
C₆–C₇		1.396			C₁–H₁	0.93	1.091		
C₅–H₁	1.082 (22)	1.094			C₂C₁S₁	118.0	117.2		
C₆–H₂		1.094			C₂C₁H₁		125.8		
C₁S₁C₄	104.1 (1.0), 100.2 (1.0), 100.4 (0.3)	99.7			H₁C₁S₁		117.0		
C₂C₁S₁	120.1 (1.0)	118.8			C₁S₁C₃	94.5	96.3		
C₅C₁S₁	119.9 (1.0)	121.5			S₁C₃S₂	114.5	112.9		
C₂C₁C₅		119.7			C₄C₃S₁	122.8	123.6		
C₁C₅C₆		120.5							
C₆C₅H₁		119.1							
C₁C₅H₁		120.4							
C₅C₆C₇		119.8							
C₅C₆H₂		120.2							
C₇C₆H₂		120.0							
Φ	131.4, 128, 128	127.4							

[a] The figures given in parentheses are reported standard deviations. [b] The double bond system was assumed to be planar. [c] From ref 16. [d] From ref 22. [e] From ref 21. [f] The STO-3G method incorrectly predicts a local minimum for the CC–SC rotation at Φ = 180° (T), see text for details. [g] A C_{3v} local symmetry was assumed for the methyl group. [h] From ref 23. [i] From ref 24. [j] From ref 25. [k] From ref 26. [l] From ref 27.

Table II. Calculated and Experimental Conformational Energies (kcal mol⁻¹)

transformations	exptl	ab initio	molecular mechanics
vinyl mercaptan (1)			
C → E	> 0ᵃ	0.5,ᵇ 1.8,ᶜ > 0ᵈ	0.6
methyl vinyl sulfide (2)			
stag, C → stag, E	0,ᶠ 1.4,ᵍ 2.3ʰ	0.7,ᵇ 0.2ᵈ	0.4
stag, C → ecl, C	3.2ⁱ	3.1ᵇ	3.3
stag, T → ecl, T		1.5ᵇ	1.8
divinyl sulfide (3)			
C₁ (CE) → C₂ (EE)	~ 0ʲ	0.2ᵈ	0.2
C₂ (CE) → Cₛ (EE)		1.2ᵈ	0.3
1,4-dithiin (4)			
C₂ᵥ(boat) → D₂ₕ(planar)	?,ᵏ > 0ˡ	3.0,ᵈ 2.6,ᵉ 2.3, 1.8	0.2
benzo-1,4-dithiin (7)			
C₁(boat) → C₂ᵥ(planar)			1.8
dibenzo-1,4-dithiin (8)			
C₂ᵥ(boat) → D₂ₕ(planar)	> 4ᵐ		4.6

[a] From ref 21c. [b] 44-31G level, from ref 16. [c] From ref 21a. [d] 3-21G level, this work. [e] 6-21G level, this work. [f] From ref 21. [g] From ref 36a. [h] From ref 36b. [i] From ref 34. [j] From ref 37. [k] From ref 43. [l] From ref 42. [m] From ref 24.

Table III. Calculated Total Energies (hartrees) for the Lowest Energy Conformation

molecule	conformation	basis set	total energy
vinyl sulfide	C	3-21G	-473.15400
methyl vinyl sulfide	stag, C	3-21G	-511.97711
divinyl sulfide	T, T	STO-3G	-548.20059
	C, E	3-21G	-549.60545
1,4-dithiin	boat	STO-3G	-938.25144
	boat	3-21G	-944.00464
	boat	6-21G	-948.51671
1,3-dithiole	planar	STO-3G	
1,4-dithiafulvene	planar	STO-3G	-938.26173

Table IV. Force-Field Parameters[a]

Natural Bond Lengths and Stretching Force Constants

bond	l_0, Å	k_1, mdyn Å⁻¹	dipole, D[b]
C_{sp^2}–S	1.765	4.0	1.15

Natural Bond Angles and Bending Force Constants

angle	θ_0, deg	k_θ, mdyn Å rad⁻²
C_{sp^3}–S–C_{sp^2}	94.0	0.60
C_{sp^2}–S–C_{sp^2}	98.0	0.80
C_{sp^2}–S–H	94.0	0.40
C_{sp^2}–C_{sp^2}–S	120.0	0.50
H–C_{sp^2}–S	115.0	0.40
S–C_{sp^2}–S	118.0	0.50

out-of-plane bending constant for S–C_{sp^2}–X bonds = 0.05 mydn Å rad⁻²

Torsional Parameters (kcal mol⁻¹)

dihedral angle	V_1	V_2	V_3
H–C_{sp^3}–S–C_{sp^2}	0.00	0.00	0.50
S–C_{sp^3}–S–C_{sp^2}	0.00	0.00	0.50
C_{sp^2}–C_{sp^2}–S–C_{sp^3}	-1.80	1.00	-0.70
H–C_{sp^2}–S–C_{sp^3}	0.00	1.00	0.00
C_{sp^2}–C_{sp^2}–S–H	-0.60	0.60	-0.40
H–C_{sp^2}–S–H	0.00	0.60	0.00
C_{sp^2}–C_{sp^2}–S–C_{sp^2}	-0.60	0.60	-0.40
H–C_{sp^2}–S–C_{sp^2}	0.00	0.60	0.00
S–C_{sp^2}–S–C_{sp^2}	0.00	0.60	0.00
C_{sp^2}–C_{sp^2}–C_{sp^2}–S	0.00	16.25	2.00
C_{sp^2}–C_{sp^2}–S	0.00	16.25	2.00
S–C_{sp^2}–C_{sp^2}–S	0.00	16.25	2.00

[a] For hydrocarbon parameters see ref 16. [b] The positive sign is defined as having the atom to the left at the positive end of the dipole and vice versa.

in mind for force field development.

