

# Are Any Ten-Valence-Electron HXY Species Bent in the Ground State? Ab Initio Optimized Energies and Shapes of HBO, HBS, HAlO, HAlS, and HCS<sup>+</sup> and Their Isomers

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**Abstract:** The potential energy surfaces of the HBO--HOB, HBS--HSB, HAlO--HAl, HAlS--HSAI, and HCS<sup>+</sup>--HSC<sup>+</sup> systems, each containing ten valence electrons, were explored by ab initio molecular orbital calculations. Since Walsh's rules predict that all of the energy minima should be linear, and since no nonlinear forms of these molecules or ions have been detected experimentally, it is interesting that theoretical calculations reveal some of them to be distinctly bent in their ground state. The five systems were studied at a minimum of nine uniform levels of theory with basis sets as large as 6-311G(2d,2p), i.e., triple- $\zeta$  plus double polarization, and with incorporation of frozen-core and full-core electron correlation at the perturbation orders MP2, MP3, and MP4. The geometry of each stationary-point structure was fully optimized at all levels. At our "best" level of theory, i.e., MP2/6-311G(2d,2p), HSB, HSAI, and HSC<sup>+</sup> are strongly bent, HOB is more weakly bent, HAlO is minutely bent, while HCS<sup>+</sup>, HBO, HBS, HAlO, and HAlS are all linear. All but HSC<sup>+</sup> lie in a deep energy well with respect to intramolecular HXY--HYX isomerization. We predict that HSB, HSAI, and HOB should exist as bent molecules under sufficiently isolated conditions, and, if one of these molecules is experimentally realized, it could become the first observed nonlinear ten-valence-electron HXY-type species.

## Introduction

One of the predictions of Walsh's rules is that molecules of the class HXY having ten valence electrons should be linear in their ground states.<sup>1</sup> Some examples of isomeric pairs of molecules or ions that conform to this rule, according to theoretical studies, are HCN--HNC,<sup>2-16</sup> HCO<sup>+</sup>--HOC<sup>+</sup>,<sup>9,17-20</sup> and HNSi--HSiN.<sup>21-29</sup>

Interest in such molecules was no doubt stimulated by the observation of several of them in interstellar space, for example, HNC,<sup>30,31</sup> HCO<sup>+</sup>,<sup>32,33</sup> HOC<sup>+</sup>,<sup>34</sup> and HCS<sup>+</sup>.<sup>35</sup> In each of these cases, laboratory or astronomical characterization was preceded by and aided by theoretical predictions.

With the object of determining whether other molecules or ions of the type HXY containing ten valence electrons would also exhibit linear equilibrium geometries, and of calculating the relative energies of the isomeric HXY and HYX structures and the potential energy barriers separating them, a systematic exploration of the ab initio Hartree-Fock STO-3G potential energy surfaces for the HXY--HYX rearrangement of some 42 HXY systems was conducted by us between 1979 and 1984.<sup>36</sup> Atoms X and Y were selected from elements of the first and second rows of the periodic table such that the resulting HXY species were neutral or singly or doubly charged. In that exploration, we located some 76 minima of which 29 HXY species appeared to be nonlinear. At the inception of that study, no other theoretical in-

- (1) Walsh, A. D. *J. Chem. Soc.* **1953**, 2288.
- (2) Pearson, P. K.; Schaefer, H. F., III; Wahlgren, U. *J. Chem. Phys.* **1975**, *62*, 350.
- (3) Komornicki, A.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Morgan, C. *Chem. Phys. Lett.* **1977**, *45*, 595.
- (4) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545.
- (5) Bartlett, R. J.; Purvis, G. D., III *Int. J. Quantum Chem.* **1978**, *14*, 561.
- (6) Redmon, L. T.; Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1980**, *72*, 986.
- (7) Gray, S. K.; Miller, W. H.; Yamaguchi, Y.; Schaefer, H. F., III *J. Chem. Phys.* **1980**, *73*, 2733.
- (8) Vazquez, G. J.; Gouyet, J. F. *Chem. Phys. Lett.* **1981**, *77*, 233.
- (9) Nobes, R. H.; Radom, L. *Chem. Phys.* **1981**, *60*, 1.
- (10) Peric, M.; Mladenovic, M.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys.* **1983**, *82*, 317.
- (11) Peric, M.; Mladenovic, M.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys.* **1984**, *86*, 85.
- (12) Glidewell, C.; Thomson, C. J. *Comput. Chem.* **1984**, *5*, 1.
- (13) Bertran, J.; Lledos, A. J. *Mol. Struct. (THEOCHEM)* **1985**, *24*, 211.
- (14) Taylor, P. R.; Backs, G. B.; Hush, N. S.; Hurley, A. C. *J. Chem. Phys.* **1978**, *69*, 1971.
- (15) Taylor, P. R.; Backs, G. B.; Hush, N. S.; Hurley, A. C. *J. Chem. Phys.* **1978**, *69*, 4669.
- (16) Dykstra, C. E.; Secrest, D. J. *Chem. Phys.* **1981**, *75*, 3967.
- (17) Wahlgren, U.; Liu, B.; Pearson, P. K.; Schaefer, H. F., III *Nature (London)* **1973**, *246*, 4.
- (18) Kraemer, W. P.; Dierksen, G. H. F. *Astrophys. J.* **1976**, *205*, L97.
- (19) Herbst, E.; Norbeck, J. M.; Certain, P. R.; Klemperer, W. *Astrophys. J.* **1976**, *207*, 110.
- (20) Bruna, P. J.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys.* **1975**, *10*, 323.
- (21) Murrell, J. N.; Kroto, H. W.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1977**, 619.
- (22) Preuss, R.; Buenker, R. J.; Peyerimhoff, S. D. *J. Mol. Struct.* **1978**, *49*, 171.
- (23) Roelandt, F. F.; Van de Vondel, D. F.; Van der Kelen, G. P. *J. Mol. Struct.* **1979**, *54*, 221.

