A Concise Set of “Large”, Symmetric Molecules for Evaluation of Modern Computational Methods

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The structures of a series of strained *in*-cyclophanes, for which good X-ray data are available, were calculated by using a variety of ab initio and hybrid density functional (HDFT) methods. The HDFT methods were found to overestimate systematically the transannular nonbonded contact distances in these molecules. A consideration of the deficiencies of existing test sets for the evaluation of modern computational methods led to the compilation of a set of larger molecules with accurately known geometries. Twenty highly symmetric molecules were selected for which there exist high-quality X-ray structures where the molecules reside at high symmetry sites with only relatively weak intermolecular interactions. The experimental structures of these molecules were compared with the structures calculated by five computational methods [HF/3-21G(*), MP2(FC)/6-31G(d), B3LYP/6-31G(d), B3PW91/6-31G(d), and B3PW91/cc-pVDZ], and the results are discussed in the context of choosing computational methods for routine geometry optimizations.

Introduction

From the perspective of organic chemists, and to a lesser extent inorganic chemists as well, the last two decades have seen the evolution of ab initio and density functional computational methods from curiosities with little predictive value to valuable guides for experimental work with sufficient precision and accuracy to challenge the results of many types of experiments. With the use of quantum chemical methods so widespread, their calibration with respect to experimental data is ever more important. A great deal of recent work has dealt with improved predictions of accurate molecular energies, but the calculation of accurate molecular geometries seems to be regarded as a solved problem, at least for closed-shell molecules. Thus, for example, the Gaussian-1, Gaussian-2, and Gaussian-3 theories for prediction of energies, which have evolved over a 10-year period,[1−3] all employ geometries calculated at the MP2/6-31G(d) level, for which the accuracy has been well documented.[4] The test sets for these theories are composed exclusively of quite small molecules, so that MP2/6-31G(d) geometry optimizations require little time. However, for most “real-world” applications, with significantly larger molecules, MP2 geometries are far too expensive to be employed, and most chemists choose low-level ab initio methods or hybrid density functional theory (HDFT) for calculation of reasonable molecular geometries. However, it is unfortunate that calculations using the very small molecules in, for example, the G2/97 test set[5] do not clearly reveal the systematic errors which can accumulate in the calculated geometry of a larger structure.

In the present work I first report the poor performance of commonly employed HDFT methods for the estimation of nonbonded contact distances in a series of strained cyclophanes. These compounds possess several structural features unlike any found in the small-molecule test sets used to calibrate modern computational methods. The poor computational results supplied the motivation to compile a suite of larger molecules, with accurately known geometries, which might provide a more realistic assessment of the accuracy of quantum chemical methods for the prediction of molecular geometries. I then outline a series of criteria for choosing such experimental structures, and select 20 diverse compounds to form a concise test set. Finally, I illustrate the use of this test set in a discussion of the accuracy of five representative computational methods.

Results and Discussion

Nonbonded Contacts in Strained in-Cyclophanes. The synthesis of small cyclophanes with functional groups pointing toward the center of an aromatic ring has been an interest of my research group for more than a decade.[6−8] Almost all of the molecules prepared have been characterized by X-ray crystallography, and the resulting structures exhibit some of the shortest known nonbonded contacts involving the π-electron systems of aromatic rings. Most of these cyclophanes were synthesized at a time when the calculation of their structures by ab initio methods would have been prohibitively expensive, but in recent years I have used a variety of computational methods to examine them and related compounds. The molecules studied are illustrated in Table 1; the C_3-symmetric cyclophanes **1**, **2**, **5**, **6**, and **7** are from my own laboratory,[6a,c,d,7a,b,8a,b] and **3** and **4**, which also display exceptionally tight transannular interactions, are taken from the literature.[9,10] A recent search of the Cambridge Structural Database (CSD)[11] revealed that compounds **2**, **4**, and **6** possess the shortest known nonbonded contacts of hydrogen, nitrogen, and phosphorus atoms, respectively, to the mean planes of aromatic rings.

Table 1 lists the experimental and calculated close intramolecular contacts for each compound. All of the values listed are distances between two non-hydrogen atoms. The closest contacts in compounds **1**, **2**, **3**, and **5** involve hydrogen atoms, but bond distances involving hydrogen atoms are not accurately determined by X-ray crystallography;[12] therefore, distances involving the attached heavy atoms were substituted. The geometries of the molecules were optimized by using several quite different computation methods: two relatively-low-level Hartree−Fock methods, HF/3-21G(*) and HF/6-31G(d),[13] the “standard” MP2/6-31G(d) method,[13] and six HDFT methods employing the

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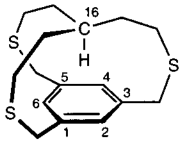
TABLE 1: Comparison of Experimental and Calculated Close Contacts in Compounds 1−7



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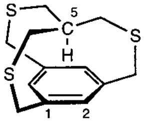

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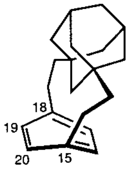

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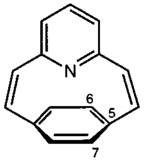

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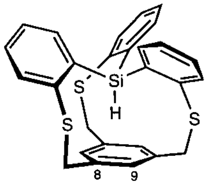

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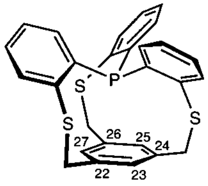

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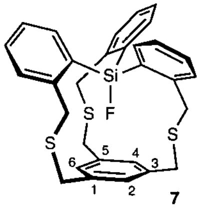

