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C(sp^2)−C(Aryl) Bond Rotation Barrier in *N*-Methylbenzamide

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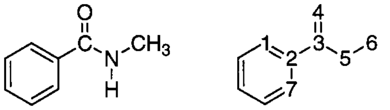
The potential energy surfaces at different levels of ab initio electronic structure theory with correlation effects included are reported for rotation about the C(sp^2)−C(aryl) bond in *N*-methylbenzamide. The results reveal a minimum at a C═C−C═O dihedral angle of ±28° with barrier heights (MP2/aug-cc-pVTZ//BLYP/DZVP2/A2) of 0.48 kcal/mol at 0° and 2.80 kcal/mol at 90°. Fully optimized geometries are in good agreement with crystal structure data, and potential energy surfaces are consistent with the experimental dihedral angle distribution. The results are used to assign MM3 force field parameters to allow calculation on *N*-methylbenzamide and other benzamide derivatives.

Introduction

Amides are a class of molecules important to several chemical disciplines. Not only are they a major functional group in organic chemistry[1] but also they form key linkages in natural macromolecules such as proteins, polypeptides, synthetic macromolecules such as nylons, and polyaramides such as Kevlar. Amides also contain oxygen and nitrogen atoms that can coordinate with metal ions.[2] Our current research centers on the development of structure−function relationships for the design of organic receptors for actinides and lanthanides. In the design of such host molecules, the amide functionality can play a role as a donor site or as a structural element for linking other donor sites.[3] Knowledge of the stable configurations of the host provides the foundation for understanding how the host structure influences guest binding. To gain this knowledge, we have been studying the conformational aspects of amides and diamides by using high-level electronic structure methods. In prior studies, we have reported detailed analyses of C(sp^2)−C(sp^3) rotation in simple aliphatic amides,[4] the stable conformations of malonamide[5] and succinamide derivatives,[6] and C−H···O hydrogen bonding between amide donors and acceptors.[7] The current study extends this work by examining the rotational potential energy surface (PES) for the C(sp^2)−C(aryl) bond in *N*-methylbenzamide (NMB; Scheme 1).

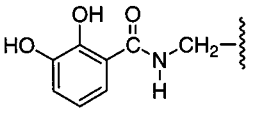
SCHEME 1



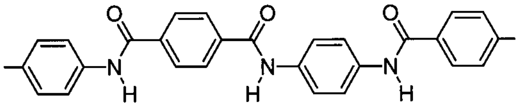
N-methylbenzamide (NMB)

We are interested in NMB as a model for a structural element that occurs in a class of siderophores known as triscatecholamides.[8] In these compounds, an amide moiety is used to link a chelating donor site, catechol, to the backbone of the host (Scheme 2). The degree of rotation about the C(sp^2)−C(aryl) bond plays an important role in directing the oxygen donors toward the guest. In this case, the rotational potential surface will be influenced by the conjugation of the amide and arene π orbitals, steric repulsions with ortho arene substituents, and intramolecular hydrogen bonding. A study of NMB provides a measure of the effect of the first two factors. Understanding C(sp^2)−C(aryl) bond rotation in NMB also has application in the conformational analysis of aramide polymers (Scheme 2).

SCHEME 2



catecholamide group



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An examination of the literature failed to reveal any reported experimental measurements of the barrier to C(sp^2)−C(aryl) rotation in NMB. Large C(sp^2)−C(aryl) rotational barriers, 12−18 kcal/mol, have been measured for *N*,*N*-dialkylbenzamide derivatives with ortho substituents on the arene.[9] These barriers approach the barriers for C(sp^2)−N(amide) rotation, suggesting that C(sp^2)−C(aryl) rotation may be coupled with C(sp^2)−N(amide) rotation in these severely sterically hindered compounds. Prior reports of theoretical studies on NMB are limited to a rotational PES obtained by molecular mechanics after fitting force field parameters to give the best agreement with X-ray crystal structure data.[10] Rotational PESs at the AM1 and HF/DZ+D level have been reported for C(sp^2)−C(aryl) rotation in the closely related molecule 1,4-phenylenediformamide.[11]

Herein we report PESs for rotation about the C(sp^2)−C(aryl) bond in NMB obtained from both density-functional theory (DFT) and Møller−Plesset theory calculations. The calculations yield a barrier height of 2.8−2.9 kcal/mol. Fully optimized

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geometries are in good agreement with crystal structure data, and the calculated PESs are consistent with an experimental dihedral angle distribution. The results are used to assign MM3 force field parameters to allow calculation on NMB and other benzamide derivatives.

