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Ab Initio Calculations on Heteroatomic Systems Using Density Functional Theory and Diffuse Basis Functions

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The enormously increased ease of performing sophisticated *ab initio* calculations has led to the publication of a multitude of fascinating results. The problem, however, as recently highlighted in a series of papers[1] on the Cope rearrangement, is to know which results can be trusted, given the fact that not all systems can be subjected to the expensive G2[2,3] treatment (which may not even be sufficient in some instances). We wish to highlight two major points here: the value of basis sets that include diffuse functions[4] and the use of density functional theory (DFT).[5] To be sure, both of these points have been made before, albeit not in the current context. It is generally understood that diffuse functions on heavy atoms are important for the proper description of anions,[6] although they were found to be unnecessary in one recent study.[7] For heteroatomic systems, particularly when lone pairs are present, diffuse functions are occasionally used,[8] but often omitted.[9] As concerns DFT (with nonlocal corrections), Houk's group has shown its efficacy in the study of pericyclic reactions,[10] although it does have some limitations.[11] Although its use appears to be growing,[7,8a,9e,12] it does not seem generally clear that this methodology may be superior, in estimating correlation energies, to MP2 or even MP4 approaches. A poignant example is that of propargylene.[13] Of the two possible singlet structures, the first a C_s acetylenic carbene and the second a C_{2v} 1,3-diradical, the former was of lower energy through the QCISD/6-31G(d) level, while the latter became the lower energy species at QCISD(T)/6-31+G(d,p) (by 0.2 kcal/mol, and 0.7 kcal/mol when the zero point energy correction was included). Using the published geometries[13] of these two species, we find the latter to be 1.2 kcal/mol[14] below the former at the UB3LYP/6-31+G(d) level (without zero point energy corrections).

Theoretical Approach

We used the G94W suite of programs.[15] The basis sets used were the standard ones included in the program, where the "+" designation indicates the inclusion of diffuse functions on heavy atoms, "++" means diffuse functions on all atoms, "(d)" means d-type polarization functions on heavy atoms, "(d,p)" means d functions on heavy atoms and p-type polarization functions on H's, and "(2df,2p)" indicates the inclusion of two sets of d polarization functions and 1 set of f polarization functions on heavy atoms together with two sets of p polarization functions on H's. The beyond Hartree−Fock (HF) methodology used to correct for correlation energy included the Moller−Plesset series of perturbation corrections, designated as MP2 (second order) and MP4 (fourth order), quadratic configuration interaction through single and double excitations (QCISD), and the Becke3LYP density functional approach, which includes nonlocal correction terms (B3LYP).[16] MP corrections were made by including all electrons in the calculation (full: Fu) or by including only valence electrons (frozen core: Fc); the extent of the corrections may include single, double, and quadruple excitations (SDQ) or these plus triple excitations (SDTQ). Characterization of a stationary point of a molecule as a minimum requires that the second-order derivative matrix (the "Hessian") have all positive eigenvalues *and* that there are no imaginary (*i.e.*, negative) vibrational frequencies (NIMAG = 0). The necessary calculation also provides the zero point vibrational energy (ZPVE) for the given geometry.

Results and Discussion

Pursuant to experimental studies involving dioxiranes and carbonyl ylides,[17] we had occasion to calculationally reexamine the parent systems (**1**, **2**). Table 1 displays

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[1] (a) Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774. (b) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072. (c) Dupuis, M.; Murray, C.; Davidson, E. R. *J. Am. Chem. Soc.* **1991**, *113*, 9756. (d) Hrovat, D. A.; Borden, W. T.; Vance, R. L.; Rondan, N. G.; Houk, K. N.; Morokuma, K. *J. Am. Chem. Soc.* **1990**, *112*, 2018 and references cited therein.

[2] For a recent extensive comparison of the results of advanced standardized calculations, including G2, see: Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299.

[3] Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

[4] By this we mean that they are included in an effort to understand the fundamental energetics of a chemical system and not as part of an effort to get more exact energies (like doing a G2 calculation or recalculating energies with a 6-311++G(2df, 2p) basis).

[5] Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford: New York, 1989.

[6] Hehre, W. J.; Radom, L.; Schleyer, P. v R.; Pople, J. A. *Ab Initio Moledular Orbital Theory*; Wiley-Interscience: New York, 1986; pp 86−88, 310−316.

[7] Wiest, O.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *117*, 11628.