(B) Comparison between ab Initio and Molecular Mechanics Structures. The ab initio calculations were carried out to provide either guidance or checks for the force field development. As can be seen from Table I, agreement between ab initio (STO-3G and 3-21G) and MM structures is generally good. Most importantly, probable systematic errors in the ab initio results have been corrected in the molecular mechanics calculations. The largest
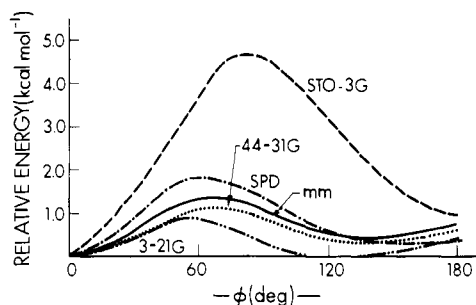
reveals that (a) the C=C bond is underestimated by 0.03 Å and (b) the C–S and S–H bonds are overestimated by 0.06 and 0.02 Å, respectively. These possible systematic errors should be kept

Figure 1. Calculated potential functions describing internal rotation (ϕ) about the CC–SH bond in vinyl sulfide.

Figure 2. Calculated potential functions describing internal rotation (ϕ) about the CC–SC$_{sp^3}$ bond in methyl vinyl sulfide.

difference occurs for the CC–SC torsional angle in the C_1 form of divinyl sulfide. These angles may have been underestimated by the 3-21G values due to its underestimation of steric congestion (vide infra). However, the CC–SC potential function is extremely flat (vide infra) and a difference ca. 10° is not unexpected. An additional structure, benzo-1,4-dithiin, for which there is currently no experimental and theoretical data, is then calculated by using the developed force field. This compound is of chemical interest because its structure is somewhere between 1,4-dithiin and dibenzo-1,4-dithiin.

(C) Comparison between Experimental and Molecular Mechanics Structures. There is a very limited amount of experimental structural data[21-27] available for organosulfur compounds containing the C_{sp^2}–S bond, which is pertinent to this study. In addition, reported standard errors in experimental structures are usually large and results on the same compounds from different laboratories may differ greatly. Thus, the accuracy of the current experimental data is probably no better than 0.02 Å for bond lengths and 2° for bond angles. In view of these limitations, we claim that the developed force field is a reasonably good one, as evidenced by the close agreement with all experimental data.

Conformational Analysis. (A) Vinyl Sulfide and Methyl Vinyl Sulfide. Conformational characteristics of vinyl sulfide and methyl vinyl sulfide have been previously explored by ab initio calculations.[16] In the same paper, conformational energies and structural variations for internal rotation along the C_{sp^2}–S bond are rationalized in terms of orbital and steric interactions. Since the rationale discussed in our previous paper[16] will provide the ground work for understanding and facilitating our discussions on more complex systems of higher sulfides, we shall summarize the part of our previous results that are pertinent to this work.

Presented in Figure 1 are potential functions describing the internal rotation of vinyl sulfide obtained from the previous ab initio calculations[16,21] (STO-3G, 44-31G, and spd) along with our current work (3-21G, and MM). Here, spd refers to a [(C/7,3), (H/4), (S/106,1)] basis contracted to [[C/4,2], [H/2], [S/6,4,1]]. The conformational characteristics of vinyl sulfide can be rationalized in terms of orbital interactions as well as steric effects. Interaction **10** between the HOMO of a double bond and the

(**10**)

(**11**)

(**12**)
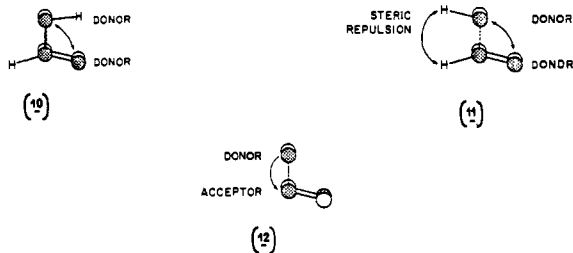
appropriate p$_z$ orbital occupied by two lone-pair electrons involves four electrons and hence is destabilizing.[30] This unfavorable interaction should lead to a bond-angle widening of $C_2C_1S_1$. Obviously, the unfavorable orbital interaction is more easily re-
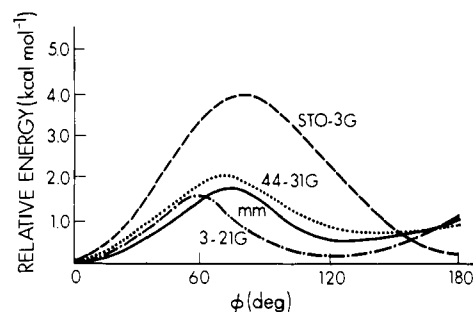
lieved in the syn (C) form **10** than in the anti (T) form **11** because of the existence of steric repulsion between a vinyl hydrogen (H$_1$) and the hydrogen (H$_4$) attached to sulfur in the latter **11**. Therefore, one expects that the anti would be less stable than the syn as predicted by calculations.[31] Interaction **12** involves two electrons and is hence stabilizing. Deviation from planarity would certainly reduce this favorable interaction. Accordingly, the C$_1$–S$_1$ bond increases its length due to the decreasing π delocalization as the dihedral angle ϕ deviates from planarity.

While it is apparent that deviation from planarity decreases the favorable two π-electron interaction, **12**, it should also be borne in mind that rotating away from planarity would, at the same time, decrease the unfavorable four π-electron interaction **10** and **11**. Therefore, there are two opposing interactions which counteract each other and the net result depends on their relative magnitudes. Since interaction **12** is not extremely strong as evidenced from experimental as well as theoretical barriers (vide infra) and interaction **11** is greater than **10**, a nonplanar form (E) occurring at ϕ = 135° is in fact not surprising. These interpretations are supported by detailed examinations of structural variations and Mulliken overlap population analysis.