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CSD refcode (compd no., site and ideal symm)	contact	d_{exptl} (Å)	d_{calcd} (Å) [$d_{\mathrm{calcd}} - d_{\mathrm{exptl}}$ (mÅ)] and E (au)								
			HF/3-21G(*)	HF/ 6-31G(d)	MP2/ 6-31G(d)	B3LYP/ 6-31G(d)	B3LYP/ 6-31+G(d)	B3LYP/ cc-pVDZ	B3LYP/ cc-pVTZ	B3PW91/ 6-31G(d)	B3PW91/ cc-pVDZ
RAZZIB	C16−C1,3,5	3.565 av[a]	3.558 [−07]	3.629 [+64]	3.519 [−46]	3.634 [+69]	3.642 [+77]	3.638 [+73]	3.631 [+66]	3.607 [+42]	3.603 [+38]
(**1**, C_1, C_3)	C16−C2,4,6	3.567 av[a]	3.564 [−03]	3.638 [+71]	3.520 [−47]	3.640 [+73]	3.648 [+81]	3.644 [+77]	3.636 [+69]	3.611 [+44]	3.608 [+41]
			−1802.26917	−1811.22387	−1813.68432	−1817.51864	−1817.53666	−1817.59765	−1817.83583	−1817.14893	−1817.23721
VAMMEB	C5−C1	3.098	3.093 [−05]	3.139 [+41]	3.073 [−25]	3.156 [+58]	3.157 [+59]	3.151 [+53]	3.144 [+46]	3.127 [+29]	3.121 [+23]
(**2**, C_3, C_3)	C5−C2	3.120	3.126 [+06]	3.177 [+57]	3.100 [−20]	3.192 [+72]	3.193 [+73]	3.187 [+67]	3.181 [+61]	3.162 [+42]	3.156 [+36]
			−1685.78381	−1694.08760	−1696.16222	−1699.55147	−1699.56710	−1699.62872	−1699.82685	−1699. 22527	−1699.30949
WAPWIT	C10−C15,18	2.906 av[b]	2.914 [+08]	2.945 [+39]	2.896 [−10]	2.954 [+48]	2.954 [+48]	2.944 [+38]	2.942 [+36]	2.930 [+24]	2.922 [+16]
(**3**, C_1, C_s)	C10−C19,20	3.003 av[b]	2.995 [−08]	3.032 [+29]	2.991 [−12]	3.054 [+51]	3.053 [+50]	3.045 [+42]	3.044 [+41]	3.030 [+27]	3.025 [+22]
			−768.20722	−772.46551	−775.09774	−777.75935	−777.77743	−777.79277	−778.01580	−777.49274	−777.53664
PYPCPE	N−C5	2.673	2.693 [+20]	2.736 [+63]	2.680 [+07]	2.734 [+61]	2.740 [+67]	2.735 [+62]	2.730 [+57]	2.717 [+44]	2.718 [+45]
(**4**, C_2, C_{2v})	N−C6,7	2.866 av[b]	2.867 [+01]	2.927 [+61]	2.865 [−01]	2.928 [+62]	2.935 [+69]	2.929 [+63]	2.927 [+61]	2.911 [+45]	2.912 [+46]
			−625.28042	−628.79297	−630.86596	−632.89052	−632.91346	−632.93012	−633.10411	−632.64825	−632.69325
VIWFAI	Si−C8	3.608	3.608 [+00]	3.674 [+66]		3.689 [+81]		3.691 [+83]		3.658 [+50]	3.657 [+49]
(**5**, C_3, C_3)	Si−C9	3.628	3.630 [+02]	3.700 [+72]		3.712 [+84]		3.714 [+86]		3.680 [+52]	3.680 [+52]
			−2504.00699	−2516.69670		−2526.17666		−2526.30251		−2525.8978	−2525.72629
KEZTIS	P−C22,24,26	3.209 av[c]	3.233 [+24]	3.338 [+129]		3.320 [+111]		3.317 [+108]		3.276 [+67]	3.273 [+64]
(**6**, C_1, C_3)	P−C23,25,27	3.223 av[c]	3.250 [+27]	3.360 [+137]		3.339 [+116]		3.335 [+112]		3.294 [+71]	3.290 [+67]
			−2555.00535	−2567.89512		−2577.41373		−2577.54542		−2576.83047	−2576.97281
HAKQOZ01	F−C1,3,5	3.137 av[c]	3.125 [−12]	3.163 [+26]		3.150 [+13]		3.132 [−05]		3.116 [−21]	3.088 [−49]
(**7**, C_1, C_3)	F−C2,4,6	3.139 av[c]	3.129 [−10]	3.167 [+28]		3.151 [+12]		3.132 [−07]		3.116 [−23]	3.087 [−52]
	Si−F	1.595	1.599 [+04]	1.598 [+03]		1.626 [+31]		1.661 [+66]		1.623 [+28]	1.659 [+64]
			−2718.91399	−2732.76334		−2743.45452		−2743.58093		−2742.78333	−2742.92300

[a] Average of nine crystallographically independent values. [b] Average of two crystallographically independent values. [c] Average of three crystallographically independent values.

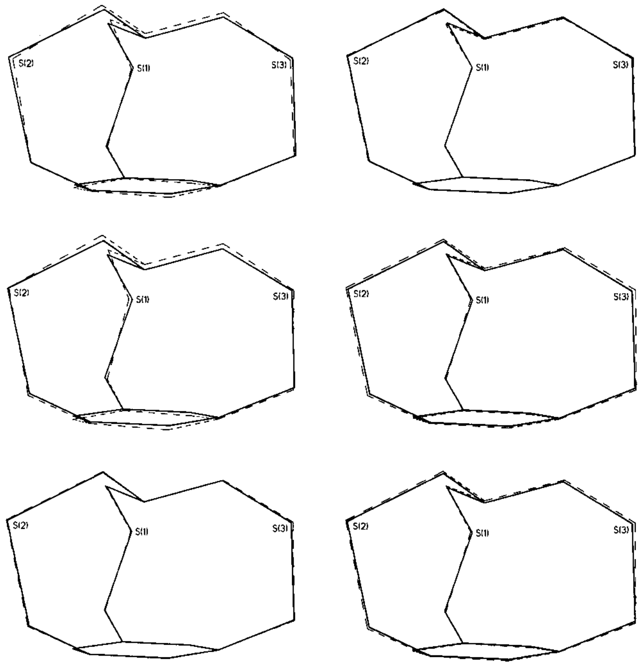


Figure 1. Superposition of the experimental (solid line) and calculated (dashed line) structures for cyclophane **2**. The computational methods employed (with rms deviations from the experimental structures) are, left column, top to bottom, AM1 (0.065 Å), PM3 (0.076 Å), and HF/3-21G(*) (0.025 Å) and, right column, MP2(FC)/6-31G(d) (0.025 Å), B3LYP/6-31G(d) (0.047 Å), and B3LYP/cc-pVTZ (0.040 Å).

