J. Am. Chem. Soc. **1993,** *115,* 10231–10236

Generalized Anomeric Effects and Hyperconjugation in $CH_2(OH)_2$, $CH_2(SH)_2$, $CH_2(SeH)_2$, and $CH_2(TeH)_2$

Ulrike Salzner and Paul von Ragué Schleyer*

Contribution from Institut für Organische Chemie I, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany

Received March 11, 1993[⊗]

Abstract: The origin of generalized anomeric effects (energy differences between gauche and anti structures) in methanediol and its sulfur, selenium, and tellurium derivatives has been examined in detail by *ab initio* calculations through the MP2 level and by NBO analyses of the Hartree–Fock wave functions. Gauche preferences of SH, SeH, and TeH substituents decrease but do not vanish. The X lone pairs as well as the CH, CX, and XH bonding electrons are slighly delocalized (X = O, S, Se, and Te). If the wave functions are expanded in terms of localized and orthogonal molecular orbitals, these delocalizations are represented by hyperconjugative orbital interactions. $p_X \rightarrow \sigma^*_{CX}$ and $\sigma_{CH} \rightarrow \sigma^*_{XH}$ hyperconjugation strongly favors gauche structures. However, other orbital interactions such as $p_X \rightarrow \sigma^*_{CH}$, $sp_X \rightarrow \sigma^*_{CX}$, and $\sigma_{XH} \rightarrow \sigma^*_{CX}$ are stronger in the anti structures and compensate the effects of the $p_X \rightarrow \sigma^*_{CX}$ and $\sigma_{CH} \rightarrow \sigma^*_{XH}$ interactions to a large extent. Nonhyperconjugative contributions to the energy difference between the gauche and anti structures are small for methanediol. Thus, dipole repulsions do not account for the anomeric effect. NBO analysis of the C–O bond rotation energies in methanediol and fluoromethanol reveals that the V_1, V_2, and V_3 Fourier components of the potential functions do not represent steric and electrostatic effects and the $p_X \rightarrow \sigma^*_{CX}$ hyperconjugation contribution adequately. In contrast to methanediol, nonhyperconjugative contributions are significant for the sulfur, selenium, and tellurium derivatives. These contributions favor the anti conformers and account for the decreased gauche preferences of $CH_2(SH)_2$, $CH_2(SeH)_2$, and $CH_2(TeH)_2$. Generalized anomeric effects (conformational preferences) and nonadditive bond separation energy behavior have complex origins (of which $p_X \rightarrow \sigma^*_{CX}$ hyperconjugation is only one contribution) and are not directly related.

Introduction

The term anomeric effect originally denoted the preference of electronegative substituents X at the anomeric center of pyranoses for the axial configuration.[1-3] In the axial conformation, the C–X bond is oriented gauche with respect to the C6–O1 bond, while in the equatorial conformer the orientation is anti (Figure 1a). Analogously, aliphatic ROCX compounds prefer gauche over anti C–O bond conformations (Figure 1b). This is known as the generalized anomeric effect.[3b]

The first explanation for the anomeric effect was offered by Edward in 1955.[1] He argued that the equatorial conformations of sugars may be destabilized by repulsions between the lone pairs of the endo- and the exocyclic oxygen atoms (Figure 2a). Similar destabilizations may arise in anti conformations of aliphatic $ROCH_2X$ compounds (Figure 2b, R = H, X = OH). A second rationalization of the anomeric effect was developed to explain distortions in the geometries of 2,5-dichloro-1,4-dioxanes:[4] unusually long exocyclic C–X bonds and short endocyclic C–O bonds. As in sugars and pyranoses, these substituent adopt axial conformations. Romers, Altona, et al.[4] suggested that in the axial conformer quantum chemical mixing may delocalize the oxygen p lone pair into the low-lying C–Cl antibonding orbital ($p_O \rightarrow \sigma^*_{CCl}$ hyperconjugation) (Figure 3). Such a stabilizing orbital interaction is not possible in the equatorial structure, since the orbtials involved are perpendicular. $p_O \rightarrow \sigma^*_{CCl}$ hyperconjugation results in a shortening of the endocyclic C2–O1 bond due to partial double character and a lengthening of the C–Cl bond due to the charge density in the antibonding C–Cl orbital.

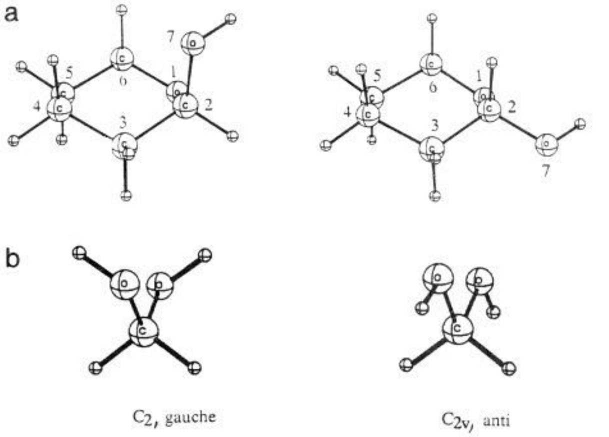

Figure 1. (a) Gauche and anti orientations of C2 substituents with respect to the O–C6 bonds in axial and equatorial conformations of 2-substituted pyrans. (b) Gauche and anti orientations of the O–H bonds with respect to the C–O bonds in the C_2 and C_{2v} conformers of $HOCH_2OH$.

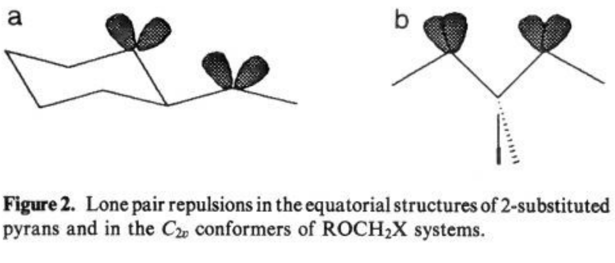

Figure 2. Lone pair repulsions in the equatorial structures of 2-substituted pyrans and in the C_{2v} conformers of $ROCH_2X$ systems.

Hartree–Fock (HF) *ab initio* calculations[5-21] reproduce the observed gauche preferences and geometric effects in pyranoses and aliphatic $ROCH_2X$ compounds. NBO analyses[22] of Hartree–

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1993.

(1) (a) Edward, J. T. *Chem. Ind.* **1955**, 1102. (b) Kabayama, M. A.; Petterson, D. *Can. J. Chem.* **1958**, *36*, 563. (c) Eliel, E. L. Kem. Tidskr. **1969**, *81*, 22.

(2) (a) Lemieux, R. U.; Chü, N. J. *Abstr. Pap.–Am. Chem. Soc.* **1958**, *133*, 31N. (b) Chü, N. J. Ph.D. Thesis, University of Ottawa, 1959.

