J. Am. Chem. Soc. 1984, 106, 3413-3415

Conclusion

For most types of nuclear spin–spin coupling, the inclusion of multicenter integrals in the semiempirical MO description leads to values of FC, OB, and SD contributions which are in reasonable accord with the ab initio results. Of particular importance is the extension of semiempirical methods to include the OB and SD contributions for coupling constants involving at least one proton. These are found to be substantial in magnitude for certain directly bonded and geminal coupling constants. Moreover, disparities between experimental values and those based on semiempirical FC terms, which are often ascribed to neglect of the OB and SD, are probably not justified. This conclusion is also supported by the insensitivity of the OB and SD contributions to substituent effects. In the tables included herein it is observed that the noncontact contributions are mainly determined by the hybridization of the atoms involved in the coupling and not by the substituent effects. For many types of spin–spin coupling the contributions of the multicenter integrals to the FC terms can be substantial, but they are not fully understood. This introduction of a reliable semiempirical method to estimate the OB and SD terms will provide the basis for further investigations of the electronic factors which determine the FC contributions.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. Services of the University of Arizona Computer Center were essential to the completion of this work.

Ab Initio Calculations of Rotational Barriers for the Diselenide Bridge in Dimethyl Diselenide[1a]

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Abstract: Ab initio calculations of the rotational barrier for the diselenide bridge, Se–Se, in dimethyl diselenide, $H_3CSeSeCH_3$, have been performed by using STO-3G and Dunning–Hay basis sets for C and H atoms and a modified Lehn–Wipff–Demuynck basis set for the Se atom consisting of a primitive [12s,8p,2d] set contracted into a [6s,4p,2d] set. Total energies as a function of $|\theta|$, the torsion angle about the Se–Se bond, and cis and trans torsional barriers are discussed in light of available experimental data.

Dimethyl diselenide ($H_3CSeSeCH_3$) is the simplest model compound containing the four consecutive atoms CSeSeC. The rotational or torsional barrier about the bond between two chalcogen atoms such as S or Se is known to be 2-fold in nature on the basis of general theoretical considerations[2] and more detailed molecular orbital (MO[3]) calculations (for specific references, see our previous papers[4,5]): the most stable conformation corresponds to a torsion angle θ[6] in the neighborhood of ±90°, and the cis barrier ($\theta = 0°$) is always calculated to be greater than the trans barrier ($\theta = 180°$).

We recently reported the results of a semiempirical CNDO/2 MO study of these barriers in dimethyl diselenide and noted that their heights were higher than the similarly calculated heights of the corresponding barriers about the S–S bond of the isologue dimethyl disulfide (H_3CSSCH_3).[4] The general shape of torsional barriers can be often be calculated, but the heights of the barriers are, in some cases, either unrealistically high or low.[7] For example, the CNDO/2 method does not adequately account for nonbonded interactions,[8] and deficiencies such as this may be, in part, responsible for the unreliable values of the calculated barrier heights. Realistic values of these heights, however, can be calculated by ab initio MO methods, provided that suitable basis sets for the MO's are chosen.[9]

Here we report an ab initio MO study of the torsional barrier about the Se–Se bond of dimethyl diselenide as part of our continuing theoretical investigation[4,5] of simple dichalcogen compounds that we are performing to learn more about the relative conformational flexibility of torsional movement about S–S, S–Se, and Se–Se bonds in cystine-containing molecules and their selenium isologues. Estimated barrier heights obtained from MO studies of these model compounds should be quite useful as input parameters in classical potential energy studies of these larger molecules—i.e., peptides. To our knowledge, this is the first report of an ab initio MO calculation of the cis and trans torsional barriers about the Se–Se bond.

Method

We performed ab initio MO calculations at two levels of refinement: at a lower level, which utilized an augmented minimal basis (AMB) set,

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(1) (a) This paper is dedicated to the memory of Professor Roderich Walter. (b) Deceased, Sept 19, 1979.

(2) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1949**, *35*, 495–499.