[8] Some recent uses of diffuse functions follow. (a) A study of $A_3H_3^+$ ions, A = C, Si, Ge, Sn, Pb: Jemmis, E. D.; Srinivas, G. N.; Leszczynski, J.; Kapp, J.; Korkin, A. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 11361. (b) Two studies of O- and S-containing compounds: Gronert, S.; Lee, J. M. *J. Org. Chem.* **1995**, *60*, 4488, 6731. (c) Study of polarizabilities of organic compounds with N, O, F: Stout, J. M.; Dykstra, C. E. *J. Am. Chem. Soc.* **1995**, *117*, 5127. (d) Calculations on Si_3O_4: Fan, J.; Nicholas, J. B.; Price, J. M.; Colson, S. D.; Wang, L.-S. *J. Am. Chem. Soc.* **1995**, *117*, 5417.

[9] Some recent examples follow. (a) Calculations involving fluorines: Jacobs, C. A.; Dailey, W. P. *J. Org. Chem.* **1995**, *60*, 7747. (b) Summary of calculations involving Si, Ge, Sn atoms: Nagase, S. *Accts. Chem. Res.* **1995**, *28*, 469. (c) Calculations on silylenes: Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691. (d) Calculations on inorganic prismanes of N, P, As, Si, Ge: Matsunaga, N.; Gordon, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 11407. (e) Calculations involving N, O, S atoms: Sustmann, R.; Sicking, W.; Huisgen, R. *J. Am. Chem. Soc.* **1995**, *117*, 9679. (f) Calculations involving P atoms: Salzner, U.; Bachrach, S. M. *J. Org. Chem.* **1995**, *60*, 7101. (g) Calculations on N- and O-substituted silylenes: Apeloig, Y.; Müller, T. *J. Am. Chem. Soc.* **1995**, *117*, 5363.

[10] (a) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036. (b) Wiest, O.; Black, K. A.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 10336 and references therein.

[11] (a) Plattner, D. A.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *117*, 4405. (b) Sulzbach, H.; Schaefer, H. F., III; Klopper, W.; Lüthi, H. P. *J. Am. Chem. Soc.* **1996**, *118*, 3519. In this case, the MP approach also failed: (c) Greer, A.; Jensen, F.; Clennan, E. L. *J. Org. Chem.* **1996**, *61*, 4107. Here, DFT fails to predict a persulfoxide to be a minimum, whereas MP2 does.

[12] (a) Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 11529. (b) Jiao, H.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R. *J. Org. Chem.* **1996**, *61*, 2826. (c) Jemmis, E. D; Srinivas, G. N. *J. Am. Chem. Soc.* **1996**, *118*, 3738. (d) Merrill, G. N.; Dahlke, G. D.; Kass, S. R. *J. Am. Chem. Soc.* **1996**, *118*, 4462. (e) Kapp, J.; Remko, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1996**, *118*, 5745.

[13] Herges, R.; Mebel, A. *J. Am. Chem. Soc.* **1994**, *116*, 8229.

[14] E (diradical) = −115.32436 au; E (carbene) = −115.32249 au.

[15] Gaussian 94, Revision B.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

[16] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[17] Warner, P. M.; Gurumurthy, R. Paper presented at the ACS Southwestern Regional Meeting, Birmingham, AL, 1994 (abstract no. 372); manuscript in preparation.

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Table 1. Energies for Dioxirane (1) and Carbonyl Oxide (2) at Various Theoretical Levels

method	basis set	geom[a]	energies (hartrees) 1	energies (hartrees) 2	$E(\mathbf{2}) - E(\mathbf{1})$ (kcal/mol)
MP4(Fc, SDQ)	6-31G(d)	D	−189.120 16	−189.070 21	31.3[b]
MP4(Fc, SDQ)	6-31G(d)	B	−189.110 75	−189.060 53	31.5
MP4(Fc, SDQ)	6-31+G(d)	C	−189.122 72	−189.077 98	28.1
MP4 (Fu, SDQ)	6-31+G(d)	B	−189.132 76	−189.087 99	28.1
MP4(Fc, SDTQ)	6-31G(d)	B	−189.128 83	−189.080 68	30.2
MP4(Fc, SDTQ)	6-311++G(d,p)	B	−189.244 71	−189.199 94	28.1
MP4(Fu, SDTQ)	6-31+G(d)	B	−189.152 65	−189.110 18	26.6
QCISD	6-31+G(d)	C	−189.123 47	−189.110 18	23.1
B3LYP	6-31+G	A	−189.548 98	−189.529 49	12.2
B3LYP	6-31G(d)	A	−189.615 55	−189.576 82	24.3
B3LYP	6-31+G(d)	A	−189.625 70	−189.591 12	21.7
B3LYP	6-31+G(d)	B	−189.625 66	−189.59118	21.6
B3LYP	6-311++G(d,p)	B	−189.676 32	−189.642 48	21.2
B3LYP/ZPVE	6-311++G(d,p)	B	−189.643 92	−189.611 48	20.4
B3LYP	6-311++G(2df,2p)	C	−189.689 22	−189.655 00	21.5

[a] Geometries optimized as follows: A, B3LYP/6-31G(d); B, B3LYP/6-311++G(d, p); C, B3LYP/ 6-311++G(2df, 2p); D,[b] MP4(Fc, SDQ)/ 6-31G(d). [b] Data from ref 18.