B3LYP and B3PW91 functionals[14−16] with a variety of basis sets. (For the larger compounds **5**−**7**, with over 30 non-hydrogen atoms, some of the more expensive calculations were not performed.)

The results are surprising, to say the least: for this series of molecules the HF/3-21G(*) calculations, of all of the methods examined, gave *by far* the most accurate estimation of the nonbonded contacts, with most of the deviations from the experimental distances being within the errors typical of high-quality X-ray structure determinations ($3\sigma \approx 0.01$ Å). This is not to say that Hartree−Fock calculations are intrinsically superior to the others; results with the larger 6-31G(d) basis set are much poorer. However, the performance of the HDFT methods was most disappointing, especially that of the extremely popular[17] B3LYP/6-31G(d) and B3LYP/6-31+G(d). In every case but one the B3LYP calculations overestimated the nonbonded contact distances. The sole counterexample, the B3LYP/cc-pVDZ calculation for **7**, is the result of a cancellation of errors: the nonbonded contact is normal because the Si−F bond length is grossly overestimated. Even when the large cc-pVTZ basis set[18] was employed, the B3LYP results were only marginally better. Interestingly, the B3PW91 functional generally gave better geometries than those from B3LYP calculations when the same basis sets were employed, but both overestimated the contact distances. In contrast, the small errors in the HF/3-21G(*) results were scattered on both sides of the experimental values, and the MP2/-6-31G(d) calculations tended to underestimate the contact distances.

The relative quality of the calculated structures is most easily seen in Figure 1, in which the experimental structure of compound **2** is superimposed[19] upon structures generated by AM1,[21] PM3,[22] HF/3-21G(*), MP2/6-31G(d), B3LYP/6-31G(d), and B3LYP/cc-pVTZ calculations. The two semiempirical methods show a variety of errors, the HF/3-21G(*) and MP2/6-31G(d) results are quite close to experiment, and the B3LYP results display the "oversized" geometries that seem to be typical of HDFT calculations on this class of compounds.[23]

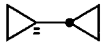
The Problem. The results presented in Table 1 indicate, at a miminum, that HDFT methods are a poor choice for routine calculations of cyclophane structures. Yet why should this be? These molecules contain no unusual bonding or unusual spin states, merely a bit of strain mainly due to nonbonded transannular interactions. Unfortunately, the calibration and testing of HDFT methods has been based primarily on experimental data from very small molecules. For example, the three parameters of the B3LYP functional were fit[14] to data from the G2 test set,[2] which contains no molecules containing rings or even any molecules with more than two non-hydrogen atoms. Subsequent tests[5,25,27] of various density functional methods tended to endorse the B3LYP functional as the "best", but none of these studies examined molecules with more than six non-hydrogen atoms.

The most extensive study was by Curtiss et al.[5] They supplemented the G2 test set with more complex molecules to give the G2/97 set, and then employed this test set to compare seven density functional methods (all using the 6-311+G(3df,2p) basis set) for the calculation of enthalpies of formation, and found that the B3LYP functional gave the best results. This careful study is one of the foundations of the current popularity of the B3LYP method, but in the context of this present paper, which focuses on the geometry of complex molecules, two points must be noted. First, Curtiss et al. used *MP2/6-31G(d) geometries* for their comparisons of DFT calculations of enthalpies of formation, but added, "The use of B3LYP/6-31G(d) geometries has little effect on the average absolute deviation." [5] Second, although the G2/97 set contains 300 molecules, only 15 of these possess even a single ring, and only two have as many as six non-hydrogen atoms. Indeed, the G2/97 test set is so heavily weighted with very small molecules that its 300 members contain a total of only 192 chemically unique bonds between two non-hydrogen atoms.

This criticism is not limited to the testing of ab initio and HDFT methods. Consider the calibration of semiempirical methods, where the computational cost is much less; perhaps large molecules would be better represented in the test sets used for the development of AM1 and PM3. In fact, the "extended tests" of AM1 utilized 138 closed-shell molecules containing C, H, N, and O, but only 19 of these molecules contained more than six non-hydrogen atoms, and for many there is no accurate experimental geometry.[21] The parametrization of PM3 utilized hundreds of molecules, and the test set is rich in heavier elements, but geometric comparisons were made for only seven molecules with more than six non-hydrogen atoms.[22] It should come as no surprise, then, that any computational method might exhibit systematic errors for some classes of complex molecules, such as those in Table 1. For this reason, a test set of larger molecules, which could be used to identify some of these errors, is extremely desirable.

Selection of the Reference Experimental Structures. The choice of very small molecules for the evaluation of computational methods is not merely one of convenience; rather, gas-phase experimental data (largely limited to small molecules) are most nearly comparable to the results of quantum calculations on isolated molecules. When considering larger species, one is inevitably required to use the results of single-crystal X-ray or neutron diffraction. The geometries obtained by X-ray analyses must differ from gas-phase data in two important respects. First, the derived bond distances involving hydrogen are systematically short,[12] due to the fact that the 1s electrons

TABLE 2: Calculated Energies and Deviations from Experimental Geometries for "Light Atom" Members of the HSX Set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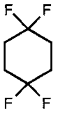

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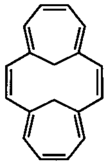
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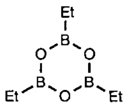

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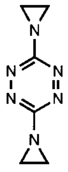

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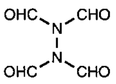

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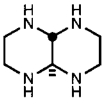

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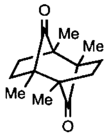

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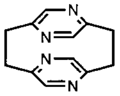

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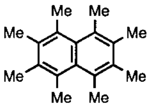