Several important points can be drawn by inspecting Figure 1. First, results obtained from the STO-3G method are quite different from all other methods. Although the STO-3G method does correctly predict that the planar C (syn) is the most stable among all conformations,[21] the barrier is overestimated and therefore the second stable conformation is incorrectly predicted to be the planar T (anti) instead of the E form. Thus, it implies that the STO-3G method tends to overestimate the C_{sp^2}–S conjugation effect **12**. It is also important to note that the weaker C_{sp^2}–S π-overlap as compared with the π character in C_{sp^2}–O distinguishes conformational characteristics between sulfur compounds and their chalcogens, oxygen compounds.[16] Secondly, the 3-21G potential function is very similar to the 44-31G. Thus, it is justified to use the cheaper 3-21G basis set for the conformational analysis of larger compounds. Thirdly, results presented in Figure 1 clearly indicate that neglecting orbitals or polarization functions would not cause any serious drawbacks for the present study as long as a 3-21G or a 44-31G basis set is employed. Finally, MM calculations do correctly simulate the potential functions of sophisticated ab initio results. The energy difference between C and E forms is estimated to be 0.6 kcal mol^{-1} and the barrier is taken as 0.9 kcal mol^{-1} for the molecular mechanics. The dipole moments obtained from STO-3G, 3-21G, and 44-31G are respectively 0.50, 1.75, and 1.55 D for the C form, while the MM method gives a value of 1.23 D.

The potential functions describing C_{sp^2}–S internal rotation in methyl vinyl sulfide are shown in Figure 2 for previous ab initio calculations[16] (STO-3G and 44-31G) and this work (3-21G and MM). As described in our previous paper, 44-31G results are in good agreement with experimental data. Potential functions obtained from 44-31G and 3-21G are very similar and this, again,

(30) Salem, L. *J. Am. Chem. Soc.* **1968**, *90*, 5431. Muller, K. *Helv. Chim. Acta* **1970**, *53*, 1112.

(31) Alternatively, the relative stabilities of syn and anti conformations may be interpreted, without the concept of orbital interactions, as due to the steric repulsion between S$_1$ and C$_2$. Population analysis indeed shows that the C$_2$...S$_1$ interaction is of antibonding nature and the interaction is larger for the anti.

justifies the economic use of the latter to calculate more complex molecules.

The STO-3G method correctly predicts that the syn (C) conformation is the most stable but it incorrectly predicts that the anti (T) is the next stable conformation. The energy barrier is also largely overestimated. Again, this is presumably due to the fact that STO-3G exaggerates the π character of the C_{sp^2}–S bond. Since there is a close contact distance between the methyl group and the ethylene fragment, one might expect the most stable conformation of methyl vinyl sulfide to be the anti. However, this is certainly not the case, both experimetally and theoretically. Apparently, the methyl vinyl sulfide molecules gain extra stability by some procedures which still need to be considered. The extra stability may be rationalized in terms of interaction **13** between the HOMO of the methyl group and the LUMO of the C=C–S fragment or interaction **14** between the LUMO of the methyl group and the HOMO of the C=C–S fragment. Another
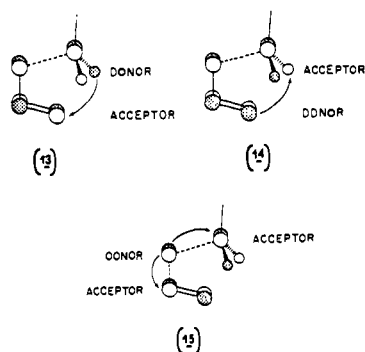
qualitative MO approach to look at this problem has been proposed by Bernardi et al.[32] for methyl vinyl ether. This would involve interaction **15** between the filled $3p_z$ orbital of S and the LUMO of the group orbitals constructed by methyl and ethylene fragments. On the other hand, the extra stability gained by orbital interactions in methyl vinyl sulfide as opposed to vinyl sulfide may simply be interpreted as saying that the former involves six π-electrons and is hence aromatic while the latter has four π-electrons and is, hence, nonaromatic.[32,33]

As can be seen from Figure 2, 44-31G and 3-21G rotational potential functions along the C_{sp^2}–S bond are quite well simulated by MM calculations. The methyl rotational barriers for the C and T forms were also studied by the MM method. The conformation involving a staggered arrangement of the methyl with respect to the C_1–S_1 bond was found to be more stable than the corresponding eclipsed form by 3.3 kcal mol^{-1} for the syn and by 1.7 kcal mol^{-1} for the anti. The barrier to internal rotation calculated for the syn form by the MM method is in good agreement with the experimental and theoretical estimates (ca. 3.2 kcal mol^{-1}).[34] The higher value for the syn methyl rotational barrier in methyl vinyl sulfide reflects the importance of interaction **13–14** and the existing unfavorable close contact between the eclipsed methyl hydrogen (H_4) and the vinyl hydrogen (H_3).

The calculated dipole moments for the staggered C form are 0.59, 1.79, 1.58 D respectively for STO-3G, 3-21G, and 44-31G calculations. The MM calculations give a value of 1.46 D, which is in good agreement with the experimental value (1.35 D).[35]

(B) Divinyl Sulfide. The conformations of divinyl sulfide have been studied by the IR and Raman vibrational spectroscopy in

Figure 3. Calculated potential functions describing internal rotation (ϕ_1) about the CC–SC$_{sp^2}$ bond in divinyl sulfide. ϕ_2 is assumed to be 180° here.

the liquid and solid phases.[37] It was suggested, on the basis of vibrational spectra, that a conformation of C_2 symmetry persists in the solid phase and that there are *probably* no more than two isomers in the liquid phase. They also suggest that the two isomers in the liquid phase are of C_2 and C_1 symmetry and that the enthalpy difference between these isomers is negligible.