- (24) Kroto, H. W.; Murrell, J. N.; Al-Derzi, A.; Guest, M. F. *Astrophys. J.* **1978**, *219*, 886.
- (25) Preuss, R.; Buenker, R. J.; Peyerimhoff, S. D. *Chem. Phys. Lett.* **1979**, *62*, 21.
- (26) Murrell, J. N.; Carter, S.; Varandas, A. J. C. *Mol. Phys.* **1978**, *35*, 1325.
- (27) Scheire, L.; Rotthier, R.; Phariseau, P. *Int. J. Quantum Chem.* **1981**, *20*, 879.
- (28) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M. B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270.
- (29) Flores, J. R.; Largo-Cabrero, J. J. *Mol. Struct. (THEOCHEM)* **1989**, *183*, 17.
- (30) Creswell, R. A.; Pearson, E. F.; Winniewisser, M.; Winniewisser, G. Z. *Naturforsch., Teil A* **1976**, *31*, 221.
- (31) (a) Snyder, L. E.; Buhl, D. *Bull. Am. Astron. Soc.* **1971**, *3*, 388. (b) Snyder, L. E.; Buhl, D. *Astrophys. J.* **1971**, *163*, L47. (c) Snyder, L. E.; Buhl, D. *Ann. N.Y. Acad. Sci.* **1972**, *194*, 17.
- (32) Buhl, D.; Snyder, L. E. *Nature (London)* **1970**, *228*, 267.
- (33) Klemperer, W. *Nature (London)* **1970**, *227*, 1230.
- (34) Woods, R. C.; Gudeman, C. S.; Dickman, R. L.; Goldsmith, P. F.; Huguenin, G. R.; Irvine, W. M.; Hjalmarsen, A.; Nyman, L. A.; Olofsson, H. *Astrophys. J.* **1983**, *270*, 583.
- (35) Thaddeus, P.; Guelin, M.; Linke, R. A. *Astrophys. J.* **1981**, *246*, L41.
- (36) (a) Huang, Y., M.S. Thesis, Wichita State University, 1983. (b) Zandler, M. E.; Huang, Y.; Talaty, E. R. Novel, Non-Linear, Ten-Valence-Electron HXY Isomers on the ab initio SCF Potential Energy Surface. Paper presented at the 187th National Meeting of the American Chemical Society in St. Louis, April 1984. (c) Talaty, E. R.; Zandler, M. E. Ab initio SCF Potential Energy Surfaces for Linear and Bent Analogues of HCN and HNC Containing Ten Valence Electrons. Paper presented at the Nineteenth Midwest Regional Meeting of the American Chemical Society, Springfield, Missouri, October 1984.

vestigation had suggested the existence of any bent molecule of this type. In fact, to this date, there is no report of an experimentally confirmed nonlinear HXY molecule or ion containing ten valence electrons.

One of the nonlinear molecules that appeared to be distinctly bent at the STO-3G level was HSC<sup>+</sup>, lying 69.2 kcal/mol above the linear HCS<sup>+</sup>, and separated from it by an intramolecular isomerization barrier of 22.5 kcal/mol.<sup>36a</sup> A contrasting result was reported by Bruna, Peyerimhoff, and Buenker,<sup>37</sup> who characterized HSC<sup>+</sup> to correspond to a linear saddle point instead of a minimum, located about 110 kcal/mol above HCS<sup>+</sup> by ab initio calculations without and with configuration interaction. In order to investigate whether our bent STO-3G structure of HSC<sup>+</sup> was a valid prediction, we carried out further calculations at systematically higher levels of theory. Our recent results (Table I) agree with those of Wong, Nobes, and Radom<sup>38</sup> and Tao,<sup>39</sup> in that a bent local minimum exists at all levels of theory for HSC<sup>+</sup>, but that there is little or no barrier for isomerization of bent HSC<sup>+</sup> to linear HCS<sup>+</sup> when large basis sets are used along with electron correlation.

Since the barrier to isomerization of HSC<sup>+</sup> to HCS<sup>+</sup> almost disappears in going from calculations at the STO-3G level to higher levels, it is of interest to investigate whether any molecule or ion of the type HXY is bent. With this object in mind, we describe here ab initio calculations on HBS, HBO, HAlS, and HAlO and their isomers. In order to obtain a valid comparison of these systems with one another as well as with the HCS<sup>+</sup> system, each set of molecules was investigated at a minimum of nine uniform levels of theory, without and with polarization functions, and by utilizing different degrees of electron correlation. Such a comparison is not currently available in the literature, although varying types of calculations have been reported for HBS,<sup>40-46</sup> HBO,<sup>47-53</sup> and HAlO.<sup>48</sup> The present calculations on HAlS are the first to be reported.

## Method and Results

A VAXstation-2000 computer was used to perform calculations by means of the GAUSSIAN 86 program.<sup>54</sup> Completely optimized geometries were determined in all cases either by using the OPT command available in the program or, when the capacity of the disk storage was exceeded, by sequential optimization of each of the two or three variable parameters. Basis sets as large as 6-311G(2d,2p) at the RHF and MP2 levels and 6-31G\*\* at MP3 and MP4(SDTQ) levels were utilized. Harmonic vibrational frequencies were also calculated, usually at the MP2(full core)/6-31G\*\* level, serving to furnish energy corrections for zero-point vibrational energy (ZPVE) and to verify the nature of stationary points on the potential energy surfaces as equilibrium structures,

(37) Bruna, P. J.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys.* **1978**, *27*, 33.

(38) Wong, M. W.; Nobes, R. H.; Radom, L. *J. Mol. Struct. (THEOCHEM)* **1988**, *163*, 151.

(39) Tao, Y. *Chem. Phys. Lett.* **1989**, *154*, 374.

(40) Thomson, C. *Chem. Phys. Lett.* **1974**, *25*, 59.

(41) Gropen, O.; Wisloff-Nilssen, E. *J. Mol. Struct.* **1976**, *32*, 21.

(42) Kroto, H. W. *Chem. Soc. Rev.* **1982**, *11*, 435.

(43) Ha, T. K.; Nguyen, M. T.; Vanquickenborne, L. G. *J. Mol. Struct. (THEOCHEM)* **1982**, *90*, 99.

(44) Nguyen, M. T.; Ruelle, P. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1225.

(45) Grein, F. *J. Mol. Spectrosc.* **1986**, *115*, 47.

(46) Largo-Cabrerizo, A.; Barrientos, C. *J. Mol. Struct. (THEOCHEM)* **1989**, *183*, 183.

(47) Thomson, C.; Wishart, B. *J. Theor. Chim. Acta* **1974**, *35*, 267.

(48) Zhubina, T. S.; Zyubin, A. S.; Gorbik, A. A.; Charkin, O. P. *Zh. Neorg. Khim.* **1985**, *30*, 2739.

(49) Tyrrell, J. *J. Phys. Chem.* **1979**, *83*, 2906.

(50) Zhubina, T. S.; Charkin, O. P.; Gurvich, L. V. *Zh. Strukt. Khim.* **1979**, *20*, 3.

(51) Botschwina, P. *Chem. Phys.* **1978**, *28*, 231.

(52) Summers, N. L.; Tyrrell, J. *J. Am. Chem. Soc.* **1977**, *99*, 3960.

(53) Harrison, J. A.; MacLagan, R. G. A. *Chem. Phys. Lett.* **1989**, *155*, 419.