Theoretical Details

Electronic Structure Calculations. Calculations on NMB were performed using both DFT and second-order Møller−Plesset perturbation theory (MP2).[12] DFT calculations were done with the DGauss program system[13] using the local density approximation (SVWN exchange-correlation functional)[14] and the generalized gradient approximation (BLYP exchange-correlation functional).[15] All DFT calculations were done using a polarized double-ζ basis set (DZVP2) optimized at the DFT level with the A2 charge-density-fitting basis set in order to get formal N^3 scaling (DFT/DZVP2/A2).[13,16] MP2 calculations were done either with the Gaussian 98 program[17] using a polarized double-ζ valence basis set for molecular orbital calculations (DZP)[18] or with the NWChem program[19] using the aug-cc-pVTZ basis set.[20]

The PES for NMB was obtained by constraining the dihedral angle Φ (C1−C2−C3−O4; see Scheme 1) to a series of values and fully optimizing the remaining geometrical degrees of freedom at the SVWN/DZVP2/A2, BLYP/DZVP2/A2, and MP2/DZP levels of theory. In addition, single-point energies were calculated at the MP2/aug-cc-pVTZ level using the BLYP geometries. The approximate location of the minimum on the PES was identified, and the full geometry optimization of the minimum energy structure for NMB was performed at the SVWN/DZVP2/A2, BLYP/DZVP2/A2, and MP2/DZP levels of theory. Frequencies were calculated analytically at the BLYP/DZVP2/A2 level.

Cambridge Structural Database. Experimental average geometric parameters and dihedral angle distribution were obtained through analysis of the Cambridge Structural Database (CSD).[21] The CSD program QUEST was used to identify structures containing a phenyl ring attached to an amide C═O in which both arene ortho positions were occupied by hydrogen atoms and the nitrogen was substituted with a hydrogen atom and a C(sp^3) carbon. A total of 170 structures were retained when the search was constrained to eliminate all structures with *R* factors greater than 10%, with errors, or with disorder. The CSD program VISTA was used to perform a statistical analysis of the geometric parameters in these structures to provide a basis for comparison with theoretical results.

Force Field Calculations. Calculations were performed with the MM3(96) program.[22] The development and validation of default amide parameters provided with the program are described elsewhere.[23] This model uses several dielectric-dependent parameters to account for changes in the amide moiety that occur on going from the gas phase to the condensed phase. These changes include an increased C═O bond length, a decreased C−N bond length, and an increase in the barrier to rotation about the C−N bond. Default gas-phase parameters ($\epsilon = 1.5$) were applied when doing MM3 calculations for fitting the PES and for comparing structural features with those obtained from electronic structure calculations. Condensed phase parameters ($\epsilon = 4$) were applied when doing MM3 calculations for comparing structural features with those obtained from X-ray data.