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compd no., CSD refcode, space group, molecular symm	E (au), rms dev (Å) from expt (rank), max dev (Å) from expt				
	HF/3-21G(*)	MP2(FC)/6-31G(d)	B3LYP/6-31G(d)	B3PW91/6-31G(d)	B3PW91/cc-pVDZ
11, BCPROP02	−231.65312	−233.73985	−234.59323	−234.51484	−234.52661
Cmca	0.006 (=1)	0.006 (=1)	0.016 (5)	0.011 (=3)	0.011 (=3)
C_{2h}	0.007	0.007	0.018	0.012	0.012
12, BOMJIW	−626.24928	−631.11334	−632.84567	−632.62068	−632.66045
Pnnm	0.048 (5)	0.024 (4)	0.013 (3)	0.012 (2)	0.009 (1)
C_{2h}	0.083	0.048	0.019	0.021	0.014
13, DEZNAX	−686.96747	−693.11295	−695.43846	−695.17331	−695.21942
Pnnm	0.038 (5)	0.012 (1)	0.020 (4)	0.017 (=2)	0.017 (=2)
C_{2h}	0.073	0.016	0.033	0.030	0.030
14, FIPDIR01	−532.04882	−536.47528	−538.24909	−538.03122	−538.05787
*P*63/*m*	0.036 (5)	0.019 (4)	0.009 (3)	0.007 (2)	0.005 (1)
C_{3h}	0.048	0.026	0.014	0.009	0.006
15, FIZJIH	−555.16458	−560.11509	−561.79152	−561.58408	−561.62220
*C*2/*m*	0.058 (5)	0.016 (1)	0.034 (4)	0.029 (3)	0.020 (2)
C_{2h}	0.086	0.021	0.046	0.044	0.032
16, FORHYZ01	−558.96554	−563.65456	−565.19826	−564.97818	−565.02413
*I*42*m*	0.013 (1)	0.025 (3)	0.028 (5)	0.022 (2)	0.026 (4)
D_{2d}	0.019	0.033	0.041	0.033	0.039
17, GAZNIE	−450.59313	−454.54274	−456.03164	−455.87176	−455.90564
*C*2/*m*	0.048 (5)	0.034 (4)	0.030 (3)	0.028 (2)	0.027 (1)
C_{2h}	0.055	0.040	0.034	0.035	0.034
18, HEJGUY	−687.71181	−693.72162	−695.97827	−695.73426	−695.77435
Cmca	0.014 (3)	0.021 (5)	0.017(4)	0.011 (2)	0.010 (1)
C_{2h}	0.024	0.042	0.020	0.014	0.011
19, KAHROA	−675.33160	−681.35153	−683.46619	−683.20958	−683.25258
Ccca	0.124 (5)	0.064 (4)	0.034 (3)	0.029 (2)	0.024 (1)
D_2	0.198	0.083	0.039	0.034	0.030
20, OMNAPH01	−691.72062	−697.94115	−700.37973	−700.12524	−700.15655
Ccca	0.041 (5)	0.040 (4)	0.035 (3)	0.032 (2)	0.023 (1)
D_2	0.077	0.072	0.059	0.055	0.036

in hydrogen are involved in bonding and are displaced toward the other atom (i.e., there is no spherical core of electron density). Second, crystal packing forces may distort the molecule from an ideal geometry. For the purposes of the present study, it is acceptable simply to ignore the hydrogen positions when experimental results are compared with calculated geometries, but to minimize the effects of crystal packing forces, the X-ray structures must be chosen very carefully.

The effects of the crystal environments on the selected molecular geometries may be reduced by excluding structures with strong intermolecular forces, such as salts or hydrogen-bonded structures. Unfortunately, even with only van der Waals forces in a crystal, there can be substantial distortions from gas-phase equilibrium geometries by packing forces. However, these distortions can be further reduced by insisting that the packing forces act equally on several parts of the molecule; thus, one should choose high-symmetry molecules in high-symmetry environments.[28] These considerations, along with the obvious requirements for good-quality X-ray structure determinations and some limit on the size of the molecules, led to the following criteria for selection of crystal structures from the CSD.[11]

(1) The molecules should contain 6−18 non-hydrogen atoms.

(2) The molecules must possess at least two nontrivial symmetry elements.

(3) The ideal molecular symmetry must equal the crystallographic site symmetry.

(4) The structures may not contain hydrogen bonds, salts, or the solvent of crystallization.

(5) The structures should exhibit no disorder.

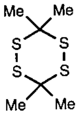
(6) For all determinations, $R(F) \leq 5.0\%$.

(7) Finally, for the present study, only hydrogen and first- and second-row elements were permitted.

These criteria are very strict; fewer than 100 structures in the CSD meet them. Criterion 3 is the most difficult to satisfy; for example, there are many structures containing molecules with ideal D_2 symmetry, but almost all of these possess only crystallographic C_2 or C_1 symmetry. However, criterion 3 was retained because it requires that the X-ray structure and the calculations have the same number of independent geometric parameters, a very desirable feature for the purposes of comparison: there is a single experimental value for each symmetry-equivalent bond, instead of the average of two or more crystallographically independent bond lengths. It should be noted that, for the molecules in Table 1, the experimental and calculated structures tend to be most similar when the crystallographic site symmetry approaches or equals the ideal molecular symmetry.

From the candidates in the CSD, 20 structures were selected; these molecules are designated the "high-symmetry X-ray set", or the "HSX set", and are illustrated in Tables 2 and 3.[30] The 10 structures in Table 2 contain only hydrogen and first-row elements, and the 10 in Table 3 contain one or more second-row elements. In choosing these structures, an effort was made to maximize the number of elements, bond types, and molecular shapes that are represented. There are 21 types of bonds in these molecules, disregarding bond order (B−C, B−O, C−H, C−C, C−N, C−O, C−F, C−Si, C−P, C−S, C−Cl, N−H, N−Si, N−P, N−S, O−P, F−P, Si−Cl, P−Cl, S−S, and S−Cl), and