(3) (a) Lemieux, R. U. In *Molecular Rearrangements*; De Mayo, P. Ed.; Interscience: New York, 1964, p 723. (b) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer Verlag: Berlin, 1983. (c) Juaristi, E.; Cuevas, G. *Tetrahedron* **1992**, *48*, 5019.

(4) (a) Altona, C. PH.D. Thesis, University of Leiden, 1964. (b) Romers, C.; Altona, C.; Buys, H. R.; Havinga, E. *Top. Stereochem.* **1969**, *4*, 39.

0002-7863/93/1515-10231$04.00/0

Figure 3. Hyperconjugation in the axial structures of 2-substituted pyrans and dioxanes.

Fock wave functions using orthogonalized atomic orbital bases support the hyperconjugation model.[23] Analyses of the wave functions employing nonorthogonal atomic orbitals reveal stabilizations arising from interference interactions.[24] In contrast to Edward's classic interpretation of the anomeric effect in terms of repulsive "rabbit ear" effects, both analyses of *ab initio* results indicate that stabilizations arising from orbital interactions involving the adjacent electronegative substituents at carbon are responsible instead.

Radom et al.[25] analyzed rotational barriers around C–Y single bonds in terms of Fourier type decompositions into 1-fold (V_1), 2-fold (V_2), and 3-fold (V_3) contributions. Fluoromethanol being taken as an example, these contributions were attributed to dipole repulsions, $p_O \rightarrow \sigma^*_{CF}$ hyperconjugation, and steric effects, respectively. Grein and Deslongchamps[26] developed this method further and applied it to neutral and protonated XH_nCH_2OH systems, X = F, O, N, and C.

The group separation reactions[27] (eq 1) of $RXCH_2YR$ systems (X, Y = NH_2, OH, and F) are endothermic.[28,29] Since $p_Y \rightarrow \sigma^*_{CX}$ hyperconjugation is eliminated on the right side of eq 1, the group separation energy has also been attributed to $p_Y \rightarrow \sigma^*_{CX}$ hyperconjugation.[28] Thus, anomeric effects and group separation energies are presumed to have the same origin. Group separation reactions were therefore taken as measures of the anomeric effect.[28,29]

$$RYCH_2XR + CH_4 \rightarrow CH_3YR + CH_3XR \qquad (1)$$

When X and Y are substituents from the third row of the periodic table (PH_2, SH, Cl), the group separation energies at the Hartree–Fock level are very small or even slightly negative. This led to the conclusion that anomeric effects are negligible when substituents of the higher rows of the periodic table are involved.[28] The absence of anomeric effects for these systems was rationalized by the fact that $p_Y \rightarrow \sigma^*_{CX}$ hyperconjugation is less effective for higher row substituents because these are poorer σ acceptors and have lower π-donor abilities than their second-row analogs.

However, XCH_2Y compounds involving P,[30] S,[31] Se,[31] and Cl[32] substituents do indeed prefer gauche conformations. Moreover, they exhibit bond length and bond angle changes indicative of $p_Y \rightarrow \sigma^*_{CX}$ hyperconjugation. For example, the calculated widening of the Se–C–Se bond angle in the C_2 conformer of $CH_2(SeH)_2$ is even larger than that in methanediol.[33]

Apeloig and Stanger[29] observed that the energy differences between the gauche and the anti conformers of $AH_2(XH)_2$, A = C, Si and X = O, S, parallel the trends of the isodesmic equations (eq 1). In contrast, Krol et al.[34] pointed out the apparent discrepancy that a compound for which reaction 1 has a negative ΔE value ($RYCH_2XR$ side less stable) can actually prefer the gauche conformation.

These discrepancies clearly demonstrate that a quantitative relationship between the anomeric effect (i.e. gauche–anti energy differences) and group separation energies does not exist. In this study we will examine the anomeric effect involving substituents of the higher rows of the periodic table[28–33] by comparison of energies of gauche and anti structures of $CH_2(XH)_2$, X = O, S, Se, and Te. The conformational energies and rotational barriers around the C–X bonds will be decomposed using the NBO method,[22] which allows the direct calculation of the hyperconjugative energy contributions to the Hartree–Fock energies and thus the separation of energy effects due to hyperconjugation and dipole repulsions. Group separation energies will be compared with the anomeric effects.

Methods

The geometries of the C_2, C_s, C_{2v}, and C_1 conformers of $CH_2(XH)_2$ (X = O, S, Se, and Te) (Figure 4) were fully optimized at the MP2 (frozen core) level using the Gaussian 90 and 92 (G90 and G92)

---

(5) (a) Jeffrey, G. A.; Pople, J. A.; Radom, L. *Carbohydr. Res.* **1972**, *20*, 440. (b) Jeffrey, G. A.; Pople, J. A.; Radom, L. *Carbohydr. Res.* **1972**, *25*, 117. (c) Jeffrey, G. A.; Pople, J. A. Radom, J. A.; *Carbohydr. Res.* **1974**, *38*, 81. (d) Jeffrey, G. A.; Pople, J. A.; Binkley, J. S.; Vishveshwara, S. *J. Am. Chem. Soc.* **1978**, *100*, 373.

(6) Bingham, R. *J. Am. Chem. Soc.* **1975**, *97*, 6743.

(7) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 1663.

(8) (a) Kost, D.; Kornberg, N. *Tetrahedron Lett.* **1978**, *35*, 3275. (b) Kost, D.; Raban, M. *J. Am. Chem. Soc.* **1982**, *104*, 2960.

(9) Pross, A.; Radom, L. *J. Comput. Chem.* **1980**, *1*, 195.

(10) (a) Williams, J. O.; Scarsdale, J. N.; Schäfer, L.; Geise, H. J. *J. Mol. Struct.* (*Theochem*) **1981**, *76*, 11. (b) Schäfer, L.; Alsenoy, C. v.; Williams, J. O.; Scarsdale, J. N.; Geise, H. J. *J. Mol. Struct.* (*Theochem*) **1981**, *76*, 349. (c) Alsenoy, C. v.; Schäfer, L.; Scarsdale, J. N.; Williams, J. O.; Geise, H. J. *J. Mol. Struct.* (*Theochem*) **1981**, *86*, 111.

(11) Schleyer, P. v. R.; Kos, A. *Tetrahedron* **1983**, *39*, 1141.

(12) Magnussen, E. *J. Am. Chem. Soc.* **1986**, *108*, 11.

(13) (a) Aped, P.; Apeloig, Y.; Ellencweig, A.; Fuchs, B.; Goldberg, I.; Karni, M.; Tartakovsky, E. *J. Am. Chem. Soc.* **1987**, *109*, 1486. (b) Aped, P.; Schleifer, L.; Fuchs, B.; Wolfe, S. *J. Comput. Chem.* **1989**, *10*, 265.