(54) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. GAUSSIAN 86; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

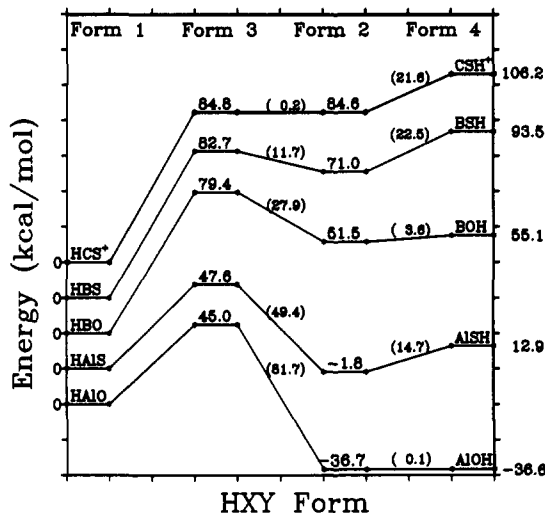


Figure 1. Relative energies (uncorrected for ZPVE) of the four forms of five HXY systems. Barrier energies are in parentheses.

transition structures, or higher-order saddle points. Following conventional procedure, the ZPVEs were all scaled by 0.93;<sup>55,56</sup> however, correction to account for ZPVE in no case changed any of our conclusions. Not included in the correction for the non-minimum structures is the translational zero-point energy corresponding to the missing vibrational degree of freedom.

In each of the five HXY systems investigated, the properties of four separate structures or forms were determined. These forms will be referred to in the rest of this paper as forms 1-4. Form 1 is an energy minimum corresponding to the linear HXY structure, that is, HCS<sup>+</sup>, HBO, HBS, HAlO, and HAlS. Form 2 represents the isomeric HXY equilibrium structure. This form is bent in all cases except HAlO, which is bent only at some levels of theory. Form 3 is the transition state or first-order saddle point (one imaginary frequency) separating forms 1 and 2 and thus represents the top of the barrier to rearrangement, that is, an "isomerization barrier". Form 4 corresponds to a forced linear HXY geometry. Except for unusual cases where form 2 is linear (HAlO), form 4 represents a second-order saddle point (two imaginary frequencies), the only importance of which is to assess a "bending energy", viz., the increase in energy in changing from bent form 2 to forced linear form 4. In the remainder of this paper, the terms "isomerization barrier" and "bending energy" will have the above meanings.

At the top of Tables I and II are displayed the relative energies (uncorrected for ZPVE) and completely optimized structures, respectively, of forms 1-4 of the HCS<sup>+</sup> system. Also included in Table I are the calculated total energies (in hartrees) of the bent HCS<sup>+</sup> cation (form 2) at the various levels of calculation along with the ZPVE of the four species. In the same tables are also shown analogous calculations for the HBO, HBS, HAlO, and HAlS systems. In the table of relative energies (Table I), increasing amounts of indentation are employed to visually indicate increasing order of incorporation of electron correlation, e.g., RHF, MP2, MP3, MP4. All bond lengths are given in angstroms and all bond angles in degrees. Semiempirical MNDO calculations are included for comparison with the ab initio results. Table III contains the calculated harmonic vibrational frequencies and zero-point energies of the various forms of the five systems mentioned above.

Schematic energy profiles representing intramolecular rearrangements on the five HXY potential energy surfaces are shown in Figure 1. For this purpose, we have used the results obtained with our largest basis set (i.e., triple- $\zeta$  with double polarization) at a moderate level of electron correlation (i.e., second-order perturbation theory); namely, the MP2/6-311G(2d,2p) level. Although we have obtained some completely optimized structures at even higher levels, such as MP4(Full Core)/6-31G(d,p) and MP4(Frozen Core)/6-311G(2d,2p), we could not find compelling reasons to investigate all systems at these rather high levels. Hence, calculations at the MP2/6-311G(2d,2p) level, which were performed for all five of the HXY systems in all four forms, will be referred to in the rest of the paper as our "best" calculations. All but the HAlS-HAlO system were calculated at the MP2(Full Core) level.

Proton affinities, bond lengths, and energies of the five XY-type diatomic structures corresponding to the five HXY systems are recorded in

(55) Hout, R. F.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234.

(56) DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333.

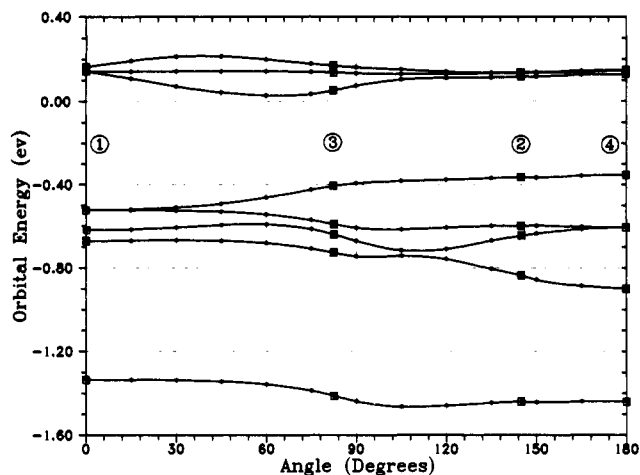


Figure 2. RHF/6-311G(2d,2p) orbital energies of five valence orbitals and three lowest virtual orbitals plotted versus the angle of the hydrogen atom from the midpoint of the BO bond in the system HBO--HOB. Circled points correspond to forms 1-4.

Table IV at selected levels of theory up to our "best" calculations. The negatively charged diatomic ions are unknown experimentally, but theoretical estimations of several of the proton affinities were reported.<sup>57,58</sup> Table V depicts the variation of the MOPAC MNDO bond order of the XY bond in going progressively from form 1 to form 4. Also shown for comparison are the bond orders of the corresponding diatomic XY species.

The angle dependence of the RHF/6-311G(2d,2p) orbital energies of the five highest occupied and three lowest unoccupied orbitals in the HBO--HOB system are plotted in Figure 2.

### Discussion

Before the publication of Wong, Nobes, and Radom,<sup>38</sup> we had investigated the HCS<sup>+</sup>--HSC<sup>+</sup> potential energy surface at many of the same levels they reported. We have verified their results, which were all obtained at the frozen-core level of electron correlation, and have extended their study to include calculations at MP4(Full Core)/6-31G\*\* and MP2(FU)/6-311G(2d,2p) levels. A similar detailed study at uniform levels of theory is being reported here for the HBS, HBO, HAlO, and HAlS systems.

By a careful exploration of the potential energy surfaces of these five systems using our previous STO-3G results as a guide, we have located two minima in each of the five systems at all levels of theory. When our "best" calculations are used, five of the ten minima consist of distinctly bent structures, viz., HSB, HSAI, HOB, HOAl, and HSC<sup>+</sup>. However, as discussed later, the "isomerization barrier" and "bending energy" vary considerably among the five systems with the result that HSB and HSAI lie in deep energy wells with respect to "bending energy", HOB lies in a distinct but shallower well, HOAl lies in an extremely shallow well, and HSC<sup>+</sup> is separated from the isomeric thioformyl cation, HCS<sup>+</sup>, by a minute barrier, at best. The remaining five of the ten minima, viz., HCS<sup>+</sup>, HBS, HBO, HAlO, and HAlS, were shown to exhibit linear geometries by exploration of the potential energy surfaces calculated at our "best" level.