(3) Abbreviations: AEB, augmented extended basis; AMB, augmented minimal basis; *b*, bond length; CNDO/2, complete neglect of differential overlap, version 2; DH, Dunning–Hay; *E*, total energy; E_0, minimum total energy; MLWD, modified Lehn–Wipf–Demuynck; MO, molecular orbital; STO , Slater-type orbital; ΔE_{cis}, $E(0°) - E_0$, height of cis barrier; ΔE_{trans}, $E(180°) - E_0$, height of trans barrier; ζ, orbital exponent; θ, torsion angle about S–S or Se–Se; θ_0, torsion angle corresponding to E_0; τ, bond angle.

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(6) Throughout this paper θ refers to the particular torsion angle defined by the four consecutive atoms A–B–B–A, where B is either S or Se. θ corresponds to the torsion angle χ^3 in the disulfide bridge region of the amino acid cystine or in the dichalcogen bridge region of selenocystine. The eclipsed cis conformation is defined as 0°, and the trans conformation as ±180°. Positive and negative torsion angles correspond to right-handed (*P*) and left-handed (*M*) screw senses, respectively. These algebraic signs are in accordance with the recommendations of the IUPAC Commission on Nomenclature of Organic Chemistry ("Nomenclature of Organic Chemistry"; Pergamon Press: Oxford, U.K., 1979; p 483).

(7) E.g., see (a) Herndon, W. C.; Feuer, J.; Hall, L. H. *Tetrahedron Lett.* **1968**, 2625–2628. (b) Gordon, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 3122–3130.

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and at a higher one, which utilized an augmented extended basis (AEB) set. For the C and H atoms, we used the STO-3G basis set[10] as part of the AMB set and the Dunning–Hay (DH) basis set[11] as part of the AEB set. In the STO-3G basis set, each Slater-type orbital (STO) is represented as a sum of three Gaussian functions, and in the DH basis set, contracted forms of the primitive sets of Huzinaga[12] are used. Both the STO-3G and DH sets were augmented with a modified Lehn–Wipff–Demuynck (LWD) set[13] for the Se atom to form the complete AMB and AEB sets, respectively. It should be noted that the MLWD set includes a *d* function. Lehn et al.[14] used their set of basis functions in an ab initio study of dimethyl selenide (H_3CSeCH_3) and its monovalent carbanion ($H_3CSeSeCH_2{}^{1-}$) and obtained reasonably good agreement between the calculated and observed values of the first and second ionization potentials. Therefore, we felt that this basis set for Se would be suitable for calculations on dimethyl diselenide.

We set bond angles and bond lengths at or near their experimentally determined values[15] and used the HONDO MO program[16] to calculate the total energy E. All calculations were performed on the CDC-7600 computer at Lawrence Berkeley Laboratory, University of California, Berkeley, CA. E was calculated as a function of $|\theta|$, the magnitude of the torsion angle about the diselenide bridge, at the following values of $|\theta|$: 0°, which corresponds to the cis conformation; 85°–95° in 2.5° intervals, which corresponds to the range expected on the basis of our previous semiempirical MO calculations[4] to be that in which E_0, the minimum of E, occurs; 180°, which corresponds to the *trans* conformation. No attempt was made to optimize the geometry to obtain the lowest possible values of E for the following reasons: (1) Experimental geometry used here was taken from the electron diffraction studies reported by D'Antonio et al.[15] (2) Our principal objective in this study was to investigate the nature of torsional barrier to Se–Se bond in dimethyl diselenide and utilize them in potential energy calculations of larger molecular constructs containing Se atom. (3) Computational costs for a complete geometry optimization, relaxing all bond lengths, bond angles, and torsion angle, θ, for the size of basis sets considered herein are prohibitive. (4) The effect of geometry optimization on the torsional barrier remains uncertain; see Renugopalakrishnan et al.[4] and van Wart et al.[17] Renugopalakrishnan et al.[4] have reported geometry optimization for dimethyl diselenide at the CNDO/2 level previously. Total energy E of $H_3C–Se–Se–CH_3$ was minimized with respect to two C–Se and Se–Se bond lengths and C–Se–Se and Se–Se–C bond angles as a function of the torsion angle, $|\theta|$, by using CNDO/2 and classical conjugate gradient method of Murtagh and Sargent.[18] The minimum value of $E(\theta)$ occurred at $|\theta| = 85°$ where difference between theoretical and experimental values for the bond lengths and bond angles were found to be 0.0435 Å, 0.001 Å, and 1.90°, respectively, for Se–Se and C–Se bond lengths and C–Se–Se and Se–Se–C bond angles, which were remarkably close to the the corresponding values from CNDO/2 calculations without geometry optimization and experimental values. In view of this earlier observation and the prohibitive computational costs, either geometry optimization or CI was considered practical.