(14) (a) Wolfe, S.; Ruak, A. *J. Chem. Soc. B* **1971**, 136. (b) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102. (c) Wolfe, S.; Whangbo, M. H.; Mitchel, D. J. *Carbohydr. Res.* **1979**, *69*, 1. (d) Wolfe, S.; Pinto, B. V.; Varma, V.; Leung, R. Y. N. *Can. J. Chem.* **1990**, *68*, 1051.

(15) Pichon-Pesme, V.; Hansen, N. K. *J. Mol. Struct.* (*Theochem*) **1989**, *183*, 151.

(16) (a) Wiberg, K. B.; Murcko, M. A. *J. Am. Chem. Soc.* **1987**, *104*, 4137. (b) Wiberg, K. B.; Murcko, M. A. *J. Phys. Chem.* **1987**, *91*, 3616. (c) Wiberg, K.; Murcko, A. *J. Am. Chem. Soc.* **1989**, *111*, 4821. (d) Wiberg, K. B.; Rablen, P. *J. Am. Chem. Soc.* **1993**, *115*, 614.

(17) (a) Sana, M.; Leroy, G.; Peeters, D.; Wilante, C. *J. Mol. Struct.* (*Theochem*) **1988**, *164*, 249. (b) Leroy, G.; Sana, M.; Wilante, C. *J. Mol. Struct.* (*Theochem*) **1991**, *234*, 303.

(18) Kysel, O.; Mach, P. *J. Mol. Struct.* (*Theochem*) **1991**, *227*, 285.

(19) Woods, R. J.; Szarek, W.; Smith, V. H., Jr. *J. Chem. Soc., Chem. Commun.* **1991**, *76*, 334.

(20) Wipff, G.; Boudon, S. In *Accurate Molecular Structures*; Domenico, A., Hargittai, J., Eds.; Oxford University, Press, 1991.

(21) (a) Meyer, M. *J. Mol. Struct.* (*Theochem*) **1992**, *257*, 157. (b) Cramer, C. J. *J. Org. Chem.* **1992**, *57*, 7034.

(22) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (c) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (d) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1978**, *101*, 1700. (e) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736.

(23) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 7362.

(24) (a) Smits, G. F.; Altona, C. *Theor. Chim. Acta* **1985**, *67*, 461. (b) Smits, G. F.; Krol, M. C.; van der Hart, W. J.; Altona, C. *Mol. Phys.* **1986**, *59*, 209. (c) Smits, G. F.; Krol, M. C.; Altona, C. *Mol. Phys.* **1988**, *63*, 921. (d) Smits, G. F.; Krol, M. C.; Altona, C. *Mol. Phys.* **1988**, *65*, 513.

(25) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371.

(26) Grein, F.; Deslongchamps, P. *Can. J. Chem.* **1992**, *70*, 604, 1562.

(27) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1985.

(28) Schleyer, P. v. R.; Jemmis, J. E.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393.

(29) Apeloig, Y.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1977**, *99*, 5901.

(30) (a) Juaristi, E.; Aguilar, M. A. *J. Am. Chem. Soc.* **1986**, *108*, 2000. (b) Juaristi, E. *Heteroat. Chem.* **1990**, *1*, 267. (c) Juaristi, E. *Acc. Chem. Res.* **1989**, *22*, 357. (d) Juaristi, E.; Flores-Vela, A.; Labastida, V. *J. Org. Chem.* **1989**, *54*, 5191.

(31) (a) Pinto, B. M.; Johnston, B. D.; Bachelor, R. J.; Einstein, F. W. B.; Gay, I. D. *Can. J. Chem.* **1988**, *66*, 2956. (b) Bachelor, R. J.; Einstein, F. W. B.; Gay, I. D.; Gu, J.-H.; Johnston, B. D.; Pinto, B. M. *J. Am. Chem. Soc.* **1989**, *111*, 6582. (c) Pinto, B. M.; Johnston, B. D.; Nagelkerke, R. *J. Org. Chem.* **1988**, *53*, 5668. (d) Pinto, B. M.; Johnston, B. D.; Bachelor, R. J.; Gu, J.-H. *J. Chem. Soc., Chem Commun.* **1988**, 1087. (e) Pinto, B. M.; Bachelor, R. J.; Johnston, B. D.; Einstein, F. W. B.; Gay, I. D. *J. Am. Chem. Soc.* **1988**, *110*, 2990.

(32) Anet, F. A. L.; Yavari, I. *J. Am. Chem. Soc.* **1977**, *99*, 6752.

(33) Salzner, U.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Comm.* **1990**, 190.

(34) Krol, M. C.; Huige, L. J. M.; Altona, C. *J. Comput. Chem.* **1990**, *11*, 765.

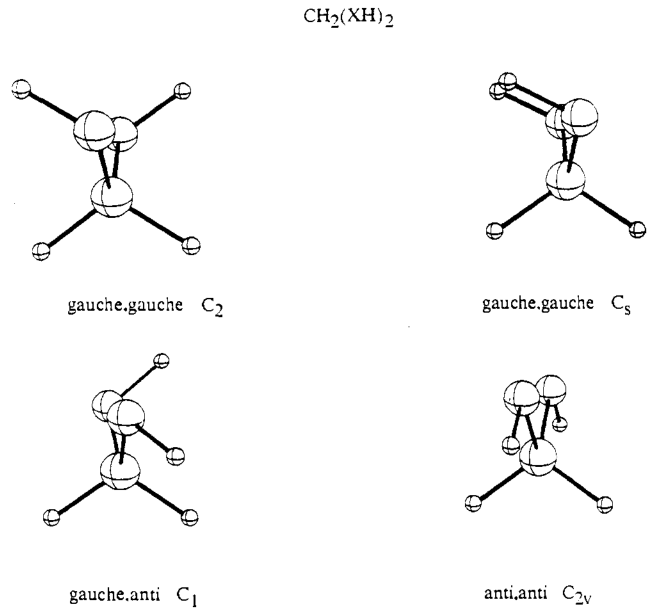

Figure 4. C_2, C_s, C_1, and C_{2v} symmetry structures of $CH_2(XH)_2$ systems.

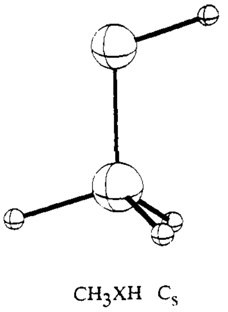

Figure 5. C_s symmetry structure of CH_3XH.

programs.[35,36] The reference CH_3XH compounds were optimized in staggered C_s symmetries (Figure 5). For X = O and S, the 6-31G** basis sets were employed. For the Se and Te compounds, effective core potentials (ECP) including relativistic corrections[37] were used. The valence basis sets for C, Se, and Te are of valence double-ζ plus polarization quality. The H basis was 6-31G**.