On the HCS<sup>+</sup> potential energy surface, the linear HCS<sup>+</sup> structure (form 1) represents the global minimum. The linear forms of HBS and HBO and the bent forms of HOAl and HSAI constitute global minima on their respective "best" potential energy surfaces. All are separated from their higher-energy isomers by a large "isomerization barrier", and all but HSAI lie considerably lower in energy than their respective isomeric equilibrium structures (HSAI is lower in energy than HAlS by only 1.8 kcal/mol when our "best" results are used).

The location of all of the global minima in deep energy wells with respect to isomerization suggests that the existence of the corresponding molecules or ion could be verified by experimental

techniques or astronomical observation. Indeed, HCS<sup>+</sup> has been observed both in interstellar space<sup>35</sup> and in the laboratory;<sup>59</sup> HBO has been detected by infrared absorption in matrix isolation experiments<sup>60</sup> and as a transient intermediate by microwave spectroscopy,<sup>61,62</sup> and HBS has been the subject of several spectroscopic studies.<sup>63-69</sup>

A consideration of the higher-energy isomeric forms shows that all but HSC<sup>+</sup> lie in deep potential wells with respect to isomerization and should also exist. The "isomerization barriers" at our "best" level of calculation for the global minima forms HCS<sup>+</sup>, HBO, HBS, HOAl, and HSAI are 84.8, 79.4, 82.7, 81.7, and 49.3 kcal/mol, respectively. Corresponding "isomerization barriers" for the higher-energy forms HSC<sup>+</sup>, HOB, HSB, HAlO, and HAlS are 0.2, 27.9, 11.8, 45.0, and 47.6 kcal/mol, respectively.

An examination of the relative energies of forms 2 and 4 in Table I of the various HYX species show that HSC<sup>+</sup>, HSB, and HSAI are distinctly bent in our "best" results, e.g., "bending energies" are 21.6, 22.5, and 14.7 kcal/mol, respectively. HOB is weakly bent with a "bending energy" of 3.6 kcal/mol, whereas HOAl has an extremely minute "bending energy" of 0.1 kcal/mol. Note that the bending frequencies of HOAl in Table III are a very low 115 cm<sup>-1</sup> at the MP2(FU)/6-31G\*\* level and 183 cm<sup>-1</sup> at the MP2(FU)/6-311G\*\* level.

The degree of bending in the bent structures, as measured by the bond angles of form 2, is least in all cases at the RHF/3-21G and RHF/6-31G levels. It increases by inclusion of polarization functions and increases even more at correlated levels of theory. HSB and HSAI are noteworthy in being substantially bent, the bond angles being 85° and 89°, respectively, in our "best" calculations. As expected from the low "bending energy" of HOB, its bond angle is 121° at the same level of calculation. The remaining two molecules exhibit a large variation of the equilibrium bond angle with the level of calculation. Reminiscent of the Hammond principle, the degree of bending of HSC<sup>+</sup> generally increases as the "isomerization barrier" decreases at higher levels of theory.

HOAl exhibits a unique and interesting dependence of its equilibrium geometry on the level of theory. As shown in Table I, this molecule is linear in all calculations employing the 6-31G\*\* basis set, with or without correlation. Especially peculiar is the bent geometry at the RHF/6-31G\* level but not at the RHF/6-31G or RHF/6-31G\*\* levels, albeit the RHF/6-31G\* "bending energy" is very small (0.04 kcal/mol). This result suggests a very flat potential energy surface and prompted us to investigate the shape of HOAl at more levels. It is linear at the RHF/6-311G\*\* level but not at the RHF/6-311G(2d,2p) level. Also, although the MP2(FU)/6-31G\*\* geometry is linear, the molecule is bent at the MP2(FU)/6-311G\*\* and MP2(FU)/6-311G(2d,2p) (i.e., "best") levels. The "bending energies" at the latter two levels are 0.038 and 0.115 kcal/mol, respectively, at the corresponding HOAl bond angles of 161.2° and 148.6°. The potential energy surface is essentially flat over a bond angle range of some 50° at our "best" level! The energy varies less than 0.2 kcal/mol over the bond angle range of 180-133°.

Although the greatest separation in energy between forms 1 and 2 of the five systems considered is encountered in the HCS<sup>+</sup> system, the "isomerization barrier" for the unimolecular rear-

(59) Gudeman, C. S.; Haese, N. N.; Piltch, N. D.; Woods, R. C. *Astro-phys. J.* **1981**, *246*, L47.

(60) Lory, E. R.; Porter, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 6301.

(61) Kawashima, Y.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1989**, *133*, 116.

(62) Kawashima, Y.; Endo, Y.; Kawaguchi, K.; Hirota, E. *Chem. Phys. Lett.* **1987**, *135*, 441.

(63) Kirk, R. W.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1967**, 18.

(64) Pearson, E. F.; McCormick, R. V. *J. Chem. Phys.* **1973**, *58*, 1619.

(65) Kroto, H. W.; Suffolk, R. J.; Westwood, N. P. C. *Chem. Phys. Lett.* **1973**, *22*, 495.

(66) Fehner, T. P.; Turner, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 7175.

(67) Pearson, E. F.; Norris, C. L.; Flygare, W. H. *J. Chem. Phys.* **1974**, *60*, 1761.

(68) Suffolk, R. J.; Cooper, T. A.; Pantelides, E.; Watts, J. D.; Kroto, H. W. *J. Chem. Soc., Dalton Trans.* **1988**, 2041.

(69) Turner, P.; Mills, I. *Mol. Phys.* **1982**, *46*, 161.

(57) Peterson, K. A.; Woods, R. C. *J. Chem. Phys.* **1989**, *90*, 7239.

(58) Botschwina, P.; Sebald, P. *J. Mol. Spectrosc.* **1985**, *1*, 110.