Table 2. Calculated Strain Energies (SE's) for 1, 3, and 4 Using Homodesmic Reaction 1

compd	strain energy (kcal/mol)	theoretical method
cyclopropane (**3**)[a]	28.7[b]	HF/6-31G(d)//HF/6-31G(d)
3	29.0	B3LYP/6-31G(d)//B3LYP/6-31+G(d)
3	27.7	B3LYP/6-31+G(d)//B3LYP/6-31+G(d)
trisilacyclopropane (**4**)	38.9[b]	HF/6-31G(d)//HF/6-31G(d)
4	35.8	B3LYP/6-31G(d)//B3LYP/6-31+G(d)
4	35.8	B3LYP/6-31+G(d)//B3LYP/6-31+G(d)
dioxirane (**1**)	33.2	HF/6-31G(d)//HF/6-31G(d)
1	24.7[c]	MP2/6-31G(d)//MP2/6-31G(d)
1	33.4	B3LYP/6-31G(d)//B3LYP/6-31+G(d)
1	32.1	B3LYP/6-31+G(d)//B3LYP/6-31+G(d)

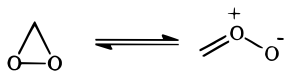
[a] Experimental SE = 28.1kcal/mol.[21] [b] Data from ref 20. [c] Data from ref 18.

Table 3. Energies Calculated for 8 and 9[a]

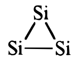
level of theory	energies, hartrees (E_{rel}, kcal/mol) 1,6-diphospha-1,5-hexadiene (**8**)	energies, hartrees (E_{rel}, kcal/mol) 3,4-diphospha-1,5-hexadiene (**9**)
HF/6-31G(d)	−837.493 58 (**0**)	−837.512 89 (**−12.1**)
HF/6-31+G(d)	−837.498 91 (**0**)	−837.520 07 (**−13.3**)
MP2 (Fc)/6-31G(d)	−838.221 10 (**0**)	−838.220 39 (**0.4**)
MP2 (Fc)/6-31+G(d)	−838.233 90 (**0**)	−838.236 50 (**−1.6**)
B3LYP/6-31G(d)	−839.874 74 (**0**)	−839.882 77 (**−5.0**)
B3LYP/6-31+G(d)	−839.882 49 (**0**)	−839.893 12 (**−6.7**)

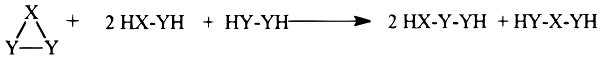
[a] All calculations are at the HF/6-31G(d)-optimized geometry.

the energies for various levels of theory. It is immediately obvious that the MP4(Fc, SDQ)/6-31G* results reported by Cremer,[18] at what was then a very high level of theory, are unreliable. Inclusion of diffuse functions improves the calculated energy gap by 3 kcal/mol; inclusion of triples [MP4(SDTQ)] has little effect, even when the core electrons are correlated [MP4(Fu)]. The QCISD/ 6-31+G(d) approach lowers the energy gap by a significant 5 kcal/mol; the energy gap might well have diminished to that found via DFT had we been able to include triples and quadruples. The results using the B3LYP methodology are also shown. Use of diffuse functions without polarization functions gives too low an energy gap due to the known propensity for split valence basis sets to disfavor small rings; omission of diffuse functions gives too large an energy gap. Significantly, once both diffuse and polarization functions are included, use of more extended basis sets results in no change in the calculated energy gap. Thus, we have adopted the 6-31+G(d) basis for the remainder of the work reported here. With the inclusion of a ZPVE correction[19] (unscaled), our best estimate of the **1**→**2** energy gap is 20.4 kcal/mol.