The NBO analyses[22] of the Hartree–Fock wave functions were carried out employing all-electron calculations (rather than ECP) for all compounds to allow a better comparison. Single points at the HF level were computed for the MP2-optimized geometries (6-31G** bases for O, S, C, and H; for Se and Te, Huzinaga's[38] 43321/4321/311 and 433321/43321/4311 bases sets were employed). Using mixed basis sets gives reliable results, since the NBO analysis is not basis set dependent.[22]

For X = O, S, and Se, additional structures with a series of fixed HXCX dihedral angles were optimized at the HF level. The HXCX dihedral angles range from 0° to 180°. The intervals are 20° (10° in the vicinity of critical points). The structures with HOCO angles from 20° to 160° have C_2 symmetry, and the 0° and 180° structures have C_{2v} symmetry (Figure 6). For these calculations, the same basis sets as described above were employed, except that for the S and Se systems the polarization functions on hydrogen were removed. The energy differences between the C_2 and the C_{2v} structures are 3.57 (X = S) and 2.20 kcal/mol (X = Se). This compares well with the HF energy differences with the larger basis sets, 3.50 and 2.30 kcal/mol.

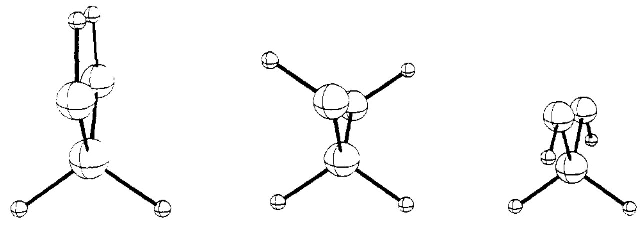

Figure 6. Structures of $CH_2(XH)_2$ arising from the rotation of both XH groups around the C–X bonds in opposite directions.

Table I. Conformational Energies (in kcal/mol) of $CH_2(OH)_2$, $CH_2(SH)_2$, $CH_2(SeH)_2$, and $CH_2(TeH)_2$, at the HF and MP2-FC Levels Using MP2-FC Optimized Geometries

	HF/MP2			
	$CH_2(OH)_2$	$CH_2(SH)_2$	$CH_2(SeH)_2$	$CH_2(TeH)_2$
C_2	0.0	0.0	0.0	0.0
C_s	3.48/+3.46	+1.27/+1.30	+0.87/+0.82	+0.50/+0.42
C_1	3.75/+4.27	+1.09/+1.42	+0.26/+0.58	−0.48/−0.35
C_{2v}	8.28/+9.19	+3.50/+4.11	+2.30/+2.71	+1.15/+1.20

The Fock matrix analyses were carried out with the NBO program,[22] which is implemented in Gaussian 90[35] and 92.[36] According to the NBO analysis, hyperconjugation represents the charge delocalization which is necessary to describe electron distributions adequately and which is not accounted for when a molecule is built up from strictly localized orbitals (NBOs). Accordingly, hyperconjugation includes all contributions from "orbital interactions" regardless of whether they are $\pi \rightarrow \sigma^*$, $\sigma \rightarrow \sigma^*$, or $\pi \rightarrow \pi^*$ symmetry. In the NLMO[22] basis, the delocalization arises from the delocalization tails of the NLMOs. The interference interactions which arise when nonorthogonal orbitals are employed[24] probably describe the same delocalization effect. Thus, hyperconjugation, delocalization tails, and interference interactions may well be different representations of the same basic physical effect.

With the NBO deletion procedure, the energies of the orbital interactions of interest are calculated by zeroing the corresponding off-diagonal Fock matrix elements. The delocalization energy is the difference relative to the total SCF energy. We will use the following abbreviations: E_{tot} is the Hartree-Fock total energy; E_{Lew} is the energy of the localized part of the wave function (Lewis structure), obtained by zeroing all orbital interactions (off-diagonal Fock matrix elements); ϵ_{del} is $E_{tot-ELew}$ (delocalization energy); E_{XCX} is the energy after zeroing the off-diagonal Fock matrix elements connecting the X lone pairs with the C–X antibonds; ϵ_{XCX} is the energy of the $lp_X \rightarrow \sigma^*_{CX}$ interactions = $E_{tot} - E_{XCX}$; E_{XCH} is the energy after zeroing the off-diagonal Fock matrix elements connecting the X lone pairs with the C–H antibonds; ϵ_{XCH} is the energy of the $lp_X \rightarrow \sigma^*_{CH}$ interactions = $E_{tot} - E_{XCH}$; $E_{XCX/H}$ is the energy after zeroing the off-diagonal Fock matrix elements connecting the X lone pairs with the C–X and C–H antibonds simultaneously; and $\epsilon_{XCX/H}$ is the energy of the simultaneous deletion of the $lp_X \rightarrow \sigma^*_{CX}$ and $lp_X \rightarrow \sigma^*_{CH}$ interactions = $E_{tot} - E_{XCX/H}$.

The $\epsilon_{XCX/H}$ term is not simply the sum of ϵ_{XCX} and ϵ_{XCH}. The energies of individual orbital interactions are not strictly additive because the charge redistributions resulting from the deletions are different.[39]

Results

Relative Energies. Table I shows the relative energies of the C_2, C_s (both gauche/gauche), C_1 (gauche/anti), and C_{2v} (anti/anti) conformers of $CH_2(XH)_2$, X = O, S, Se, and Te, at the HF and the MP2 frozen core (MP2-FC) levels. The relative energies are very similar at both levels. For O, S, and Se, C_2 structures are favored. The C_s and C_1 structures are close in energy. For X = Te, the C_1 conformer is more stable than the C_2. The least stable C_{2v} conformers are rotation transition states for all four substituents. In going down the group of the periodic table, C_1 structures are increasingly favored over C_2 and C_s forms. The energy differences between the C_2 and the C_{2v} structures drop from 9.2 (X = O) to 1.2 kcal/mol (X = Te). Note that the

---

(35) *Gaussian 90*, Revision F; Frisch, M. J., Head-Gordon, M., Trucks, G. W., Foresman, J. B., Schlegel, H. B., Raghavachari, K., Robb, M., Binkley, J. S., Gonzalez, C., Defrees, D. J., Fox, D. J., Whiteside, R. A., Seeger, R., Melius, C. F., Baker, J., Martin, R. L., Kahn, L. R., Stewart, J. J. P., Topiol, S., Pople, J. A., Eds.; Gaussian, Inc.: Pittsburgh, PA, 1990.

(36) *Gaussian 92*, Revision, A; Frisch, M. J., Trucks, G. W., Head-Gordon, M., Gill, P. M. W., Wong, M. W., Foresman, J. B., Johnson, B. G., Schlegel, H. B. Robb, M. A., Replogle, E. S., Gomperst, R., Andres, J. L., Raghavachari, K., Binkley, J. S., Gonzalez, C., Martin, R. L., Fox, D. J., Defrees, D. J., Baker, J., Stewart, J. J. P., Pople, J. A., Eds.; Gaussian, Inc.: Pittsburgh, PA, 1992.