**Table I.** Relative Energies of Four HXY Forms and Absolute Energy and HXY Bond Angle of Form 2<sup>c</sup>

method basis	relative energies, kcal/mol				angle, deg form 2	energy, hartree form 2
	form 1	form 3	form 2	form 4		
$\text{H}-\text{C}-\text{S}^+ \cdots \text{C}-\text{S}-\text{H}^+$	$\text{H}-\text{C}-\text{S}^+$	$\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{C}-\text{S}^+ \end{array}$	$\text{C}-\text{S}^+-\text{H}^+$	$\text{C}-\text{S}-\text{H}^+$		
MNDO	-89.10	28.13	0.00	5.09	116.7	336.00 <sup>a</sup>
RHF/STO-3G	-69.11	22.60	0.00	35.56	92.4	-430.749972
RHF/3-21G	-79.77	21.29	0.00	19.46	99.3	-433.290941
RHF/6-31G	-76.04	22.30	0.00	21.87	99.3	-435.415242
RHF/6-31G*	-71.83	13.21	0.00	39.70	88.2	-435.495885
RHF/6-31G**	-70.40	11.19	0.00	39.53	86.9	-435.500359
MP2(FU)/6-31G**	-88.20	0.38	0.00	20.53	60.5	-435.743255
MP3(FC)/6-31G**	-79.49	2.97	0.00	27.67	77.5	-435.748414
MP4(FC)/6-31G**	-81.87	2.01	0.00	15.51	71.6	-435.770086
MP4(FU)/6-31G**	-82.44	1.95	0.00	15.63	71.2	-435.784608
RHF/6-311G**	-68.77	9.39	0.00	40.49	83.9	-435.533804
MP4(FC)/6-311G**	-77.86	1.55	0.00	17.49	67.2	-435.817047
RHF/6-311G(2d,2p)	-68.67	9.60	0.00	43.24	84.5	-435.541740
<b>MP2(FU)/6-311G(2d,2p)<sup>b</sup></b>	<b>-84.57</b>	<b>0.19</b>	<b>0.00</b>	<b>21.64</b>	<b>62.4</b>	<b>-435.943225</b>
.93*ZPVE	8.37	(4.50)	5.21	(4.77)		
$\text{H}-\text{B}-\text{O} \cdots \text{B}-\text{O}-\text{H}$	$\text{H}-\text{B}-\text{O}$	$\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{B}-\text{O} \end{array}$	$\text{B}-\text{O}-\text{H}$	$\text{B}-\text{O}-\text{H}$		
MNDO	-17.31	73.58	0.00	0.00	180.0	-50.96 <sup>a</sup>
RHF/STO-3G	-71.31	48.95	0.00	2.62	123.7	-98.713264
RHF/3-21G	-38.04	58.11	0.00	0.15	151.6	-99.545324
RHF/6-31G	-39.91	59.01	0.00	0.04	160.8	-100.054986
RHF/6-31G*	-47.30	44.94	0.00	3.92	121.4	-100.090775
RHF/6-31G**	-43.15	47.65	0.00	4.02	122.2	-100.098414
MP2(FU)/6-31G**	-56.25	26.36	0.00	3.11	121.0	-100.349289
MP3(FC)/6-31G**	-47.73	32.27	0.00	3.71	120.3	-100.352515
MP3(FU)/6-31G**	-48.13	32.09	0.00	3.49	120.6	-100.359631
MP4(FC)/6-31G**	-52.98	27.32	0.00	3.59	120.5	-100.366185
MP4(FU)/6-31G**	-53.42	27.15	0.00	3.38	120.5	-100.373319
RHF/6-311G**	-41.34	48.39	0.00	4.31	121.8	-100.128357
MP4(FU)/6-311G**	-50.31	27.93	0.00	4.39	116.2	-100.457815
RHF/6-311G(2d,2p)	-40.36	48.28	0.00	4.69	122.0	-100.135016
<b>MP2(FU)/6-311G(2d,2p)<sup>b</sup></b>	<b>-51.45</b>	<b>27.91</b>	<b>0.00</b>	<b>3.64</b>	<b>121.4</b>	<b>-100.459036</b>
MP4(FC)/6-311G(2d,2p)	-48.39	28.47	0.00	4.13	120.4	-100.446186
.93*ZPVE	8.50	(5.34)	7.86	(7.41)		
$\text{H}-\text{B}-\text{S} \cdots \text{B}-\text{S}-\text{H}$	$\text{H}-\text{B}-\text{S}$	$\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{B}-\text{S} \end{array}$	$\text{B}-\text{S}-\text{H}$	$\text{B}-\text{S}-\text{H}$		
MNDO	-38.68	36.67	0.00	5.26	111.8	45.88 <sup>a</sup>
RHF/STO-3G	-85.20	37.44	0.00	39.35	92.7	-417.989487
RHF/3-21G	-70.58	32.83	0.00	17.42	100.4	-420.585170
RHF/6-31G	-70.56	32.63	0.00	18.06	100.5	-422.637642
RHF/6-31G*	-67.81	28.63	0.00	31.08	93.3	-422.684015
RHF/6-31G**	-65.94	28.13	0.00	30.87	92.8	-422.688158
MP2(FU)/6-31G**	-76.02	11.89	0.00	22.48	86.0	-422.890073
MP3(FC)/6-31G**	-69.23	15.07	0.00	24.53	87.5	-422.900715
MP4(FC)/6-31G**	-71.55	12.82	0.00	21.24	86.7	-422.912673
RHF/6-311G(2d,2p)	-62.73	26.89	0.00	34.11	91.1	-422.726120
<b>MP2(FU)/6-311G(2d,2p)<sup>b</sup></b>	<b>-70.95</b>	<b>11.77</b>	<b>0.00</b>	<b>22.52</b>	<b>84.5</b>	<b>-423.091796</b>
.93*ZPVE	7.39	(4.05)	5.51	(4.59)		
$\text{H}-\text{Al}-\text{O} \cdots \text{Al}-\text{O}-\text{H}$	$\text{H}-\text{Al}-\text{O}$	$\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{Al}-\text{O} \end{array}$	$\text{Al}-\text{O}-\text{H}$	$\text{Al}-\text{O}-\text{H}$		
MNDO	38.68	106.89	0.00	0.00	180.0	-61.09 <sup>a</sup>
RHF/STO-3G	44.93	104.31	0.00	5.48	113.2	-313.411765
RHF/3-21G	67.59	116.85	0.00	0.00	180.0	-315.668450
RHF/6-31G	71.40	124.07	0.00	0.00	180.0	-317.360850
RHF/6-31G*	51.07	108.33	0.00	0.04	155.0	-317.381951
RHF/6-31G**	55.37	112.49	0.00	0.00	180.0	-317.389744
MP2(FU)/6-31G**	37.46	82.70	0.00	0.00	180.0	-317.634594
MP3(FC)/6-31G**	50.69	90.50	0.00	0.00	180.0	-317.630038
MP4(FC)/6-31G**	33.74	77.80	0.00	0.00	180.0	-317.642377
RHF/6-311G**			0.00	0.00	180.0	-317.427797
MP2(FU)/6-311G**			0.00	0.04	161.2	-317.823219
RHF/6-311G(2d,2p)	52.38	110.48	0.00	0.19	148.5	-317.434649
<b>MP2(FU)/6-311G(2d,2p)<sup>b</sup></b>	<b>36.75</b>	<b>81.73</b>	<b>0.00</b>	<b>0.11</b>	<b>148.6</b>	<b>-317.863074</b>
.93*ZPVE	5.22	(3.88)	6.91	(6.91)		
$\text{H}-\text{Al}-\text{S} \cdots \text{Al}-\text{S}-\text{H}$	$\text{H}-\text{Al}-\text{S}$	$\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{Al}-\text{S} \end{array}$	$\text{Al}-\text{S}-\text{H}$	$\text{Al}-\text{S}-\text{H}$		
MNDO	9.04	61.09	0.00	5.39	112.9	21.65 <sup>a</sup>
RHF/STO-3G	7.05	83.03	0.00	27.31	94.1	-632.745974
RHF/3-21G	6.63	65.24	0.00	8.14	105.0	-636.761333
RHF/6-31G	8.31	66.48	0.00	8.31	106.7	-639.980680