Input files for NMB were created using standard MM3 atom types: 1 (alkane carbon), 3 (carbonyl carbon), 50 (benzene carbon), 7 (amide oxygen), 9 (amide nitrogen), 5 (C−H), and 28 (N−H). It is not possible to perform calculations on NMB with the default MM3(96) parameter set because of missing parameters. The default MM3(96) parameter set was used after the following modifications and additions. Using the same stretching force constant as a type 50−50 bond, 6.56 mdyn/Å^2, the bond 3−50 was assigned an r_0 of 1.485 Å to reproduce the average bond length observed in crystal structures. After a bending force constant of 1.00 (mdyn Å)/rad^2 was assigned, which is similar in magnitude to values used for 1−3−7 and 7−3−9 bends, the 9−3−50 bend (missing in the default parameter set) was assigned a θ_0 of 114.0° to reproduce the average bond angle observed in crystal structures. On the basis of prior work with *N*-benzylformamide,[24] parameters $\epsilon^* = 0.400$ and $r^* = 2.580$ Å were assigned to a 5−7 hydrogen bond. Finally, the V_2 parameters for 7−3−50−50 and 9−3−50−50 (missing in the default parameter set) torsion interactions were adjusted to fit PES for C(sp^2)−C(aryl) bond rotation at the MP2/aug-cc-pVTZ level of theory, yielding values of 3.300 and 0.700 kcal/mol, respectively.

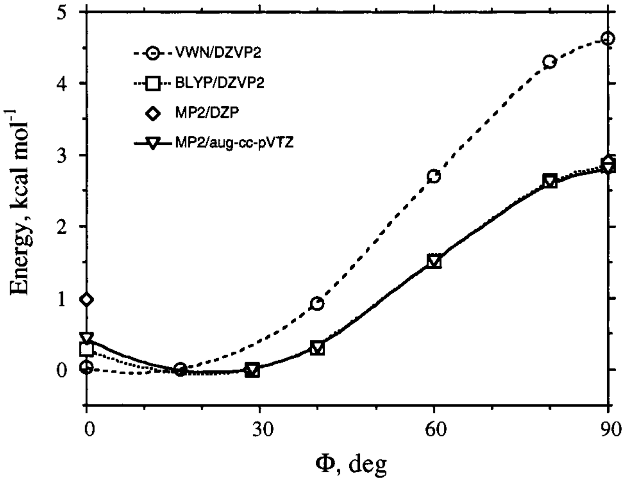

Figure 1. PES for C(sp^2)−C(aryl) bond rotation in NMB where Φ is the C1−C2−C3−O4 dihedral angle (see Scheme 1).

TABLE 1: Relative Energies (kcal/mol) for the C(sp^2)−C(aryl) Rotational PES[a]

Φ	SVWN	BLYP	MP2/DZP	MP2/aug-cc-pVTZ[b]
0.0	0.02	0.28	0.98	0.43
16.3	0.00			
28.3			0.00	
28.6		0.00		0.00
40.0	1.39	0.32		0.31
60.0	3.01	1.52		1.52
80.0	4.37	2.65		2.62
90.0	4.54	2.85	2.91	2.80

[a] Total energies at the minimum: E(SVWN/DZVP2/A2) = −436.572 175 au; E(BLYP/DZVP2/A2) = −440.207 116 au; E(MP2/DZP) = −438.967 651 au; E(MP2/aug-cc-pVTZ) = −439.584 784 au [b] Single-point energy calculation on the BLYP/DZVP2/A2 geometry.

Results and Discussion

The PESs for rotation about the C(sp^2)−C(aryl) bond in NMB at the different levels of theory are shown in Figure 1, and the energy values are given in Table 1. Given the symmetry of this PES, we present only values from 0 to 90°. The form of the PES for the different methods is very similar with all levels of theory, showing a low barrier at 0° and a high barrier at 90°. The BLYP/DZVP2/A2, MP2/DZP, and MP2/aug-cc-pVTZ barrier heights are very close in energy at 90°, 2.80−2.91 kcal/mol, whereas the SVWN/DZVP2/A2 method gives a 90° barrier