(37) Bergner, A.; Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. To be published.

(38) Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: New York, 1984.

(39) Tyrell, J.; Weinstock, R. B.; Weinhold, F. *Int. J. Quantum Chem.* **1981**, *19*, 781.

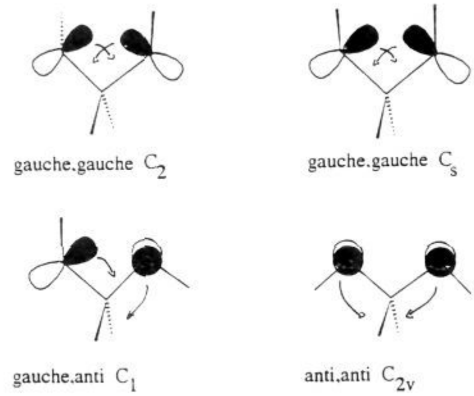

Figure 7. Orientation of the p_X lone pairs in the C_2, C_s, C_1, and C_{2v} structures of $CH_2(XH)_2$, X = O, S, Se, and Te.

Table II. Energy Contributions of $lp_X \rightarrow \sigma^*_{CX}$ (ϵ_{XCX}) and $lp_X \rightarrow \sigma^*_{CH}$ (ϵ_{XCH}) Hyperconjugation and of All Orbital Interactions (ϵ_{del}) in $CH_2(OH)\infty 2$, $CH_2(SH)_2$, $CH_2(SeH)_2$, and $CH_2(TeH)_2$, in C_2 and C_{2v} Symmetry

	$CH_2(OH)_2$		$CH_2(SH)_2$		$CH_2(SeH)_2$		$CH_2(TeH)_2$	
	C_2	C_{2v}	C_2	C_{2v}	C_2	C_{2v}	C_2	C_{2v}
ϵ_{XCX}	26.7	9.8	15.9	0.0	12.3	0.2	8.4	1.0
ϵ_{XCH}	19.0	32.9	11.5	21.0	7.5	13.3	5.1	8.9
$\epsilon_{XCX/H}$	46.5	42.8	27.6	21.0	19.8	13.5	13.6	10.0
ϵ_{del}	103.0	96.4	68.9	61.7	57.8	52.9	56.6	53.6

rotation energies of the first ($\Delta E(C_2–C_1)$) and the second ($\Delta E(C_1–C_{2v})$) substituent from the gauche to the anti position are not equal: the values are 4.3 vs 4.9 kcal/mol (X = O), 1.4 vs 2.7 kcal/mol (X = S), 0.6 vs 2.1 kcal/mol (X = Se), and –0.4 vs 1.6 kcal/mol (X = Te). Thus, the anomeric effect decreases significantly but does not vanish with the higher row substituents SH, SeH, and TeH. Due to the nonadditivity of the anomeric stabilizations, the C_1 structures gain importance for the Se and Te substituents.

Analysis of the Hyperconjugation Contribution to the Energies of C_2 and C_{2v} Conformers of $CH_2(XH)_2$, X = O, S, Se, and Te. The energy difference between the gauche/gauche and the anti/anti structures of methanediol has frequently been rationalized in terms of $p_O \rightarrow \sigma^*_{CO}$ hyperconjugation. The NBO analysis reveals that two off-diagonal Fock matrix elements do in fact relate the p_O orbitals with the adjacent σ^*_{CO} antibonds in the C_2 structure. The stabilization due to each of these matrix elements is 13 kcal/mol according to the NBO deletion procedure. Since $p_O \rightarrow \sigma^*_{CO}$ orbital interactions are absent in the C_{2v} conformer (compare Figure 7), a 26 kcal/mol stabilization of the C_2 vs the C_{2v} structure results.

Hyperconjugative interactions involving the sp lone pairs are usually regarded to be negligible compared to those of the p orbitals because sp orbitals have higher s character and lower energy.[9,29] However, the NBO analysis reveals that the two $sp_O \rightarrow \sigma^*_{CO}$ interactions in the C_{2v} conformer contribute about 5 kcal/mol each. In the C_2 form, $sp_O \rightarrow \sigma^*_{CO}$ interactions amount to 1 kcal/mol. Thus, $sp_O \rightarrow \sigma^*_{CO}$ hyperconjugation favors the C_{2v} over the C_2 conformer by 9 kcal/mol. This demonstrates clearly that the sp orbital contributions are not negligible. In the following discussion, the hyperconjugative interactions of the lone pair orbitals will include the contributions from both lone pairs, p and sp, and will be abbreviated as $lp_X \rightarrow \sigma^*$.

The NBO analysis further indicates the importance of $lp_O \rightarrow \sigma^*_{CH}$ hyperconjugation (Table II). The sum of all p and sp interactions with the C–O and C–H antibonds leads to a net stabilization of the C_2 conformer with respect to the C_{2v} form of 3.7 kcal/mol (Table III). The hyperconjugative energy contributions to the total energies and to the energy differences between C_2 and C_{2v} structurs of methanediol and its S, Se, and Te analogs are summarized in Tables II and III, respectively.

Table III. Contributions of $lp_X \rightarrow \sigma^*_{CX}$ ($\Delta\epsilon_{XCX}$), $lp_X \rightarrow \sigma^*_{CH}$ ($\Delta\epsilon_{XCH}$), and $lp_X \rightarrow \sigma^*_{CX}$ and $lp_X \rightarrow \sigma^*_{CH}$ ($\Delta\epsilon_{XCX/H}$) Orbital Interactions, Hyperconjugation as a Total ($\Delta\epsilon_{del}$), and Lewis Energies (ΔE_{Lew}) to the Energy Differences (ΔE_{tot}) between the C_2 and C_{2v} Structures of $CH_2(XH)_2$, X = O, S, Se, and Te

	$CH_2(OH)_2$	$CH_2(SH)_2$	$CH_2(SeH)_2$	$CH_2(TeH)_2$
$\Delta\epsilon_{XCX}$	16.9	15.9	12.1	7.4
$\Delta\epsilon_{XCH}$	–13.9	–9.5	–5.8	–3.8
$\Delta\epsilon_{XCX/H}$	3.7	6.6	6.3	3.6
$\Delta\epsilon_{del}$	6.6	7.2	4.9	3.0
$\Delta\epsilon_{Lew}$	1.7	–3.7	–2.8	–2.0
ΔE_{tot}	8.3	3.5	2.2	1.0

Table IV. Contributions (in kcal/mol) of the Lewis Energies (ΔE_{Lew}) and the Hyperconjugation Energies ($\Delta\epsilon_{del}$) to the Rotational Barriers (ΔE_{tot}) around the C–X Bonds in $CH_2(XH)_2$, X = O, S, and Se[a]