Table I. Total Energy (E) of Dimethyl Diselenide as a Function of the Magnitude of the Torsion Angle about the Diselenide Bond ($|\theta|$)[a]

	E, au	
$|\theta|$, deg	STO-3G[b]	DH/MLWD[c]
0	−4823.042786585	−4872.508549091
80	−4823.060326755	*d*
82.5	−4823.060462895	−4872.537108876
85	−4823.060558698	−4872.537300255
87.5	−4823.060616503	−4872.537396246
90	−4823.060638305	−4872.537399513
92.5	−4823.060626128	*d*
95	−4823.060581674	*d*
180	−4823.052894684	−4872.519041539
$|\theta_0|$,[e] deg	90.4[f]	88.8
E_0,[e] au	−4823.060640798[f]	−4872.537409809

[a] Values of E were calculated by the HONDO MO program,[16] which made use of C_2 symmetry about the center of the Se–Se bond. Bond lengths (b's) and bond angles (τ's) were set at the following values, which are at previously calculated[4] or experimentally determined[15] values: b(Se–Se), 2.3695 Å (ref 4); b(C–Se), 1.954 Å (ref 15); b(C–H), 1.131 Å (ref 15); τ(Se–Se–C), 98.8° (ref 15). The methyl C's were assumed to be tetrahedral, so that all τs involving H–C were set at 109.47°. Both methyl groups were assumed to be staggered (i.e., the methyl H's and their vicinal Se form torsion angles of +60°, −60°, and 180°). [b] STO-3G basis set.[10] [c] Dunning–Hay/modified Lehn–Wipff–Demuynck basis set.[11,13] [d] Calculation did not converge. [e] Values of E_0 and $|\theta_0|$ were estimated from a least-squares fit of data corresponding to values of $|\theta|$ between 80° and 95° to a quadratic equation—i.e., data were fit to an equation of the form $E(|\theta|) = A|\theta|^2 + B|\theta| + C$; E_0, the minimum value of E, which is given by $-B/4A + C$, occurs at a value of $|\theta|$, designated by $|\theta_0|$, given by $-B/2A$. [f] When the least-squares fit was made to data corresponding to values of $|\theta|$ between 82.5° and 90°, $|\theta_0| = 90.2°$ and $E_0 = -4823.060638319$ au—i.e., when values of E corresponding to the same range of $|\theta|$ used in calculating E_0 and $|\theta_0|$ for the DH/MLWD basis set were used in the least-squares fit, there was only a small effect on the values of E_0 ($\delta E_0 \approx +2.5 \times 10^{-6}$ au) and $|\theta_0|$ ($\delta|\theta_0| \approx -0.2°$).