We have carried out extensive calculations using STO-3G and 3-21G basis sets to assess structural variations and conformational energies of divinyl sulfide. Our calculated results are displayed in Figure 3 for rotational functions and are tabulated in Table I for equilibrium geometries. To understand the conformational characteristics of divinyl sulfide, it would be beneficial to examine the rotational curve along the C_{sp^2}–S bond as shown in Figure 3. The STO-3G curve is basically similar in shape to the corresponding ones in Figure 1 and 2. The only major difference occurs at $\phi = 0°$, which can be attributed to the highly steric congestion **16** in the TC form of divinyl sulfide. Importantly, the 3-21G
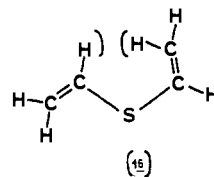
potential function is completely different from the corresponding ones in Figures 1 and 2. However, this is no surprise if one takes into account the steric congestion **16** and low C_{sp^2}–S π character. Furthermore, examination of Figures 1–3 suggests that the 3-21G syn barrier (1.5 kcal mol^{-1}) may be underestimated since it requires a syn barrier of ca. 4 kcal mol^{-1} to convert the shape of the corresponding curves of Figures 1 and 2 to the one found in Figure 3. Our speculation is inspired by the fact that the 3-21G S–C bond length is about 0.06 Å too long and this may unduly and drastically reduce the steric congestion. Thus, our MM syn barrier (4.2 kcal mol^{-1}) is larger than the 3-21G value.

As suggested previously, the STO-3G method exaggerates the π character of the C_{sp^2}–S bond and, hence, unduly estimates the TT form (S-trans, S-trans) as being the most stable conformation. On the other hand, the extended basis set, 3-21G, reasonably predicts that there are two stable conformations, CE (C_1 symmetry) and EE (C_1 symmetry) which are very close in energy, with the former being only marginally lower in energy than the latter. Molecular mechanics calculations give similar results. Both 3-21G and MM suggest the existence of a third isomer EE' (C_s symmetry), even though they do not agree well on its stability relative to the two more stable forms. However, we should point out that the EE' is disfavored by dipolar interactions and 3-21G may overestimate these interactions. Thus, MM results may be more reliable. Our interpretation is consistent with the observation that the dipole moment of divinyl sulfide (1.48 D) calculated by the MM method is in better agreement with the experimental value (1.20 D)[38] while the one (1.91 D) obtained from 3-21G is about 40% too large.

(32) Bernardi, F.; Epiotis, N. D.; Yates, R. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 2385.

(33) Cremer, K.; Binkely, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1974**, *96*, 6900. Lister, D. G.; Palmieri, P. *J. Mol. Struct.* **1976**, *32*, 355. Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941.

(34) Penn, R. E.; Curl, R. F., Jr. *J. Mol. Spectrosc.* **1967**, *24*, 235. Bock, H.; Wagner, G.; Wittel, K.; Sauer, J.; Seebach, D. *Chem. Ber.* **1974**, *107*, 1869.

(35) Trofimov, B. A.; Modonov, V. B.; Frolov, U. L.; Vyalykh, E. P.; Badjenova, T. N.; Gusanova, N. K.; Efremova, G. G.; Amosova, S. V.; Keyko, V. V. *Reakts. Sposobn. Org. Soedin.* **1976**, *13*, 57.

(36) (a) Fabian, J.; Krober, H.; Mayer, R. *Spectrochim. Acta, Part A* **1968**, *24*, 727. (b) Muller, C.; Schafer, W.; Schweig, A.; Thon, N.; Vermeer, H. *J. Am. Chem. Soc.* **1976**, *98*, 5440.
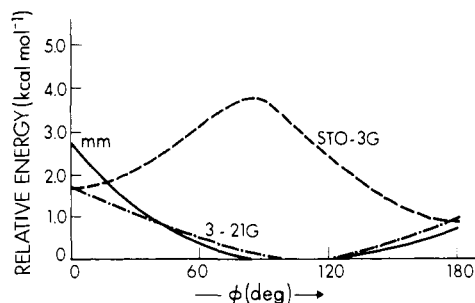
(37) Fortunato, B.; Giorgini, M. G. *Gazz. Chim. Ital.* **1976**, *106*, 1005.

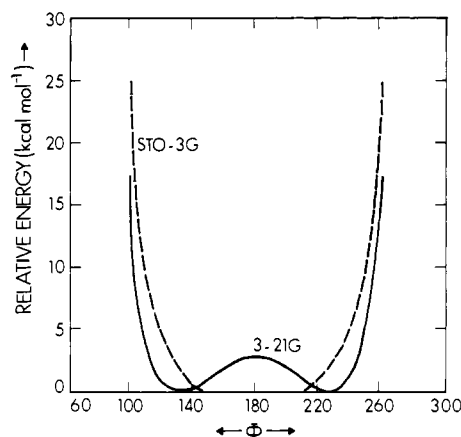(38) Hannay, N. B.; Smyth, C. P. *J. Am. Chem. Soc.* **1946**, *68*, 1005.

5330 *J. Am. Chem. Soc., Vol. 107, No. 19, 1985*

Kao et al.

Figure 4. Calculated potential functions describing the butterfly-flapping (Φ) motion of 1,4-dithiin.