TABLE 3: Calculated Energies and Deviations from Experimental Geometries for "Heavy Atom" Members of the HSX Set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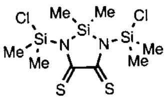
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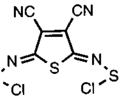
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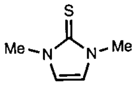
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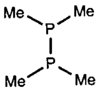
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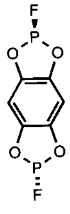
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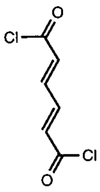
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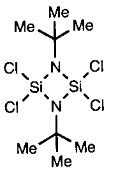
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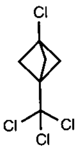
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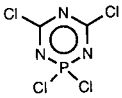
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compd no., CSD refcode, space group, molecular symm	*E* (au), rms dev (Å) from expt (rank), max dev (Å) from expt				
	HF/3-21G(*)	MP2(FC)/6-31G(d)	B3LYP/6-31G(d)	B3PW91/6-31G(d)	B3PW91/cc-pVDZ
21, BAHRIL	−1815.57959	−1825.53223	−1828.63410	−1828.35716	−1828.44919
$I4_1/acd$	0.026 (2)	0.015 (1)	0.053 (5)	0.032 (=3)	0.032 (=3)
D_2	0.031	0.022	0.058	0.035	0.035
22, BOHBUV	−2989.00141	−3005.49520	−3010.75395	−3010.24939	−3010.38437
Cmcm	0.046 (=2)	0.037 (1)	0.055 (4)	0.046 (=2)	0.065 (5)
C_{2v}	0.064	0.058	0.087	0.077	0.103
23, CLCNTP	−2544.20286	−2558.40944	−2562.49898	−2562.05853	−2562.19906
Cmcm	0.090 (5)	0.051 (1)	0.063 (4)	0.056 (3)	0.053 (2)
C_{2v}	0.150	0.117	0.118	0.110	0.113
24, DMIMZT02	−696.88478	−701.49747	−703.04696	−702.88530	−702.92239
Cmcm	0.014 (1)	0.020 (=4)	0.018 (=2)	0.018 (=2)	0.020 (=4)
C_{2v}	0.023	0.025	0.025	0.023	0.026
25, KAKGEI	−835.80284	−840.64853	−842.37227	−842.22186	−842.25885
$C2/m$	0.016 (=1)	0.016 (=1)	0.040 (5)	0.028 (3)	0.031 (4)
C_{2h}	0.019	0.020	0.047	0.034	0.036
26, LAKVIC	−1401.10024	−1410.28273	−1413.23146	−1412.85549	−1412.92422
$C2/m$	0.029 (2)	0.036 (5)	0.031 (3)	0.021 (1)	0.034 (4)
C_{2h}	0.046	0.054	0.071	0.044	0.072
27, MUCONC10	−1291.89623	−1299.56946	−1301.86417	−1301.60765	−1301.68216
Cmca	0.026 (1)	0.043 (4)	0.050 (5)	0.041 (2)	0.042 (3)
C_{2h}	0.037	0.067	0.070	0.059	0.063
28, RIXVOJ	−2824.99229	−2840.49122	−2845.29087	−2844.83312	−2844.95199
Cmca	0.032 (3)	0.020 (1)	0.040 (4)	0.031 (2)	0.042 (5)
C_{2h}	0.049	0.032	0.054	0.046	0.066
29, SEGWIK	−2058.92279	−2069.85173	−2072.94943	−2072.66587	−2072.76666
$R3m$	0.038 (4)	0.024 (1)	0.042 (5)	0.032 (2)	0.034 (3)
C_{3v}	0.056	0.032	0.054	0.037	0.041
30, YINHUY	−2406.45759	−2419.11426	−2422.62846	−2422.28099	−2422.39923
Cmcm	0.031 (3)	0.024 (1)	0.037 (4)	0.027 (2)	0.039 (5)
C_{2v}	0.040	0.038	0.066	0.048	0.069

six point groups are represented (C_{2v}, C_{3v}, C_{2h}, C_{3h}, D_2, and D_{2d}).

It is obvious that such a small set cannot represent all classes of molecules containing even these few elements equally well; the symmetry requirement alone ensures that the distribution is atypical. Moreover, all but three of the compounds contain at least one ring. This is an unintended feature of the HSX set, but ring structures tend to have greater rigidity and may be more likely to resist deformation by packing forces and thus may be biased to crystallize in higher symmetry lattices. On the other hand, ring structures are almost entirely absent fromt the G1, G2, and G2/97 test sets, so the HSX set provides a welcome complement. In addition, these 20 molecules contain 95 chemically unique bonds between two non-hydrogen atoms, nearly half as many as contained in the *entire* G2/97 test set. Overall, the structures of the HSX set are of sufficient variety to provide a wide array of computational challenges, yet the set is small enough to be evaluated by most computational methods in a reasonable amount of time.

Selection of Computational Methods. To illustrate the value of the HSX set, the geometries of these molecules were evaluated by five different computational methods: (1) HF/3-21G(*), (2) MP2(FC)/6-31G(d),[13] (3) B3LYP/6-31G(d), (4) B3PW91/6-31G(d), and (5) B3PW91/cc-pVDZ.[14−16,18] The first three of these are extremely popular. The low-level Hartree−Fock method, HF/3-21G(*), may be employed easily for molecules with 100 or more non-hydrogen atoms on common computer workstations. The MP2(FC)/6-31G(d) method has long been a standard for reliable geometries, but because of its computational demands, it is rarely used for molecules with more than 25 non-hydrogen atoms. It is for this reason that the much more efficient B3LYP/6-31G(d) method seems to have replaced MP2 calculations for routine determination of organic molecular geometries and energies.[17] I have included the less-common B3PW91/cc-pVDZ method for no other reason than that I and my collaborators have found it to be highly reliable; it was the best of the HDFT methods for the cyclophanes in Table 1, and it has given excellent results in our studies of strained polycyclic aromatic compounds.[24,31] Finally, the B3PW91/6-31G(d) method was added to compare, using the same basis set, the B3LYP and B3PW91 functionals with the MP2 method; it will be seen that this was a fortunate addition. The calculations and experimental comparisons which follow are meant merely to be an illustrative—not comprehensive—evaluation of this subset of commonly available methods using the HSX set.