Table II. Calculated Values of the Heights of Torsional Barriers about Symmetrical Dichalcogen Bonds (ΔE)[a]

			ΔE, kcal/mol	
compd	bond	barrier[b]	STO-3G/ MLWD[c]	DH/ MLWD[c]
dimethyl diselenide	Se–Se	cis	11.19	18.09
		trans	4.86	11.51
compd	bond	barrier[b]	STO-3G[d]	DH + d[d,e]
dimethyl disulfide	S–S	cis	12.68	16.49
		trans	6.27	8.00

[a] Ab initio MO calculations. Bond lengths and bond angles were set at or near their experimentally determined values. [b] $\Delta E_{cis} \equiv E(0°) - E_0$ and $\Delta E_{trans} \equiv E(180°) - E_0$, where E_0 is the minimum energy at θ_0. [c] Values are calculated from data given in Table I; see footnotes *b* and *c* of Table I for definitions of these basis sets. [d] Values are taken from Table II of Renugopalakrishnan et al.[5] [e] DH + d ≡ Dunning–Hay basis set with inclusion of d orbitals: same as the DH basis set[11] except that the contracted set for S (Table A.3 of ref 11) was augmented with a 3d function—i.e., for S, the contracted set was [6s,4p,1d]; for the d orbital, ζ, the orbital exponent was taken to be 0.45.

Results and Discussion

Table I shows the results of our calculations. The values of the heights of the cis and trans torsional barriers are shown in Table II. Note that the calculated cis and trans barrier heights for the Se–Se bond of dimethyl diselenide are 1.49 and 1.41 kcal/mol *lower* than the corresponding heights for the S–S bond of dimethyl disulfide when the requisite augmented or nonaug-

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(10) STO-3G basis set: minimal basis set in which each Slater-type orbital (STO) is represented as a sum of three Gaussian functions. (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657–2664. (b) Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *Ibid.* **1970**, *52*, 2769–2773.

(11) Dunning–Hay basis set: contracted Gaussian basis sets obtained from the primitive sets of Huzinaga;[12] for H, C, and S, the primitive sets (4s), (9s,5p) and (11s,7p) were contracted into [2s], [3s,2p], and [6s,4p], respectively. Dunning, Th. H., Jr.; Hay, P. J. In "Methods of Electronic Structure Theory"; Schaefer, H. F., Jr., Ed.; Plenum Press: New York, 1977; pp 1–27 (Tables A.1, A.2, and A.3).

(12) Huzinaga, S. "Approximate Atomic Wave Functions, II"; Department of Chemistry Technical Report, University of Alberta, Edmonton, Alberta, Canada, 1971.

(13) Modified Lehn–Wipff–Demuynck basis set for Se: Lehn et al.[14] contracted the primitive (12s,8p,2d) set into a [5s,4p,2d] set, but we contracted it into a [6s,4p,2d] set; we used the same groupings for contractions as did Lehn et al.,[14] with following exception—the s functions characterized by values of 34.47 and 15.1604 for their orbital exponents were left uncontracted (s functions characterized by values of 4.40667 and 1.92114 for their orbital exponents were contracted together using the contraction coefficients shown in Table I of Lehn et al.[14]).

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mented STO-3G basis set is used but the these respective barriers are *higher* by 1.60 and 3.51 kcal/mol when the requisite augumented DH basis set is used.

A direct comparison of the calculated values of the corresponding heights in the isologues dimethyl diselenide and dimethyl disulfide might not be warranted for calculations based on the augumented or nonaugumented STO-3G basis sets inasmuch as the levels of refinement used for the bases of the Se and S atoms are quite different; futhermore, the set of functions used for the Se atom, namely, a primitive [12s,8p,2d] set contracted into a [6s,4p,2d] set, is much more extensive than the minimal basis set comprised of only three Gaussian functions that is used for the S atom. On the other hand, fairly extensive sets are used for both the Se and S atoms when the augmented DH set is used, and so a comparison of corresponding barrier heights might well be justified in this case.

We conclude that it is possible to calculate reasonable values of both cis and trans barriers in dichalcogen compounds, but it is difficult to decide on the basis of these calculations whether corresponding barrier heights are higher in the diselenide isologue or in the disulfide isologue[19].