	ΔE_{tot}			ΔE_{Lew}			$\Delta\epsilon_{del}$		
θ_{HXCX}	O	S	Se	O	S	Se	O	S	Se
180	8.35	3.57	2.15	1.47	–3.86	–3.20	6.88	7.43	5.35
160	8.20	3.27	1.73	1.01	–4.00	–3.28	7.19	7.27	5.01
140	7.73	3.49	1.79	0.06	–4.40	–3.51	7.67	7.89	5.30
120	6.51	4.22	2.78	–0.35	–3.71	–2.74	6.86	7.93	5.52
100	4.11	3.53	2.74	0.12	–1.72	–1.02	3.99	5.25	3.76
90	2.66	2.56	2.09	0.45	–0.85	–0.29	2.20	3.41	2.39
80	1.32	1.46	1.26	0.55	–0.25	0.04	0.76	1.72	1.22
70	0.35	0.53	0.47	0.29	0.01	0.18	–0.04	0.52	0.29
60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	2.13	1.09	0.56	–0.76	0.06	–0.08	2.89	1.03	0.64
20	7.52	4.52	3.12	–0.13	–0.14	0.21	7.65	4.66	2.91
0	10.62	6.71	4.87	0.55	0.09	0.77	10.07	6.63	4.11

[a] Angles are given in degrees.

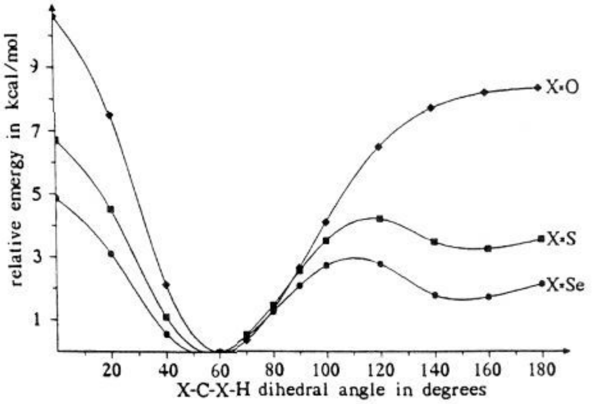

Figure 8. Rotational barriers (rotation of both XH substituents around the C–X bonds in opposite directions) of $CH_2(XH)_2$, X = O, S, and Se.

Both components (ϵ_{XCX} and ϵ_{XCH}) together give only about 30–40% of the total hyperconjugation (ϵ_{del}). Further important interactions are, for instance, $\sigma_{CH} \rightarrow \sigma^*_{XH}$, $\sigma_{XH} \rightarrow \sigma^*_{CX}$, and $lp_X \rightarrow C^*$ (C*'s are carbon Rydberg orbitals). In methanediol, $\sigma_{CH} \rightarrow \sigma^*_{OH}$ interactions contribute 3.8 kcal/mol in favor of the C_2 form. Hence, the energy difference between gauche and anti structures cannot be rationalized quantitatively by $p_X \rightarrow \sigma^*_{CX}$ orbital interactions alone.

NBO Analysis of the Rotational Barriers around the C–X Bonds in $CH_2(XH)_2$, X = O, S, and Se. A series of structures with fixed H–X–C–X dihedral angles ranging from 0° to 180° was optimized for $CH_2(XH)_2$ X = O, S, and Se (see Figure 6). The relative total energies of the various conformers as well as the hyperconjugative and Lewis energy contributions to the relative energies are summarized in Table IV and are plotted in Figures 8–10.

Decreasing hyperconjugative contributions (Figure 9) correlate with decreasing ΔE_{tot} values (Figure 8) for X–C–X–H dihedral angles between 0° and 60°. The smaller energy differences for the structures with X–C–X–H dihedral angles between 60° and 180° are mainly due to negative Lewis energy contributions

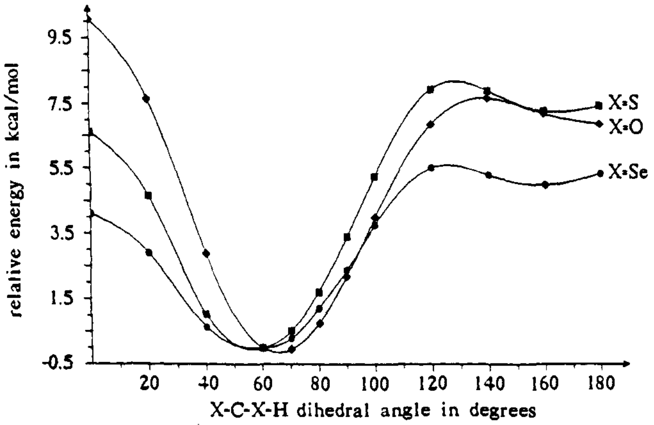

Figure 9. Dependence of the hyperconjugation contributions on the X–C–X–H dihedral angles in $CH_2(XH)_2$, X = O, S, and Se.

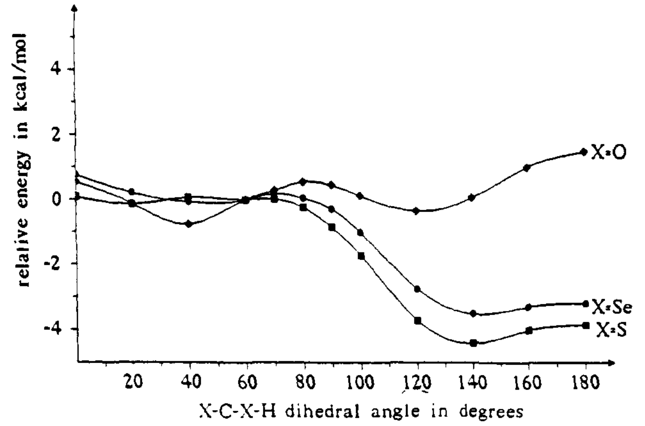

Figure 10. Dependence of Lewis energies on the X–C–X–H dihedral angles in $CH_2(XH)_2$, X = O, S, and Se.

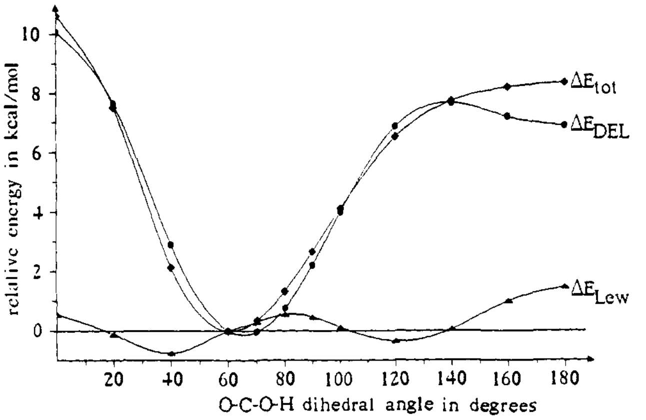

Figure 11. Contribution of hyperconjugation and the Lewis energy to the rotational barrier around the C–X bonds in $CH_2(OH)_2$.