Table I (Continued)

method basis	relative energies, kcal/mol				angle, deg form 2	energy, hartree form 2
	form 1	form 3	form 2	form 4		
RHF/6-31G*	3.99	65.20	0.00	16.71	96.4	-640.020505
RHF/6-31G**	6.00	66.88	0.00	16.62	95.8	-640.024692
MP2(FU)/6-31G**	2.22	49.67	0.00	14.63	89.5	-640.214450
MP3(FC)/6-31G**	6.67	50.97	0.00	15.55	90.2	-640.217854
MP4(FC)/6-31G**	4.56	47.10	0.00	15.07	89.6	-640.226808
RHF/6-311G(2d,2p)	4.98	66.26	0.00	18.39	93.3	-640.070230
MP2(FC)/6-311G(2d,2p) <sup>b</sup>	<b>1.76</b>	<b>49.33</b>	<b>0.00</b>	<b>14.67</b>	<b>88.6</b>	<b>-640.269599</b>
.93*ZPVE	4.99	(3.14)	5.07	(4.47)		

<sup>a</sup> Heat of formation in kcal/mol for form 2. <sup>b</sup> "Best" calculation. <sup>c</sup> All energies uncorrected for zero-point vibrational energy.

range of HSC<sup>+</sup> is smallest. This barrier decreases from about 22 to 11 kcal/mol upon inclusion of polarization functions, and then it nearly disappears upon inclusion of electron correlation (e.g., the barrier is 0.2 kcal/mol in our "best" results, the smallest value to be reported thus far). This observation corroborates the conclusion<sup>38</sup> that HSC<sup>+</sup> is unlikely to be detected experimentally.

A comparison of the relative energies of forms 2 and 3 in Table I reveals that the other bent molecules also exhibit a marked variation of this barrier with the level of theory employed. In general, there is a small but consistent reduction of the height of the barrier upon inclusion of polarization functions, but a much bigger diminution (10–30 kcal/mol) of the barrier by further incorporation of electron correlation so that the overall barrier reduction from RHF/6-31G calculations to our "best" calculations is quite large. However, despite such large reduction in height, the "isomerization barrier" remains large for HOB, HSB, HOAl, and HSAI. Among the different correlated levels, MP3 calculations always indicated a distinctly higher value of both the "isomerization barrier" and the "bending energy" than the closely comparable MP2 and MP4 calculations. These results, particularly those for the HCS<sup>+</sup> system, emphasize the fact that inclusion of electron correlation is essential for gauging the relative heights of "isomerization barriers" of these ten-valence-electron HXY systems.

The geometries of the various species depicted in Table II show some variation with the level of theory. Because very few of these species have been studied experimentally (only form 1), it is difficult to decide which level of calculation is most suited for structural predictions. However, on the basis of what few comparisons with experimental values can be made, it appears that MP3 results give the best estimates of observed geometries. MP2 calculations overestimate the lengths of XY bonds and MP4 calculations overestimate them even more. This trend has been reported previously for HCS<sup>+</sup><sup>38</sup> and is now encountered in all of the systems investigated in this paper.

The harmonic vibrational frequencies assembled in Table III were calculated at generally higher levels than those in the literature.<sup>38,39,46</sup> If Table V can be used as a guide to the type of bonding in the various forms of HXY (vide infra), then a decrease in the stretching frequency of the XY bond is to be expected when form 1 is compared with form 2, as is observed in Table III, column 5. Although the bending frequencies follow the same pattern, HOAl is noteworthy in exhibiting remarkably low values, below 200 cm<sup>-1</sup>, whether linear or bent. This observation is consistent with HOAl being linear at many levels of calculation in contrast to HSAI and HOB.

A comparison of the "best" calculated bond lengths of the diatomic XY species in Table IV with the corresponding XY bond lengths for the triatomic species in Table III shows that the bond length of the diatomic system is consistently longer than that of form 1 but shorter than that of form 2. HOAl exhibits the smallest such difference. The "best" proton affinity of CS in Table IV (193.1 kcal/mol) is very close to the best previous theoretical estimate (191 kcal/mol),<sup>38</sup> after correction for the zero-point energy (ZPVE) difference of 7.1 kcal/mol from Table III. The proton affinities of BO<sup>-</sup> and BS<sup>-</sup> are also in general agreement with those reported previously at the MP4 level.<sup>57</sup> However, note the large difference between the values calculated at the triple- $\zeta$  double-polarization level [i.e., MP2/6-311G(2d,2p) level] com-

pared to the double- $\zeta$  single-polarization level (i.e., MP2, MP3, and MP4/6-31G\*\* levels). Since CS is the only diatomic species for which an experimental value of proton affinity is available (recent value of 188 kcal/mol<sup>70</sup>), one cannot decide which level of theory will be generally suitable for reproducing experimental values.

One reason for carrying out this study was to assess the level of theory required to confidently predict structures and energies of small isomeric systems. For this reason we include semiempirical results at the MNDO level, calculated by means of MOPAC.<sup>71</sup> Although MNDO was not expected to perform well for these species, consistent parameters were not available for all atoms at the superior AM1 or never PM3 semiempirical levels.

The bond lengths from MNDO are far shorter than our "best" calculations, agreeing best with the STO-3G level, which is known to give rather poor predictions compared to the split valence 3-21G level and higher levels. The semiempirical bond angles were generally too large, yielding in the extreme a linear HOB structure. The relative MNDO energies of the four HXY--HXY forms were qualitatively correct, but quantitatively very poor.

Especially interesting are the MOPAC MNDO XY bond orders, presented in Table V, as a function of the angle made by the hydrogen atom from the midpoint of the XY bond. Notice that the X–Y bond order decreases by approximately one bond in going from form 1 to form 2 (or 4). The quasi-Lewis structures shown at the top and bottom of the Table V are intended to indicate possible bonding patterns. While the bond order of HCS<sup>+</sup> is near 3, that of HBO and HBS is near 2.5, that of HAIO, HAIS, and HSC<sup>+</sup> is near 2.0, that of HOB and HSB is near 1.5, and that of HOAl and HSAI is near 1.0. One might speculate that the lower bond order results in an increase of electron population on the O and S atoms leading to increased nonlinear p<sup>2</sup> (90°) bonding instead of linear sp bonding. From this viewpoint, the linearity of HOAl at several levels is surprising.

Calculations at a reasonably high level as reported in Tables I and II are essential in gauging the usefulness of earlier qualitative theories of shapes of molecules,<sup>72</sup> such as those of Walsh,<sup>1</sup> Schnuelle and Parr,<sup>73</sup> and VSEPR theory.<sup>74–76</sup> From orbital overlap arguments, Walsh stated that the energies of the five filled valence-shell molecular orbitals of molecules of the type discussed in the present paper should either increase in energy or remain unchanged when the HXY angle varies from 180° and 90°, and hence he concluded that all HXY species having ten valence electrons should be linear in their ground states. However, it is the total energy and not the sum of the orbital energies that determines the shapes of molecules (the difference being a large contribution from electron repulsion that changes in subtle ways with bond angle).