1 **2**


3


4


(1)

No significant changes in the calculated geometries for **1** and **2** are observed at the various correlated levels of theory. We next address the strain energy (SE) of **1**, which was calculated[18] as 24.7 kcal/mol via the homodesmic reaction (1). This reaction has also been applied to cyclopropane (**3**) and trisilacyclopropane (**4**), yielding SE's of 28.7 kcal/mol and 38.9 kcal/mol, respectively, at the HF/6-31G(d) level.[20] Our results, shown in Table 2, demonstrate that correlation energy is not an issue for

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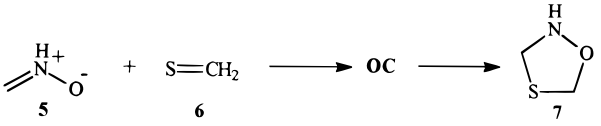
(18) Cremer, D.; Schmidt, T.; Gauss, J.; Radhakrishnan, T. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 427.

(19) Frequency analyses show that both **1** and **2** are energy minima (NIMAG = 0).

(20) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60.

3, but inclusion of diffuse functions has a small effect, consistent with “pseudo-π” bonding in **3**, which brings the calculated SE very close to the experimental value.[21,22] For **4**, correlation decreases the apparent SE by 3 kcal/mol; the lack of a diffuse function effect may be related to the imputed lack of “bent bonding” in **4**.[9b] For the DFT approach, a very small correlation effect is seen for **1**, along with a somewhat larger effect of diffuse functions. The net SE is 32.1 kcal/mol, which would make **1** about 4 kcal/mol more strained than **3**. This makes sense, since the lone pair repulsions between the oxygens would be expected to raise the energy of **1** more than do the H−H eclipsing interactions present in **3**. We do not know why the MP4 results[18] were so different.



Having seen the potential importance of diffuse functions, we became intrigued by the calculated intermediacy of an orientation complex (**OC**) for the reaction of nitrone (**5**) with thioformaldehyde (**6**),[23] ultimately to give **7**. At the B3LYP/6-31G(d) level, these authors found the **OC** to be 5.48 kcal/mol more stable than the starting materials (SM) (not counting ZPVE); we find the same difference. However, at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level, the **OC** is only 3.57 kcal/mol below the SM (at B3LYP/6-311++G(d, p)//B3LYP/6-31G(d), the number is 3.60 kcal/mol). When the ΔZPVE[23] is included, this leaves the **OC** at only 1.8 kcal/mol below the SM. This is a small enough stabilization to call into question the conclusion that the **OC** would be below the SM in solution.[23,24] We do note, however, that an electron-donating substituent (OH) on the carbon atom of **5** and an electron-withdrawing substituent (BH_2) on the nitrogen atom each led to a ca. 6.5 kcal/mol stabilization of the **OC** relative to SM at the B3LYP/6-31+G(d) level.

Lastly, we address the recent[9f] calculation that placed 3,4-diphospha-1,5-hexadiene (**9**) only 1.73 kcal/mol below 1,6-diphospha-1,5-hexadiene (**8**), with 1.3 kcal/mol of that amount being due to ΔZPVE; this result was obtained at the QCISD(T)/6-31G(d) level. We located the minima called **conformation 1** and **conformation 16** by Salzner and Bachrach, which we call **8** and **9**, respectively. Our results at the HF/6-31G(d) level are the same as reported;[9f] our MP2/6-31G(d) results differ very slightly because we did not reoptimize the geometry. The effect of diffuse functions to relatively lower the energy of **9** is seen at the HF and MP2 levels; the effect is slightly larger than what is gained by going from MP2 to QCISD(T). More significantly, perhaps, is the result using DFT. Now **9** stands 6.7 kcal/mol below **8** (without ZPVE correction). This value is more in line with Appel's[25] estimate of 4 kcal/mol and certainly allows for the relative destabilization of **9** by bulky substituents on phosphorus.

In conclusion, diffuse functions can be important in properly assessing energies of heteroatomic systems, especially when lone pairs are present. Additionally, DFT appears to be more effective, particularly when cost is considered, at recovering the correlation energies present in these molecules.

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(21) (a) Schleyer, P. v R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377. (b) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York: 1976, Table A2, p. 271−310; (c) see also Beckhaus, H.-D.; Rüchardt, C.; Kazhushkov, S. I.; Belov, V. N.; Verevkin, S. P.; de Meijere, A. *J. Am. Chem. Soc.* **1995**, *117*, 11854.

(22) Note that none of the SE calculations mentioned have been corrected for ZPVE effects.

(23) Sustmann, R.; Sicking, W.; Huisgen, R. *J. Am. Chem. Soc.* **1995**, *117*, 9679.

(24) Neither this nor the previous[23] calculations included any correction for basis set superposition errors, which would artificially favor the starting materials relative to the OC; the correction might be on the order of 1 kcal/mol.

(25) Appel, R. in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; pp 172−181.