Table V. Decomposition of the Hyperconjugation Contribution $\Delta\epsilon_{del}$ to the Rotational Barrier of Methanediol into $lp_O \rightarrow \sigma^*_{CO}$ ($\Delta\epsilon_{OCO}$), $lp_O \rightarrow \sigma^*_{CH}$ ($\Delta\epsilon_{OCH}$), and Other Contributions[a]

θ_{HOCO}	$\Delta\epsilon_{OCO/CH}$	$\Delta\epsilon_{OCO}$	$\Delta\epsilon_{OCH}$	$\Delta\epsilon_{others}$
180	3.07	17.34	–14.86	3.81
160	3.15	15.35	–12.67	4.04
140	3.41	10.02	–6.99	4.26
120	1.86	3.78	–2.10	5.00
100	–0.55	–2.55	1.69	4.54
90	–1.28	–3.91	2.34	3.48
80	–1.33	–3.67	2.13	2.08
70	–0.52	–1.80	1.21	–0.48
60	0.00	0.00	0.00	0.00
40	3.78	7.24	–3.47	–0.89
20	7.38	12.68	–5.77	0.27
0	16.57	14.40	–4.77	–6.50

[a] Energies are given in kcal/mol, angles in degrees.

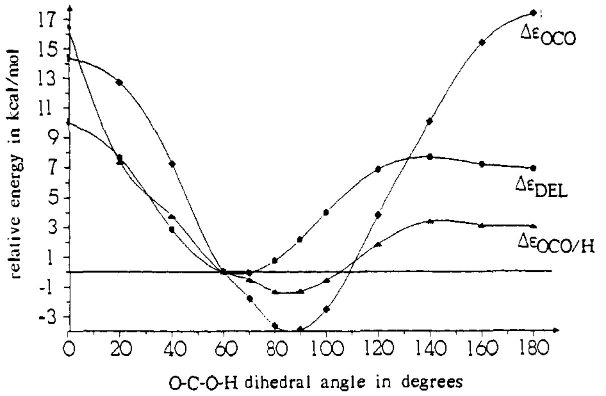

Figure 12. Contributions of $lp_O \rightarrow \sigma^*_{CO}$ (OCO) and $lp_O \rightarrow \sigma^*_{CH}$ (OCO/H) interactions and of the sum of all orbital interactions (DEL) to the rotational barrier of $CH_2(OH)_2$.

(Figure 10). Thus, for example, the Lewis energy term is small and positive for methanediol, but it is relatively large and negative for its higher row analogs.

The hyperconjugative energy changes represent the total energy curve almost perfectly for methanediol (Figure 11). Therefore, steric and electrostatic effects appear to be rather small. $lp_O \rightarrow \sigma^*_{CO}$ interactions (p and sp included) are greatest for H–O–C–O dihedral angles of 90° (Figure 12, Table V). The contribution to the energy difference between the 90° and the 180° conformer is 21 kcal/mol. This large energy contribution is nearly compensated by the opposite effect due to $lp_O \rightarrow \sigma^*_{CH}$ interactions. These stabilize the 180° compared to the 90° structure by 17 kcal/mol. However, the hyperconjugative energy effects are not fully represented by these two terms (Figure 12). Other interactions also contribute. The observed preference for H–O–C–O dihedral angles of about 60° is a compromise between the dihedral angle dependence of various orbital interactions. The contribution from hyperconjugation as a total leads to a 70° dihedral angle in methanediol. The final shift to 60° is due to the Lewis energy.

Thus, NBO analysis indicates that the potential energy function for the rotation around the C–O bonds in methanediol is the result of a rather complicated interplay of numerous orbital interactions. Dipole repulsions and steric effects are of minor importance. In contrast, Radom et al.[3c] rationalized the potential function for the C–O bond rotation in fluoromethanol in terms of the V_1, V_2, and V_3 Fourier components which were attributed to dipole repulsions, $p_O \rightarrow \sigma^*_{CF}$ interactions, and steric effects, respectively.[3c] We therefore optimized the cis, trans, and gauche ($\theta_{H-O-C-F}$ = 64°) conformers of fluoromethanol at the HF/6-31G** level and carried out NBO analyses. The relative energies are gauche 0.0, cis +2.42, and trans +4.79 kcal/mol. (Radom et al.[3c] obtained relative energies of 0.0, +1.31, and +5.60 kcal/mol at HF/4-31G in the rigid rotor approximation.) The V_2 Fourier term, which was attributed to $p_O \rightarrow \sigma^*_{CF}$ hyperconjugation, contributes about 1.5 kcal/mol in the gauche conformer.[3c] According to the NBO analysis, however, the $p_O \rightarrow \sigma^*_{CF}$ interaction amounts to 18 kcal/mol in the gauche conformer. Thus, V_2 certainly does not represent the $p_O \rightarrow \sigma^*_{CF}$ hyperconjugation. Orbital interactions involving the sp_O lone pair were claimed to be negligible in ref 3c. In contrast, the $sp_O \rightarrow \sigma^*_{CF}$ interactions contribute to 7 kcal/mol in the cis and trans structures. Both oxygen lone pairs also interact with the C–H antibonds. This leads to a 3-fold rather than a 1-fold contribution of hyperconjugation. Furthermore, if V_3 represented steric interactions, it would not be symmetrical as in ref 3c, since the three substituents are not equivalent. Thus, each of the three Fourier components comprises different energy contributions with the same periodicity, and unsymmetrical physical effects give rise to more than one Fourier component. This means that the number of Fourier components necessary to simulate a potential function

Table VI. Group Separation Energies $CH_2(XH)_2 + CH_4 \rightarrow 2CH_3XH$ (Eq 1), X = O, S, Se, and Te, at the HF and MP2-FC Levels (in kcal/mol)

	HF/MP2			
	$CH_2(OH)_2$	$CH_2(SH)_2$	$CH_2(SeH)_2$	$CH_2(TeH)_2$
C_2	+15.61/+17.09	−0.29/+2.62	−1.09/+2.33	−2.19/+0.32
C_s	+11.85/+13.64	−1.67/+1.32	−2.13/+1.51	−2.78/+1.05
C_1	+12.12/+12.82	−1.51/+1.19	+1.80/+1.75	−1.80/+1.82
C_{2v}	+7.25/+7.90	−3.86/−1.49	−3.32/−0.38	−3.80/+0.28

is not equivalent to the number of physical effects which contribute to the energy changes. Moreover, the mathematical separation of the potential function does not separate the *physical* components.

Trend in Hyperconjugation along the Series $CH_2(XH)_2$, X = O, S, Se, and Te. The contributions of hyperconjugation (ϵ_{del}) in the C_2 structures of $CH_2(XH)_2$, X = O, S, Se, and Te, are 109, 67, 57, and 56 kcal/mol, respectively, when all types of orbital interactions are included (Table II). The trends are roughly parallel for ϵ_{del} and for the components ϵ_{XCX} and ϵ_{XCH}. As previously suggested,[28] the delocalization energies decrease from O to Te. The largest difference is observed between the first and the second row of the periodic table.