An examination of Figure 2 for the HBO--HOB system shows that although the various RHF/6-311G(2d,2p) orbital energies

(70) Smith, D.; Adams, N. E. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 149.

(71) Stewart, J. J. P. MOPAC 4.0, QCPE, Indiana University, Bloomington, Indiana 47405.

(72) Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980.

(73) Schnuelle, G. W.; Parr, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 8974.

(74) Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* **1957**, *11*, 339.

(75) Gillespie, R. J. *J. Chem. Educ.* **1963**, *40*, 295.

(76) Gillespie, R. J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 819.



Table II (Continued)

HAlS-HSAI	form 1		form 3				form 2			form 4	
	R <sub>HAl</sub>	R <sub>AlS</sub>	R <sub>HAl</sub>	R <sub>AlS</sub>	R <sub>SH</sub>	∠AlSH	R <sub>AlS</sub>	R <sub>SH</sub>	∠AlSH	R <sub>AlS</sub>	R <sub>SH</sub>
MP2(FU)/6-31G**	1.5601	2.0042	1.6457	2.0753	2.0945	46.49	2.2344	1.3370	89.53	2.1747	1.3296
MP3(FC)/6-31G**	1.5601	1.9990	1.6520	2.0827	2.1395	46.04	2.2378	1.3385	90.15	2.1758	1.3297
MP4(FC)/6-31G**	1.5643	2.0179	1.6586	2.0995	2.1155	46.34	2.2419	1.3418	89.55	2.1813	1.3334
RHF/6-311G(2d,2p)	1.5543	1.9903	1.6429	2.0632	2.2106	45.05	2.2624	1.3315	93.35	2.2130	1.3221
MP2(FC)/6-311G(2d,2p) <sup>a</sup>	1.5599	2.0170	1.6473	2.0824	2.1053	46.33	2.2626	1.3394	88.61	2.2055	1.3325

<sup>a</sup> "Best" calculation. <sup>b</sup> Reference 59. <sup>c</sup> Reference 61. <sup>d</sup> Reference 68.

Table III. Harmonic Frequencies Calculated by MP2(FU)/6-31G\*\*

molecule	form	frequencies, <sup>a</sup> cm <sup>-1</sup>				ZPVE, <sup>b</sup> kcal/mol
		bending		stretch		
H-C-S <sup>+</sup>	1	767.2	767.2	1404.1	3358.2	9.00
	3		(785.8i)	1269.1	2115.4	(4.84)
H-S-C <sup>+</sup>	2		435.1	1189.4	2292.4	5.60
	4	(225.7i)	(225.7i)	1123.0	2466.5	(5.13)
C-S				1313.6		1.88
H-B-O	1	785.0	785.0	1831.0	2994.7	9.14
	3		(1753.7i)	1681.2	2334.9	(5.74)
H-O-B	2		570.0	1419.3	3918.6	8.45
	4	(438.6i)	(438.6i)	1497.1	4080.2	(7.97)
B-O <sup>-</sup>				1709.1		2.44
H-B-S	1	702.8	702.8	1225.4	2929.0	7.95
	3		(1644.7i)	1027.3	2025.2	(4.36)
H-S-B	2		549.6	810.2	2783.2	5.92
	4	(583.2i)	(583.2i)	835.6	2619.0	(4.94)
B-S <sup>-</sup>				1022.6		1.46
H-Al-O	1	406.0	406.0	1039.8	2071.7	5.61
	3		(1210.4i)	1082.7	1837.6	(4.17)
H-O-Al <sup>c</sup>	2	115.0	115.0	869.7	4094.4	7.43
	4	115.0	115.0	869.7	4094.4	7.43
Al-O <sup>-</sup>				938.3		1.34
H-Al-S <sup>d</sup>	1	465.5	465.5	717.6	2110.0	5.37
	3		(1290.1i)	603.9	1757.3	(3.38)
H-S-Al	2		431.8	533.1	2847.0	5.45
	4	(548.0i)	(548.0i)	446.5	2917.8	(4.81)
Al-S <sup>-</sup>				610.7		0.87

<sup>a</sup> Values in parentheses represent imaginary frequencies. <sup>b</sup> Translational zero-point energy not included. <sup>c</sup> Frequencies calculated at the MP2-(FU)/6-311G\*\* level for the bent form 2 of HOAl are 183.1, 864.9, and 4065.7, and for the forced linear form 4 they are (143.1i), (143.1i), 870.9, and 4081.5. <sup>d</sup> All HAlS--HSAI frequencies calculated at the RHF/6-31G\*\* level.

at optimized bond lengths change as the bond angle is varied, no uniform conclusions similar to those of Walsh are discernible. Similar plots for other systems at other levels provide even less insight. One point of interest is that the degenerate  $\pi$  orbitals of linear HBO represent the HOMO, whereas the similar degenerate orbitals of HOB are substantially lower than the HOMO. This indicates that there may be a significant change in the relative importance of the  $\pi$  bond in going from form 1 to form 2, as suggested in the discussion of the MOPAC bond orders above.

### Concluding Remarks

The question we posed in the title of the present paper can now be answered more definitively, namely, Are any ten-valence-electron HXY species bent in the ground state? In contrast to the near disappearance at higher levels of the substantial STO-3G "isomerization barrier" for the bent HSC<sup>+</sup> cation, the small RHF/6-31G "bending energy" for HOB increases to 4.1 kcal/mol at the MP4(Frozen Core)/6-311G(2d,2p) level while the very high STO-3G "isomerization barrier" to HBO is greatly reduced, but still remains at a large value of 28.5 kcal/mol at this level. HSB and HSAI remain substantially bent at the highest levels of calculation, lying in energy wells at least as deep as 10 kcal/mol in our "best results". However, HOAl loses its large STO-3G "binding energy" and becomes linear or is very weakly bent at higher levels. The variation of potential energy with bending angle for HOAl is so remarkably flat that there is little possibility for specific determination of its linearity or nonlinearity.

Thus, out of the various species in the five systems examined at a reasonably high level of theory, we have located three

molecules, viz., HSB, HSAI, and HOB, that are distinctly bent and possess a sufficiently high isomerization barrier to predict with some degree of confidence that in a sufficiently isolated state these molecules should exist with bent geometry. HSAI has the additional advantage of being the global minimum, thus making detection of the bent HSAI molecule as likely or even more likely than the linear HAlS molecule lying 1.8 kcal/mol higher in energy in our "best" calculations. No previous ab initio calculations of this type have been reported for HSB and HSAI and no previous such calculations on the other species were performed in which geometries were completely optimized at all levels. Also, there is no previous report of the extreme flatness of the potential energy curve with respect to bond angle in HOAl.