Acknowledgment. This work was supported, in part, by National Institutes of Health Grant AM-18399. V. R. is deeply indebted to Dr. Michel Dupuis, National Resource for Computation in Chemistry, University of California, Berkeley, CA for his aid in performing these calculations and for his poignant comments on this manuscript, to Dr. Harry F. King for his help with one of the references, and to Mrs. Sara W. Leake for her aid in preparing the manuscript.

Registry No. Dimethyl diselenide, 7101-31-7.

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(19) Infrared and Raman spectroscopic data (ref 19a-c) and thermodynamic data (ref 19d) on dimethyl disulfide and dimethyl diselenide have been published. Although these data do contain information on barrier heights about the dichalcogen bridge, careful comparative studies of these two isologues have not, to our knowledge, been reported, and so it is not possible at present to decide on the basis of experimental studies whether corresponding barrier heights are higher in the disulfide or in the diselenide compound. (a) Scott, D. W.; Finke, H. L.; Gross, M. E.; Guthrie, G. B.; Huffman, H. M. *J. Am. Chem. Soc.* **1950**, *72*, 2424-2430. (b) Crowder, G. A.; Scott, D. W. *J. Mol. Spectrosc.* **1965**, *16*, 122-129. (c) Green, W. H.; Harvey, A. B. *J. Chem. Phys.* **1968**, *49*, 3586-3595. (d) Hubbard, W. N.; Douslin, D. R.; McCullough, J. P.; Scott, D. W.; Todd, S. S.; Messerly, J. F.; Hossenlopp, I. A.; George, A.; Waddington, G. *J. Am. Chem. Soc.* **1958**, *80*, 3547-3554.

Matrix Isolation Studies of Nucleic Acid Constituents. 2. Quantitative ab Initio Prediction of the Infrared Spectrum of In-Plane Modes of Uracil

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Abstract: The dipole moment derivatives (or atomic polar tensors (APTs)) for the atoms in uracil have been calculated in an ab initio quantum mechanical calculation, using the GAUSSIAN 76 program with 4-31G basis functions. The frequencies and normal coordinate transformation matrices have been calculated from the force constants obtained from the ab initio quantum mechanical calculations by Nishimura et al. These are combined with our calculated APTs to predict absolute intensities and to give a prediction from ab initio calculations of the entire infrared spectrum for the in-plane modes of the isolated uracil molecule. This predicted spectrum is in excellent agreement with the experimental spectrum (from Szczesniak et al.) of uracil isolated in a matrix. This result indicates that it is possible at present to make good quantitative predictions that are very useful in assignment and interpretation of vibrational spectra even for molecules that are as complicated as uracil. Comparisons are given between experimental and predicted spectra for matrix isolated uracil and for N_1,N_3-dideuteriouracil, and the predicted spectra are also tabulated for C_5,C_6-dideuterated, N_1,N_3,C_5,C_6-perdeuterated, C_5-deuterated, C_6-deuterated, N_1-deuterated, and N_3-deuterated uracils. The calculated APTs are also tabulated for use in future predictions of intensities of other nucleic acid constituents by transfering APTs.

Recently, it has been shown that it is possible to predict with considerable accuracy the infrared absorption spectra of small molecules.[1-3] These predictions are made by using normal coordinate analyses based on force constants and intensity parameters transferred from related molecules or from ab initio quantum mechanical calculations. Comparisons between the experimental spectra and the predicted spectra for these molecules have shown that the predictions of absolute intensities can be expected to be in agreement with the experimental spectra within a "factor of two".[4] While it may seem that the typical "factor-of-two" agreement that we expect between the predicted and experimental intensities may be too poor to be of any value, this magnitude of agreement is sufficient to be very useful to the experimental spectroscopist.[4] It is important to realize that when the predicted spectral patterns (within a factor of two, or even three) are compared with an experimental spectrum (for example, see reference 4 or Figure 2 of this paper) the usual agreement is close enough to be "very good" and "quantitative" enough to be useful in several applications. For one thing, predictions of this type for species (such as *isolated* uracil molecules) which are difficult to obtain in a bottle[5] are expected to be of considerable importance in the interpretation of experimental studies of these species in

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