The reason for smaller interaction energies with the higher row substituents SH, SeH, and TeH can be rationalized by means of second-order perturbation theory (eq 2),[40] which estimates the

$$\Delta E = -qF_{ij}^{\ 2}/(\epsilon_i - \epsilon_j) \qquad (2)$$

stabilization as the ratio between the square of the Fock matrix element and the energy difference between the interacting orbitals. The interactions of the p_X lone pairs with the σ^*_{CX} antibonds, for instance, amount to 18, 9, 8, and 5 kcal/mol for O, S, Se, and Te according to second-order perturbation theory. The energy differences between donor and acceptor orbitals in the denominator decrease from O to Te (1.11, 0.75, 0.65, and 0.57 au, respectively). Thus, the smaller ΔE values with higher row substituents are due to smaller Fock matrix elements between the interacting orbitals (0.126, 0.073, 0.063, and 0.049 au). Therefore, the magnitude of hyperconjugation is dominated by the size of the Fock matrix elements (which enter eq 2 in the second power) rather than energy differences between interacting orbitals.

Isodesmic Equations. The C_2 conformation of methanediol (X = O) is stabilized by 17.1 kcal/mol at the MP2-FC level according to the reaction

$$CH_2(XH)_2 + CH_4 \rightarrow 2CH_3XH$$

The C_2 forms of X = S, Se, and Te compounds are stabilized by 2.6, 2.3, and 1.5 kcal/mol, respectively (Table VI). The stabilization energies decrease from X = O to X = S by 14.5 kcal/mol. The values for X = S, Se, and Te are similar. At the HF level, the reaction energies are reduced by about 3–4 kcal/mol for all substituents. Thus, the negative group separation energies at the HF level[28] involving higher row compounds are due to the neglect of correlation.

An interesting aspect of the group separation energies is that the C_{2v} conformer of methanediol is stabilized by nearly 8 kcal/mol, although $P_O \rightarrow \sigma^*_{CO}$ hyperconjugation is absent. This stabilization is mainly due to the $sp_O \rightarrow \sigma^*_{CO}$ interactions in methanediol, since $p_O \rightarrow \sigma^*_{CH}$ hyperconjugation in $CH_2(OH)_2$ is almost identical with that in $2CH_3OH$.

Since in the usual interpretation the C_{2v} structures are not supposed to have anomeric interactions, the group separation energies cannot be a reliable measure of the anomeric effect (see also refs 17 and 34). Moreover, the trends in anomeric and group separation energies for the C_2 conformers in the series X = O, S, Se, and Te are *not* parallel. Since orbital interactions other than $p_X \rightarrow \sigma^*_{CX}$ contribute, the group separation energies also cannot be employed to estimate the strength of $p_X \rightarrow \sigma^*_{CX}$ hyperconjugation (see ref 41).

Conclusions

Anomeric effects (i.e. gauche conformational preferences) of $CH_2(XH)_2$ compounds are smaller for X = S, Se, and Te than for X = O. However, even for $CH_2(TeH)_2$, the C_2 and C_1 conformers are more stable than the C_{2v} form.

NBO analyses of the Hartree–Fock wave functions reveal that delocalization effects (i.e. hyperconjugation) are responsible for the anomeric stabilizations. Steric and electrostatic contributions are rather small for methanediol. For the S, Se, and Te analogs, nonhyperconjugative effects favor the anti conformers. The familiar $p_X \rightarrow \sigma^*_{CX}$ orbital interactions are the largest individual hyperconjugative contributions. However, other orbital interactions such as $p_X \rightarrow \sigma^*_{CH}$, $sp_X \rightarrow \sigma^*_{CX}$, $sp_X \rightarrow \sigma^*_{CH}$, and bond–antibond interactions also are present. The individual terms are small, but their sum amounts to about 60% of the total delocalization. Gauche structures are favored by $p_X \rightarrow \sigma^*_{CX}$, $sp_X \rightarrow \sigma^*_{CH}$, and $\sigma_{CH} \rightarrow \sigma^*_{XH}$ interactions. Anti structures are stabilized by $p_X \rightarrow \sigma^*_{CH}$, $sp_X \rightarrow \sigma^*_{CX}$, and $\sigma_{XH} \rightarrow \sigma^*_{CX}$. The anomeric effect arises from the difference between the stabilizations in the gauche and the anti structures.

Orbital interactions are less effective with the higher row substituents SH, SeH, and TeH than with OH, although the energy difference between the donor and the acceptor orbitals decreases in going down the group. The smaller stabilizations are due to smaller Fock matrix elements between the donor and the acceptor orbitals.

Although the magnitude of the orbital interactions is significantly smaller for the higher row substituents SH, SeH, and TeH than for OH, the difference between the stabilizations in the gauche and the anti structures is larger for SH than for OH and is only slightly attenuated for SeH and TeH. The smaller anomeric effects of the higher row compounds are due to nonhyperconjugative (e.g. steric and electrostatic) contributions, which increasingly favor the anti structures in going down the group.

Group separation reactions at the MP2 level indicate stabilizations for the C_2 conformers of all four $CH_2(XH)_2$ derivatives, X = O, S, Se, and Te. However, the ca. 8 kcal/mol stabilization of the anti/anti (C_{2v}) conformer of methanediol according to eq 1 (mainly due to $sp_O \rightarrow \sigma^*_{CO}$ hyperconjugation) indicates that the group separation energies measure neither the anomeric effect nor the effect of $p_X \rightarrow \sigma^*_{CX}$ hyperconjugation.

NBO analysis of the C–O bond rotational barrier in methanediol indicates that numerous orbital interactions contribute and that steric and electrostatic effects are of minor importance. NBO analysis of the relative energies of the cis, trans, and gauche conformers of fluoromethanol reveals that the number of Fourier components necessary to reproduce the rotational potential function does not correspond to the number of contributing *physical* effects. Contributions with the same periodicity are absorbed in the same Fourier component. Unsymmetrical contributions such as steric effects involving different substituents give rise to more than one Fourier component. Thus, the V_1, V_2, and V_3 terms do not represent dipole repulsions, $p_O \rightarrow \sigma^*_{CF}$ hyperconjugation, and steric effects adequately. The application of Fourier analysis as a measure of these effects is discouraged.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, the Stiftung Volkswagenwerk, and the Deutsche Forschungsgemeinschaft. We thank Dr. A. Dorigo and Dipl. Chem. Ch. Maerker for their assistance, and F. Grein, M. Pinto, K. Houk, Y. D. Wu, E. Juaristi, and K. Wiberg for reprints and communications.

---

(40) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley and Sons: New York, 1985.

(41) Salzner, U.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1992**, *5*, 190.