(C) 1,4-Dithiin. The preferred structure of 1,4-dithiin (4) has attracted considerable attention from both experimental and theoretical chemists, because of the continuing interest in the biological and chemical properties and stereochemistry of itself[39] and of related molecules such as 1,4-dioxin,[40] dibenzo-1,4-dithioxin, and dibenzo-1,4-dithiin.[41] According to X-ray diffraction studies,[23] the 1,4-dithiin ring is, in the solid state, nonplanar with a butterfly-flapping angle Φ of 137 or 141° between the two SCCS planes. This result is consistent with the recent dipole moment measurements[42] on 1,4-dithiin in CCl_4 and cyclohexane which suggests a boat conformation with Φ = 136 ± 7°. However, experimental studies[43] of the ultraviolet photoelectron spectrum and NMR proton coupling constants in a nematic phase were unable to choose between a boat, planar, or rapidly inverting structure.

Theoretical calculations have produced conflicting results pertaining to the 1,4-dithiin ring structure. HMO and EHT semiempirical calculations[44] claimed the boat structure to be more stable than the planar form by 6.4 and 2.2 kcal mol^{-1}, respectively. On the other hand, MNDO semiempirical calculations,[45] including Fletcher–Powell minimization, indicated the planar form to be favored over the boat structure by 0.4 kcal mol^{-1}. There is also disagreement among two previous ab initio calculations[45,46] using the STO-3G basis set. Upon partial optimization, Galasso[46] calculated a boat form (Φ = 131°) to be favored over the planar form by 14.6 kcal mol^{-1}. On the other hand, Hayakawa[45] et al. reported that the boat and planar conformations had virtually identical energies, with the former (Φ = 153°) being only 0.4 kcal mol^{-1} higher in energy.

In the light of the apparently confusing results, we carried out more extensive theoretical calculations in attempting to solve the problems. As shown in Figure 4, our STO-3G calculations indicated

that the butterfly-flapping function is very flat and that the boat form is the minimum with Φ = 161°. The energy difference between the boat and planar forms is only 0.03 kcal mol^{-1} according to the STO-3G theory. Since the STO-OG basis set tends to overestimate the rotational barrier about the C_{sp^2}–S bond, as shown in Figures 1–3, *this negligible energy difference would imply that the boat form should be more stable than the planar form*. In fact, calculations using the larger 3-21G basis set yield a similar potential curve (Figure 4), but the energy difference between boat (Φ = 133°) and planar forms is much larger (3.0 kcal mol^{-1}). Calculations using the 6-21G basis set with fully structural optimization predict a slightly smaller value, 2.6 kcal mol^{-1}. The MM energy difference (0.2 kcal mol^{-1}) between boat (Φ = 150°) and planar conformations is considerably smaller than the 3-21G and 6-21G values.

It is important to note that after our calculations were completed, Saebo et al.[47] reported their calculations on 1,4-dithiin using STO-3G, 3-21G*, and 6-31G* basis sets. Their STO-3G results are identical with ours. The butterfly-flapping angle obtained from 3-21G* calculations (137°), which include d-functions on sulfur,[48] are comparable to our 3-21G results (135°). However, the energy difference between boat and planar forms is reduced from 3.0 kcal mol^{-1} for the 3-21G to 2.3 kcal mol^{-1} for the 3-21G*. The 6-31G* single point calculations, which include d-type polarization functions on carbon and on sulfur, further reduce the energy difference to 1.8 kcal mol^{-1}. It is interesting to note that the reduction in the boat–planar energy difference in going from the 3-21G to the 3-21G* basis set is about the same as the one in going from the 6-21G to the 6-31G* basis set. Thus, addition of polarization functions to an extended basis set significantly reduces the boat–planar energy difference of 1,4-dithiin by almost a constant amount (0.7 kcal mol^{-1}).

The calculated dipole moment decreases as the size of basis set is increased from 3-21G, 6-21G, 3-21G*, to 6-31G* (1.85, 1.79, 1.52, and 1.48 D, respectively). The same trend is observed for the calculated boat–planar energy difference (3.0, 2.6, 2.3, and 1.8 kcal mol^{-1} respectively for 3-21G, 6-21G, 3-21G*, and 6-31G*). However, the 6-31G* dipole moment is still about 30% larger than the experimental value (1.14 D).[42] On the other hand, the MM method gives a dipole moment of 0.95 D, which is in better agreement with the experimental value than any ab initio theories can do. Thus, we feel the boat–planar energy difference predicted by the largest basis set (employed so far for 1,4-dithiin) is probably still too large. The value predicted by molecular mechanics may be an acceptable one, although it may be slightly too low. Our best guess is that the real boat–planar energy difference in 1,4-dithiin should not be more than 1 kcal mol^{-1}.

The conformational preference of 1,4-dithiin is thus different from its congener, 1,4-dioxin, whose planarity has been assessed both experimentally and theoretically.[39] According to molecular mechanics calculations, the major factor to account for this is the very different natural bond angles for C–S–C and C–O–C. The smaller natural bond angles of 1,4-dithiin cause the ring to flap in order to release unfavorable ring strains in the planar form.

In summary, theoretical calculations predict that, in the gas phase, the dithiin molecule is very flexible, with the boat form being the minimum in energy. However, since the butterfly-flapping potential is extremely shallow, conformational equilibrium can easily be modified by solvent or other effects. This is particularly true for polar solvents, since the boat form is disfavored by dipolar interactions according to molecular mechanics calculations. If the above conformational characteristics of 1,4-dithiin are assumed, it is not difficult to explain the apparent conflicting experimental results.

(D) Dibenzo-1,4-dithiin and Benzo-1,4-dithiin. Dibenzo-1,4-dithiin has been the subject of many experimental and theoretical studies. X-ray diffraction studies[25,26] reveal that the molecule exists

(39) (a) Breslow, D. S.; Skolnik, H. "Multi-Sulfur and Sulfur and Oxygen Five- and Six-Membered Heterocycles"; Interscience: New York, 1966; Part II, Chapter 12 and references therein. (b) Gershbein, L. L. *Res. Commun. Chem. Pathol. Pharmacol.* **1975**, *11*, 445.