Comparison of Experimental and Computed Structures. Hartree−Fock calculations were carried out by using SPARTAN Version 5.0[32] or GAUSSIAN 98.[33] HDFT calculations were

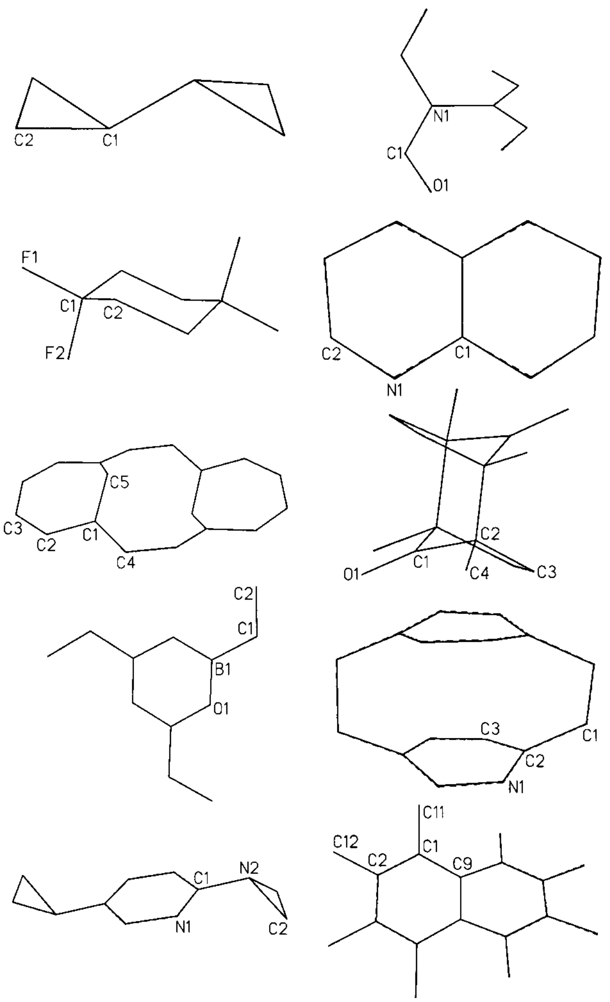

Figure 2. Superposition of the experimental (solid line) and the *best* calculated (dashed line) structures of each of the light atom members of the HSX set: left column, top to bottom, **11**−**15**; right column, **16**−**20**. The crystallographic numbering schemes for the symmetry-independent atoms are given.

carried out with GAUSSIAN 94 or GAUSSIAN 98,[33] and all MP2 calculations were carried out with GAUSSIAN 98.[33] Each geometry optimization was carried out under a symmetry constraint identical to the site symmetry of the molecule in its experimental crystal structure determination; default convergence criteria were employed in all cases.

The results of these calculations are summarized in Tables 2 and 3. Each entry in the tables gives the calculated energy of the optimized geometry (merely for the purpose of reproducing the calculation) as well as the rms and maximum deviations (Å) of the calculated geometry from the experimental one. The best fits and the deviations were calculated by using the OFIT function in Siemens SHELXTL,[20] and all non-hydrogen atoms were used for the fitting. Next to the rms deviation entry for each calculation, the rank of this result among the five methods examined (1 = best) is given. Thus, rather than compiling extensive tables of bond lengths and angles for each computed structure (which tends to obscure the forest with trees), I have chosen to rank the results on the basis of the *overall* agreement with the experimental structures.

The first thing to notice is the generally very high quality of the calculated structures. For each of the molecules in the HSX set, one or more of the methods examined gave geometries in excellent agreement with experiment, an observation that tends to support the notion that high-symmetry molecules in relatively noninteracting, high-symmetry environments do not deviate too greatly from their gas-phase structures. This is dramatically illustrated in Figures 2 and 3, in which the experimental structure of each of the 20 molecules is superimposed with its best calculated geometry; the differences between the two, in nearly every case, are barely visible at this scale.

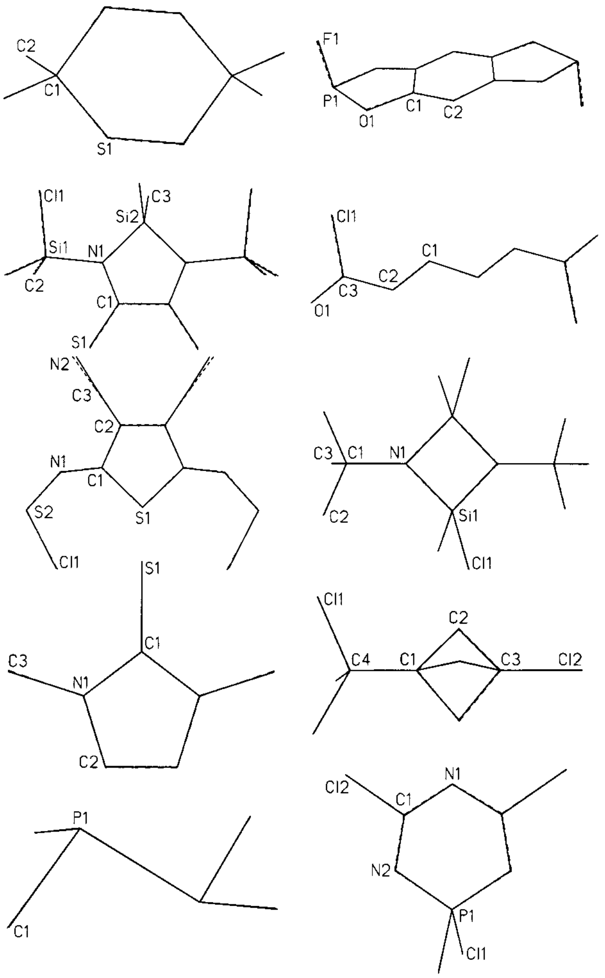

Figure 3. Superposition of the experimental (solid line) and the *best* calculated (dashed line) structures of each of the heavy atom members of the HSX set: left column, top to bottom, **21**−**25**; right column, **26**−**30**. The crystallographic numbering schemes for the symmetry independent atoms are given.

The trends in the quality of the calculated structures are most easily grasped by examining the matrix below, which simply displays the relative ranks (based on agreement with experiment) of the five calculations performed on each of the 20 molecules (ties are underlined; LT and HT are the totals of the ranks for the light atom and heavy atom calculations, respectively).