After a review of all of the results at correlated levels, it appears that MP2 and MP4 calculations are similar in their predictions but both yield results that are somewhat different from MP3 calculations. Although MP3 may be more accurate for bond lengths and angles, the similarity of MP2 and MP4 results suggests that MP2 may be sufficient with a large enough basis set to make reasonably confident predictions. For the molecules and ions studied, no serious error in prediction would occur from using the much less computationally intensive MP2/6-31G\*\* level of theory rather than our "best" calculations or the higher-level MP3 and MP4 calculations. Inclusion of some electron correlation is essential to correctly predict "isomerization barriers" and "bending energies" for these systems, but it affords little improvement in bond lengths and angles.

At this point, it may be worthwhile to review the conclusions of our earlier extensive STO-3G study<sup>36</sup> of HXY--HYX systems

**Table IV.** Bond Lengths, Energies, and Proton Affinities of Five XY Systems<sup>a</sup>

method basis	$R_{XY}$	energy, hartrees	proton affinity, <sup>b</sup> kcal/mol	
C-S	C-S	C-S	H-C-S <sup>+</sup>	H-S-C <sup>+</sup>
RHF/3-21G	1.5636	-433.122928	185.20	105.44
RHF/6-31G**	1.5197	-435.304316	193.42	123.02
MP2(FU)/6-31G**	1.5445	-435.557681	(-7.1) 204.66	(-3.7) 116.45
MP3(FC)/6-31G**	1.5317	-435.551933	202.78	123.29
MP4(FC)/6-31G**	1.5723	-435.579635	201.38	119.52
<b>MP2(FU)/6-311G(2d,2p)<sup>a</sup></b>	<b>1.5413</b>	<b>-435.758863</b>	<b>200.27</b>	<b>115.71</b>
B-O <sup>-</sup>	B-O <sup>-</sup>	B-O <sup>-</sup>	H-B-O	H-O-B
RHF/3-21G	1.2526	-98.986552	388.68	350.64
RHF/6-31G**	1.2770	-99.539760	393.71	350.56
MP2(FU)/6-31G**	1.2546	-99.803200	(-6.7) 398.93	(-6.0) 342.68
MP3(FC)/6-31G**	1.2433	-99.795971	396.96	349.24
MP4(FC)/6-31G**	1.2626	-99.815246	398.70	345.72
<b>MP2(FU)/6-311G(2d,2p)<sup>a</sup></b>	<b>1.2422</b>	<b>-99.931927</b>	<b>382.21</b>	<b>330.77</b>
B-S <sup>-</sup>	B-S <sup>-</sup>	B-S <sup>-</sup>	H-B-S	H-S-B
RHF/3-21G	1.7336	-420.095907	377.58	307.01
RHF/6-31G**	1.7069	-422.175256	387.79	321.86
MP2(FU)/6-31G**	1.6997	-422.378351	(-6.5) 397.13	(-4.5) 321.11
MP3(FC)/6-31G**	1.7008	-422.381117	395.30	326.07
MP4(FC)/6-31G**	1.7152	-422.395160	396.29	324.73
<b>MP2(FU)/6-311G(2d,2p)<sup>a</sup></b>	<b>1.6980</b>	<b>-422.595253</b>	<b>382.54</b>	<b>311.59</b>
Al-O <sup>-</sup>	Al-O <sup>-</sup>	Al-O <sup>-</sup>	H-Al-O	H-O-Al
RHF/3-21G	1.6313	-315.032021	331.78	399.38
RHF/6-31G**	1.6096	-316.766537	335.70	391.06
MP2(FU)/6-31G**	1.6693	-317.036698	(-4.3) 337.71	(-6.1) 375.17
MP3(FC)/6-31G**	1.6315	-317.012372	336.91	387.60
MP4(FC)/6-31G**	1.7243	-317.050487	337.67	371.42
<b>MP2(FU)/6-311G(2d,2p)<sup>a</sup></b>	<b>1.6556</b>	<b>-317.265069</b>	<b>338.50</b>	<b>375.25</b>
Al-S <sup>-</sup>	Al-S <sup>-</sup>	Al-S <sup>-</sup>	H-Al-S	H-S-Al
RHF/3-21G	2.1611	-636.235784	323.18	329.80
RHF/6-31G**	2.0905	-639.486078	(-4.5) 331.99	(-4.6) 338.00
MP2(FU)/6-31G**	2.0902	-639.676127	335.59	337.81
MP3(FC)/6-31G**	2.0858	-639.673334	335.01	341.68
MP4(FC)/6-31G**	2.1050	-639.685068	335.39	339.95
<b>MP2(FC)/6-311G(2d,2p)<sup>a</sup></b>	<b>2.1112</b>	<b>-639.737299</b>	<b>332.25</b>	<b>334.02</b>

<sup>a</sup>"Best" calculation. <sup>b</sup>Values in parentheses represent zero-point vibrational energy corrections calculated at the level indicated. The correction for bent HOAl calculated at the MP2(FU)/6-311G\*\* level is -6.0. <sup>c</sup>All energies uncorrected for zero-point vibrational energy.

**Table V.** MOPAC MNDO Bond Order of the XY Bond in Five XY and Five HXY Species as a Function of Hydrogen Angle from the Midpoint of the XY Bond

angle	H-C-S <sup>+</sup>	H-B-O	H-B-S	H-Al-O	H-Al-S
	:C=S:	:B=O:	:B=S:	:Al=O:	:Al=S:
	2.53	2.28	2.09	2.17	2.07
	H-C≡S <sup>+</sup>	H-B≡O:	H-B≡S:	H-Al=O:	H-Al=S:
0.0 <sup>a</sup>	2.84	2.45	2.49	2.18	2.25
30.0	2.82	2.44	2.46	2.18	2.25
60.0	2.67	2.36	2.22	2.18	2.22
90.0 <sup>b</sup>	1.94	1.70	1.39	1.33	1.07
120.0	1.82 <sup>c</sup>	1.43	1.30 <sup>c</sup>	1.09	1.04 <sup>c</sup>
150.0	1.90	1.47 <sup>c</sup>	1.29	1.10	0.99
180.0 <sup>d</sup>	2.02	1.57	1.36	1.17 <sup>c</sup>	0.98
	:C=S-H <sup>+</sup>	:B=O-H	:B=S-H	:Al=O-H	:Al=S-H

<sup>a</sup>Form 1. <sup>b</sup>Approximate form 3. <sup>c</sup>Approximate form 2. <sup>d</sup>Form 4.

containing ten valence electrons. At this level, it appeared that for X less electronegative<sup>77</sup> than Y, (1) HXY (i.e., form 1) is linear, while (2) HXY (i.e., form 2) may be bent, especially if Y is an element of the second row of the periodic table. The "best" results in the present paper as well as other recent reasonably high level calculations<sup>39</sup> are in agreement with these conclusions. However, ab initio calculations at a high level for more HXY-HYX systems or more experimentally observed structures are

needed before the general validity of these conclusions can be ascertained. A study of several of the other HXY systems containing ten valence electrons, previously surveyed with STO-3G, is well under way with the MP2/6-31G\*\* level of theory and, where necessary, higher levels of theory.

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(77) Simons, G.; Zandler, M. E.; Talaty, E. R. *J. Am. Chem. Soc.* **1976**, *98*, 7869.