(40) (a) Beach, J. Y. *J. Chem. Phys.* **1941**, *9*, 54. (b) Connett, J. E.; Creighton, J. A.; Green, J. H. S.; Kynaston, W. *Spectrochim. Acta* **1966**, *22*, 1959. (c) Tinland, B.; Decoret, C. *J. Mol. Struct.* **1971**, *9*, 205.

(41) Aroney, M. J.; LeFevre, R. J. W.; Saxby, J. D. *J. Chem. Soc.* **1965**, 571. Laur, P. H. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; M. Dekker: New York, 1972; Vol. 3; Chapter 24, p 91. Colonna, F. P.; Distefano, G.; Galasso, V.; Irgolic, K. J.; King, C. E.; Pappalardo, G. C. *J. Organomet. Chem.* **1978**, *146*, 235. Fronza, G.; Ragg, E. *J. Chem. Soc., Perkin Trans. 2*, **1982**, 291. Cairns, T.; Fishbein, L.; Mitchum, R. K. *Biomed. Mass Spectrom.* **1980**, *7*, 484 and references therein.

(42) Mirarchi, D.; Phillips, L.; Ritchie, G. L. D. *Aust. J. Chem.* **1982**, *35*, 2335.

(43) Long, R. C.; Goldstein, J. H. *J. Mol. Spectrosc.* **1971**, *40*, 632. Russell, J. *Org. Magn. Reson.* **1972**, *4*, 433. Colonna, F. P.; Distenfano, G.; Galasso, V. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 75.

(44) Kreevoy, M. M. *J. Am. Chem. Soc.* **1958**, *80*, 5543. Ray, N. K.; Narasimham, P. T. *J. Mol. Struct.* **1968**, *1*, 489.

(45) Hayakawa, K.; Mibu, N.; Osawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* **1982**, *104*, 7136.

(46) Galasso, V. *THEOCHEM.* **1981**, *85*, 159.

(47) Saebo, S.; Radom, L.; Ritchie, G. L. D. *J. Mol. Struct.* **1984**, *108*, 59.

(48) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

Table V. Theoretical and Experimental Ionization Energies (eV) of 1,4-Dithiin

Xα–SW		VEH	STO-3G	3-21G	6-21G	
KT[a]	TS[b]	KT[a]	KT[a]	KT[a]	KT[a]	exptl[c]
5.56 π(6a₁)	8.3	7.97 π(6a₁)	5.02 π(6a₁)	8.60 π(6a₁)	8.49 π(6a₁)	8.2
7.83 π(4b₁)	10.6	10.54 π(4b₂)	8.70 π(4b₂)	10.67 π(4b₂)	10.73 π(4b₂)	10.1
7.92 π(4b₂)	10.7	11.14 π(4b₁)	9.50 π(4b₁)	11.27 π(4b₁)	11.24 π(4b₁)	10.3
9.60 σ(5a₁)	12.3	11.97 σ(5a₁)	10.05 σ(5a₁)	12.41 σ(5a₁)	12.38 σ(5a₁)	11.4
9.86 σ(3b₂)	12.7	12.68 σ(3b₂)	10.26 σ(3b₂)	12.49 σ(3b₂)	12.47 σ(3b₂)	12.2
10.30 σ(2a₂)	13.2	12.99 σ(2a₂)	10.48 σ(2a₂)	12.89 σ(2a₂)	12.83 σ(2a₂)	12.2
10.67 π(4a₁)	13.5	13.59 π(4a₁)	12.22 π(4a₁)	14.48 π(4a₁)	14.40 π(4a₁)	13.1
13.26 σ(3b₁)	16.2	16.66 σ(3b₁)	14.11 σ(3b₁)	16.26 σ(3b₁)	16.20 σ(3b₁)	14.9
14.48 σ(2b₂)		17.39 σ(2b₁)	15.56 σ(2b₁)	18.08 σ(2b₁)	18.01 σ(2b₁)	15.3
15.04 σ(2b₁)		18.08 σ(2b₂)	16.45 σ(2b₂)	18.98 σ(2b₂)	18.96 σ(2b₂)	16.3
15.14 σ(3a₁)		18.32 σ(3a₁)	16.90 σ(3a₁)	19.05 σ(3a₁)	18.99 σ(3a₁)	16.3

[a] Koopmans' theorem, see ref 53. [b] Transition state concept, see ref 9. [c] From ref 52.

as a folded C_{2v} configuration with a butterfly-flapping angle of 128°. A dipole moment study of dibenzo-1,4-dithiin in benzene solution gave 144 ± 8° for the butterfly-flapping angle.[49] A dielectric study in a polymer matrix[50] gave 3.6 ± 0.7 kcal mol⁻¹ for the inversion barrier, while LCAO–MO calculations[51] yielded a value of 6–7 kcal mol⁻¹ for the barrier. The recent electron diffraction analysis[24] found 128–130° for the butterfly-flapping angle and estimated that the inversion barrier should be greater than 4 kcal mol⁻¹.

Our molecular mechanics calculations suggest the C_{2v} boat form, with a butterfly-flapping angle of 130°, to be the energy minimum. This is in good agreement with X-ray and electron diffraction data. An inversion barrier of 4.6 kcal mol⁻¹ is predicted by the MM method, which is in line with the value suggested by the electron diffraction study; however, it is about 1 kcal mol⁻¹ larger than the one estimated by the dielectric study in a polymer matrix. Dibenzo-1,4-dithiin is calculated to have a dipole moment of 1.74 D, which is larger than the one of dithiin.