	Light	atom	molecules								Heavy	atom	molecules								LT	HT
HF/3-21G(*)	$\underline{1}$	5	5	5	5	1	5	3	5	5	2	$\underline{2}$	5	1	$\underline{1}$	2	1	3	4	3	40	24
MP2/6-31G(d)	$\underline{1}$	4	1	4	1	3	4	5	4	4	1	1	1	$\underline{4}$	$\underline{1}$	5	4	1	1	1	31	20
B3LYP/6-31G(d)	5	3	4	3	4	5	3	4	3	3	5	4	4	$\underline{2}$	5	3	5	4	5	4	37	41
B3PW91/6-31G(d)	$\underline{3}$	2	$\underline{2}$	2	3	2	2	2	2	2	$\underline{3}$	$\underline{2}$	3	$\underline{2}$	3	1	2	2	2	2	22	22
B3PW91/cc-pVDZ	$\underline{3}$	1	$\underline{2}$	1	2	4	1	1	1	1	$\underline{3}$	5	2	$\underline{4}$	4	4	3	5	3	5	17	38

The data for the light atom and heavy atom structures are rather different.

(1) For the light atom structures, the B3PW91/cc-pVDZ results are superior; they are in the best agreement with the experimental data in 6 of the 10 cases. The B3PW91/6-31G(d) method is almost as good, giving the second-best structure in 8 of 10 cases. Both B3PW91 methods seem superior to the

TABLE 4: "Head-to-Head" Comparisons of the Relative Accuracy of the Five Computational Methods Used for the Calculations on the HSX Set in Tables 2 and 3

	HF/ 3-21G(*)	MP2(FC)/ 6-31G(d)	B3LYP/ 6-31G(d)	B3PW91/ 6-31G(d)	B3PW91/ cc-pVDZ
HF/3-21G(*)		5−13−2	12−8−0	6−13−1	10−10−0
MP2(FC)/6-31G(d)	13−5−2[a]		12−8−0	10−10−0	11−8−1
B3LYP/6-31G(d)	8−12−0	8−12−0		0−19−1	5−15−0
B3PW91/6-31G(d)	13−6−1	10−10−0	19−0−1		9−8−3
B3PW91/cc-pVDZ	10−10−0	8−11−1	15−5−0	8−9−3	

[a] As an example, this entry (13−5−2) indicates that the MP2(FC)/6-31G(d) method gave more accurate structures than the HF/3-21G(*) method in 13 cases and less accurate structures in 5 cases, and 2 were of the same accuracy.

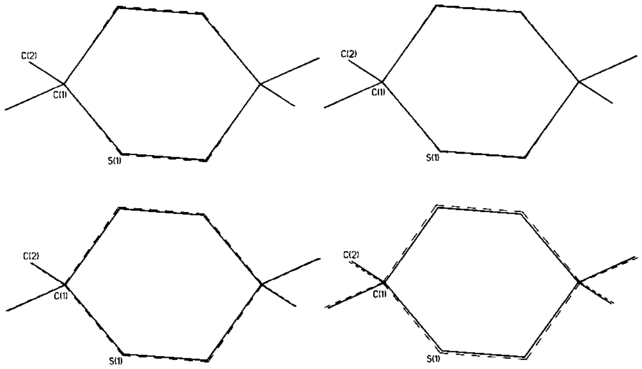

Figure 4. Superposition of the experimental (solid line) and calculated (dashed line) structures for 3,3,6,6-tetramethyl-*s*-tetrathiane (**21**). The computational methods employed are (clockwise from upper left) HF/3-21G(*), MP2(FC)/6-31G(d), B3LYP/6-31G(d), and B3PW91/cc-pVDZ.

B3LYP/6-31G(d) and MP2/6-31G(d) calculations. The HF/3-21G(*) calculations are generally poorest, but gave the best results in two cases.

(2) For the heavy atom structures, MP2/6-31G(d) geometries are superior; they are in the best agreement with the experimental data in 7 of the 10 cases. The B3PW91/6-31G(d) and, surprisingly, the HF/3-21G(*) calculations are nearly as good, but the other two HDFT methods—B3LYP/6-31G(d) and B3PW91/cc-pVDZ—gave significantly poorer results.

An alternative way to analyze the data is to make pairwise, "head-to-head" comparisons of the five computational methods; the results are given in Table 4. In these comparisons, the MP2-(FC)/6-31G(d) and B3PW91/6-31G(d) methods have "winning records" against each of the other three methods and tie with each other (10−10−0) for overall accuracy. *However, the surprising entry is the 19−0−1 record of B3PW91/6-31G(d) vs B3LYP/6-31G(d); that is, in 19 out of 20 cases the former gives a more accurate geometry than the latter, and the remaining case is a tie.*

In terms of the rms deviations from the experimental structures (see Tables 2 and 3), the HF/3-21G(*) method gives similar results for light atom and heavy atom structures, and the same is true for the MP2/6-31G(d) method. However, all three HDFT methods show significantly larger deviations for heavy atom structures than for the light atom structures. This finding is most pronounced for the B3LYP/6-31G(d) and B3PW91/cc-pVDZ methods, but it is also true for B3PW91/6-31G(d).

The reason for this is obvious when one examines the calculated structures: HDFT methods systematically overestimate bond lengths involving second-row elements. This problem is well illustrated by Figure 4, which gives the experimental and computed structures for 3,3,6,6-tetramethyl-*s*-tetrathiane (**21**). The MP2/6-31G(d) geometry is very close to the experimental structure, and the HF/3-21G(*) result is only slightly worse. However, the HDFT methods clearly overestimate the size of this molecule, with the B3LYP/6-31G(d) geometry substantially poorer than the B3PW91 structures. This phenomenon is well-known, even appearing in user manuals for computational packages,[26,34] but this does not seem to have inhibited the use of HDFT methods for such molecules (perhaps because the energies are reported to be more reliable than those obtained by Hartree−Fock calculations[27,35]). However, one may ask to what degree the choice of basis sets influences the results. Table 5 gives the deviations from the experimental structure for the geometries of compound **21** calculated by using a variety of basis sets for each method. No strong dependence on the basis set is observed; the rms deviations of calculated structures from experiment are more closely related to the type of method chosen. Larger basis sets give some improvement in the quality of the HDFT geometries, but even with quite large basis sets, no HDFT method gives results superior to those from the MP2/6-31G(d) calculations, and no B3LYP geometry is superior to the HF/3-21G(*) result.