It is interesting to note that although a boat conformation with $\Phi \cong 130°$ is the most stable form for both dibenzo-1,4-dithiin and 1,4-dithiin, the energy difference between the boat and planar forms (or the inversion barrier) is much bigger in dibenzo-1,4-dithiin (ca. 4 kcal mol⁻¹) than in 1,4-dithiin (ca. 1 kcal mol⁻¹). Apparently this difference comes from interactions between dithiin and benzene rings. According to molecular mechanics calculations, the extra rigidity introduced by the benzene rings makes the boat form of dibenzo-1,4-dithiin relatively more stable than the boat form of 1,4-dithiin. The V_3 term of the C_{sp^2}–C_{sp^2}–S–C_{sp^2} torsional function in the E form accounts, in part, for the extra stabilization of the boat vs. planar forms in dibenzo-1,4-dithiin. There are four such interactions in dibenzo-1,4-dithiin while there are none in 1,4-dithiin. Contribution of the V_3 term is zero for the planar form because of its 3-fold nature. The contributions of the V_3 term are 0.5 kcal mol⁻¹ (4 × 0.13) for the boat form. Alternatively, one may obtain similar results by calculating the energy difference between $\Phi = 120$ and 180° from Figure 3 and multiplying it by 4 to get the total torsional contributions.

From the structural point of view, benzo-1,4-dithiin is the average of 1,4-dithiin and dibenzo-1,4-dithiin. In fact, the stable boat form is calculated to have a butterfly-flapping angle (Φ) of 135°; this is close to the average of the corresponding values for 1,4-dithiin and dibenzo-1,4-dithiin. Moveover, the calculated boat–planar energy difference for dithiin is also about the average of corresponding values for 1,4-dithiin and dibenzo-1,4-dithiin. The calculated dipole moment for benzo-1,4-dithiin is 1.49 D, which is compatible to the average of those found in dithiin and dibenzo-1,4-dithiin (0.95 and 1.74 D, respectively).

Electronic Structures. It has been demonstrated that an understanding of chemical and electronic properties of molecules

Table VI. Theoretical[a] and Experiment Lowest Ionization Potentials (eV)

compound	exptl.	STO-3G	3-21G	VEH
vinyl mercaptan		6.70	9.24	8.91
methyl vinyl sulfide	8.21[b,c]	6.42	8.81	8.82
divinyl sulfide	8.25[b], 8.42[d]	6.16	8.83	8.85
dithiin	8.15[e]	5.04	8.61	7.98
1,3-dithiole				8.26
1,4-dithiafulvene		5.33		7.88
benzo-1,4-dithiin				8.23
dibenzo-1,4-dithiin	7.80[f]			8.45
2,2'-bi-1,3-dithiole				7.25

[a] Obtained by the Koopman's theorem for the lowest energy conformation. [b] From ref 54. [c] Approximated by the value of ethyl vinyl sulfide. [d] From ref 55. [e] From ref 52. [f] From ref 56.

can be aided by quantum chemical calculations. The electronic structures of organosulfur compounds have recently attracted considerable attention because of the growing interest in organic polymers and conductors.

The photoelectron spectra of 1,4-dithiin[52] have recently been examined. The negatives of the occupied molecular orbital energies from various calculations are given in Table V for 1,4-dithiin, together with the available experimental data on ionization potentials (IP). The ionization potentials calculated by Koopmans' theorem[53] (KT) neglect the relaxation of the molecular orbitals which occurs upon ionization. Thus, the absolute values of the ionization potentials obtained from Koopman's theorem are probably not meaningful. There have been many applications of quantum chemical calculations in aiding spectral interpretation. The most important consideration for this type of application is for the ordering of calcuated molecular orbitals to be correct, then the derived ionization potentials can be correlated with the observed spectra.

As can be seen from Table V, all ab initio and VEH calculations give identical orbital ordering even though the orbital energies are different. The Xα–SCF method also gives the same orbital ordering with the exception of switching b₁ and b₂ symmetry orbitals. The ionization potentials obtained by ab initio and VEH calculations can be related to the experimental values by a linear relation such as IP(exptl) = $a_0 + a_1$·IP(calcd). For instance, the equation IP(exptl) = 3.770 − 0.737·IP(STO-3G) was proposed for 1,4-dioxin[52] and related systems. Interestingly, the IP values calculated by the Xα–SCF method using the Koopmans' theorem can be corrected to the experimental values by simply adding a constant term; i.e., IP(exptl) = 2.6 + IP(Xα–SCF). This simplicity may give the Xα–SCF method an edge over other methods.

(49) Aroney, M. J.; LeFevre, R. J. W.; Saxby, J. D. *J. Chem. Soc.* **1965**, 571.

(50) Kamiya, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3929. Chandra, A. K. *Tetrahedron* **1963**, *19*, 471.

(51) Davies, M.; Swain, J. *Trans. Faraday Soc.* **1971**, *67*, 1637.

(52) Colonna, F.; Distefano, G. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 75.

(53) Koopmans, T. *Physica (Amsterdam)* **1933**, *1*, 104.

(54) Trofimov, B. A.; Melder, U. K. H.; Pukver, R. I.; Vyalykh, E. P. *Theor. Eksp. Khim.* **1975**, *11*, 1965.

(55) Weiner, M. A.; Lattman, M. *Inorg. Chem.* **1978**, *17*, 1084.

(56) Kamiya, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3929. Lamatte, B.; Berthier, G. *J. Chem. Phys.* **1966**, *63*, 369.

(57) Sappenfield, D. S.; Kreevey, M. *Tetrahedron* **1963**, *19*, suppl. 2, 157.