TABLE 5: Energies (au) and Deviations (Å) from the Experimental Geometries for 3,3,6,6-Tetramethyl-*s*-trithiane (21) Calculated by a Variety of Methods

computational level	E	rms dev	max dev
HF/3-21G(*)	−1815.57959	0.026	0.031
HF/6-31G(d)	−1824.23376	0.038	0.046
HF/cc-pVDZ	−1824.33188	0.037	0.043
HF/6-311+G(2d,p)	−1824.41175	0.039	0.045
HF/cc-pVTZ	−1824.46531	0.037	0.042
MP2(FC)/6-31G(d)	−1825.53223	0.015	0.022
MP2(FC)/cc-pVDZ	−1825.73337	0.027	0.037
MP2(FC)/6-311+G(2d,p)	−1825.95979	0.018	0.027
MP2(FC)/cc-pVTZ	−1826.22417	0.014	0.018
B3LYP/6-31G(d)	−1828.63410	0.053	0.058
B3LYP/cc-pVDZ	−1828.72022	0.053	0.057
B3LYP/6-311+G(2d,p)	−1828.82780	0.051	0.058
B3LYP/cc-pVTZ	−1828.86798	0.046	0.052
B3PW91/6-31G(d)	−1828.35716	0.032	0.035
B3PW91/cc-pVDZ	−1828.44919	0.032	0.035
B3PW91/6-311+G(2d,p)	−1828.54449	0.029	0.034
B3PW91/cc-pVTZ	−1828.58522	0.024	0.028

As noted previously, for each HSX set member, at least one method examined gave a structure in excellent agreement with the experimental geometry. However, crystal packing forces can sometimes intrude to a significant degree, and by the same token, some molecules are computationally especially challenging. One example, the heteroatom-rich structure **23**, seems to show both characteristics; its computed and experimental geometries are illustrated in Figure 5. All four calculated geometries find the two cyano groups [C(3)−N(2)] to be splayed more widely than in the experimental structure. An examination of the crystal packing shows that there are close contacts between the cyano group nitrogens and the sulfur atoms [S(2)] of adjacent molecules, perhaps forcing the cyano groups closer together. The other bond angles in the structure are well reproduced by the B3PW91 calculations (only B3PW91/cc-pVDZ is shown) and the MP2/6-31G(d) calculation, but all tend to overestimate the bond lengths in this case. The B3LYP/6-31G(d) structure suffers from the same problems, but in addition, its exocyclic C(1)−N(1)−S(2) and N(1)−S(2)−Cl(1) bond angles are significantly worse. In contrast, the experimental bond distances are rather well reproduced in the HF/3-21G(*) structure, but the overall geometry is the worst of the five because of substantial errors in the exocyclic bond angles.

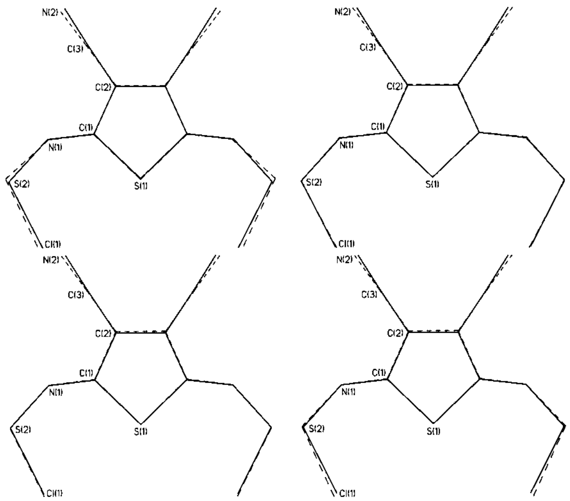

Figure 5. Superposition of the experimental (solid line) and calculated (dashed line) structures for 2,5-bis(chlorothioimino)-3,4-dicyanothiophene (**23**). The computational methods employed are (clockwise from upper left) HF/3-21G(*), MP2(FC)/6-31G(d), B3LYP/6-31G(d), and B3PW91/cc-pVDZ.

Conclusion

Most chemists employ computational methods to guide their research or to provide explanations for unusual or unexpected results. For this reason, modern computational methods should be tested to as great a degree as possible on systems of a complexity comparable to those encountered in the laboratory. The intent of this study has not been to recommend one particular computational method. Instead, it is more important to emphasize that the computational methods discussed here, and, more generally, all methods which can be applied to large molecules using currently available computers, involve significant approximations, and that one should not automatically assume that the "higher" computational level is more reliable for *all* classes of compounds (as seen in Table 1).

For most light atom structures, common HDFT methods give superior geometries at a low computational cost, but for complex structures containing second-row elements, the choices are less clear. Of the methods examined in the present study, B3PW91/6-31G(d) is a good first choice if an "all-purpose" method is desired that is computionally efficient enough to be used on relatively large molecules. This method gives excellent results on light atom structures, and it suffers least from the problems associated with heavy atoms common to HDFT methods. In this respect, B3PW91/6-31G(d) appears to be a fortunate combination of functional and basis sets; certainly, there is no reason to expect, a priori, that this combination should be so much better than B3LYP/6-31G(d) or B3PW91/cc-pVDZ. However, that seems to be the case, and all of the data contained in Tables 1−3 suggest that B3LYP/6-31G(d), currently the most commonly employed method for geometry optimization,[17] should be replaced by B3PW91/6-31G(d), which requires essentially identical computational resources. This choice may change, of course, as faster computers or newer methodologies become available.

The HSX set provides a good first test for the calculation of geometries, and it may be used to see whether a particular method is likely to be satisfactory for the problem at hand. Consider again the cyclophanes in Table 1; five of these contain second-row elements. It would be obvious from tests with the HSX set that most HDFT methods are at a significant disadvantage for that reason, regardless of any other unique features of these molecules. If HDFT methods are chosen for the problem anyway, it would be clear that the B3PW91 functional would be a better choice than the B3LYP functional for geometry optimizations. (On the other hand, the HSX set does not predict that the HF/3-21G(*) would be so nearly perfect for this particular class of molecules, merely that it should give reasonable results.)

Finally, if the HSX set proves to be useful for the evaluation of the present and future computational methods, then it may be desirable to determine the experimental enthalpies of formation for several of these compounds so that they can be employed for evaluation of both calculated geometries and energies on a routine basis.

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