Table VII. Calculated and Experimental Electronic spectra (eV) of 1,4-Dithiin and Dibenzo-1,4-dithiin

	Xα–SW	experimental
1,4-dithiin		
$\pi(6a_1) \rightarrow \pi^*(5b_1)$	4.55	
$\pi(6a_1) \rightarrow \pi^*(7a_1)$	4.66	4.59[a]
$\pi(6a_1) \rightarrow \pi^*(5b_2)$	5.33	
$\pi(6a_1) \rightarrow \pi^*(8a_1)$	5.37	5.75
dibenzo-1,4-dithiin		
$\pi(11a_1) \rightarrow \pi^*(7a_2)$	3.92	
$\pi(8b_2) \rightarrow \pi^*(7a_2)$	4.25	4.13[b]
$\pi(11a_1) \rightarrow \pi^*(9b_2)$	4.39	
$\pi(11a_1) \rightarrow \pi^*(10b_1)$	4.40	4.81
$\pi(11a_1) \rightarrow \sigma^*(12a_1)$	4.88	
$\pi(11a_1) \rightarrow \sigma^*(11b_1)$	5.14	
$\pi(11a_1) \rightarrow \sigma^*(13a_1)$	5.19	
$\pi(11a_1) \rightarrow \pi^*(8a_2)$	5.32	5.10
$\pi(11a_1) \rightarrow \pi^*(14a_1)$	5.62	
$\pi(11a_1) \rightarrow \pi^*(10b_2)$	5.80	5.93

[a] From ref 57. [b] From ref 50.

However, the VEH method would be more appropriate for this type of routine application, because it is very easy to use and it gives ab initio quality results with negligible computer time.

The negatives of the highest occupied molecular orbital (HOMO) energies for various compounds are presented in Table VI, together with the available experimental data on ionization potentials. Theoretical values differ from one method to another. However, the order of experimental values across compounds within a particular method are essentially preserved. The only exception occurs at dibenzo-1,4-dithiin. Our theoretical calculations predict that there is about an 0.5 eV increase in IP from 1,4-dithiin to dibenzo-1,4-dithiin, while the experimental data indicates a decrease of 0.35 eV. It is interesting to note that previous semiempirical SCF–MO–CI calculations[50] also predicted a net IP increase of 0.6 eV in going from 1,4-dithiin to dibenzo-1,4-dithiin.

For the calculation of spectroscopic quantities within the Xα methodology, Slater has proposed the transition-state concept.[9]

Within this method, the ionization potentials are approximated as the energy of the orbital from which one-half unit of electronic charge has been removed. A SCF calculation is then performed for the transition state, which allows the orbital to relax and thus to overcome the basic deficiency in the KT treatment of ionization potentials. Calculated results using the transition state concept are also listed in Table V for 1,4-dithiin. The transition-state approach, indeed, gives the best overall results of all the methods.

The transition-state concept is also used to predict energies of optical transitions for both 1,4-dithiin and dibenzo-1,4-dithiin. As can be seen from Table VII the calculated results are in good agreement with experimental spectra. Importantly, the theoretical calculations provide the nature of virtual orbitals and the characteristics of electronic transitions.

Conclusions

We have described the potential of the complementary use of theoretical tools to study geometrical structures, energies, conformations, and electronic structures of large molecules. A force field has been developed, on the basis of experimental and ab initio data, permitting molecular mechanics calculations to be performed on large molecules which is necessary for deriving structures within a negligible CPU time. Undoubtedly, the best set of parameters can only be reliably evaluated when new experimental values are available and the older ones redetermined. Nevertheless, we do expect that this is a reasonable force field and its predictions are at least qualitatively correct. A physical linkage has been made between the molecular mechanics method and the VEH method so that one can easily use molecular mechanics geometries along with the VEH approach in obtaining molecular orbitals and energies of ab initio quality with inexpensive CPU time. The Xα–SCF method has been shown to produce very good optical transitions, and its development and applications for large organic molecules should be encouraged. It is our hope that this work will stimulate further theoretical and experimental research in this area.

Ab Initio Studies of the C₃H₄ Surface. 1. SCF and CI Study of Structures and Stabilities of Isomers

N. Honjou, J. Pacansky, and M. Yoshimine*

Contribution from the IBM Research Laboratory, San Jose, California 95193. Received February 5, 1985

Abstract: SCF and CI calculations have been performed to study structures and stabilities of possible C₃H₄ isomers. The stable singlet isomers considered are methylacetylene (0), allene (0.7), cyclopropene (22.5), propenylidene (43.6), and cyclopropylidene (63.3), where calculated relative energies in kcal/mol are given in parentheses. For reactive intermediates, vinylmethylenes, low-lying states for six possible conformations (trans or cis planar carbene; trans or cis planar and bisected diradicals) are studied. Our best results show that the ³A″ states of trans and cis planar carbene structures are the most stable and isoenergetic lying 50.5 kcal/mol above the singlet methylacetylene. The lowest singlet vinylmethylene is the ¹A′ state of planar carbene which lies 10 kcal/mol above the ³A″ states of vinylmethylene. A study of the rotation of the CH₂ group revealed that both singlet and triplet bisected diradicals and also the triplet planar diradicals are not stable. A study of cis–trans isomerization for vinylmethylene conformers indicates 7–8 kcal/mol potential energy barriers for the singlet carbenes and diradicals and 5 kcal/mol for the triplet carbenes. From the analysis of the relative stabilities of the singlet C₃H₄ isomers, a new possible mechanism that involves propenylidene emerged for the thermal cyclopropene to methylacetylene isomerization.

I. Introduction

Many of the mechanisms for the thermal interconversion of isomers on the C₃H₄ surface play a central role in organic chemistry. Thus, they not only serve as models for much larger systems, but also provide a fundamental basis for reactions of hydrocarbons.

In Scheme I (see also Figure 1) a number of possible thermal reactions are shown that provide the basis for our ab initio study.