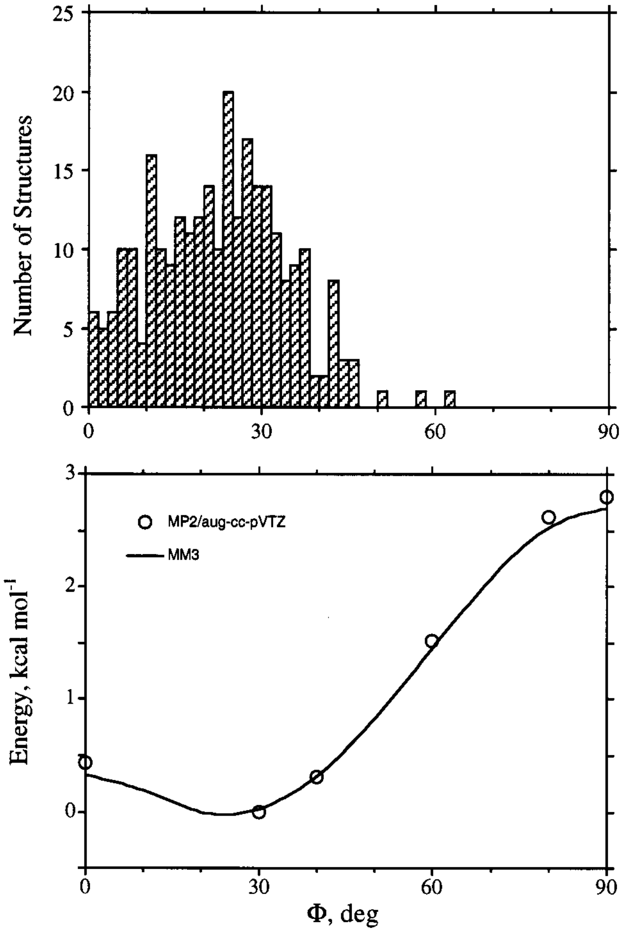

Figure 2. Comparison of experimental distribution of Φ (top) with the PES obtained at the MP2/aug-cc-pVTZ level of theory (bottom). The solid curve in the lower plot shows the MM3 fit to the MP2/aug-cc-pVTZ energies.

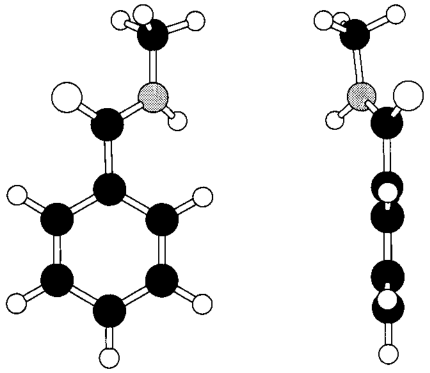

Figure 3. Two views of the MP2/DZP minimum energy structure of NMB.

of almost 2 kcal/mol higher. The spread in barrier heights is larger for the 0° barrier, where SVWN/DZVP2/A2 gives 0.02 kcal/mol, BLYP/DZVP2/A2 gives 0.28 kcal/mol, MP2/aug-cc-cpVTZ gives 0.48 kcal/mol, and MP2/DZVP gives 0.98 kcal/mol. The results support the prior PES obtained by fitting force field parameters to X-ray structure in which the calculated barriers were found to be 2.6 and 0.4 kcal/mol, respectively.[10]

MM3 parameters for the two torsional interactions, 7−3−50−50 and 9−3−50−50, were adjusted to fit the MP2/aug-cc-cpVTZ PES to within an average error of ±0.05 kcal/mol as shown in Figure 2. The fit was obtained by assigning barrier heights for twofold periodicity only, i.e., V_2 parameters. This result suggests that there is an intrinsic preference for the amide to remain coplanar with the arene. A tendency toward planarity is consistent with the fact that coplanar orientation would align π orbitals resulting in stabilization through delocalization of electron density.

After locating the approximate positions of the rotational minima, full geometry optimizations were performed at the SVWN/DZVP2/A2, BLYP/DZVP2/A2, and MP2/DZP levels of theory. Vibrational frequencies, calculated at the BLYP/DZVP2/A2 level, established the absence of any negative modes, verifying the structure obtained at this level of theory to be a true minimum on the PES. The lowest frequency, which corresponds to the torsion about the C(sp^2)−C(aryl) bond, is 56 cm^{-1} (0.16 kcal/mol). This value is only 0.12 kcal/mol less than that of the torsional barrier at this level of theory, suggesting that there are at most a couple of modes bound by the 0° barrier. Calculated frequencies of 1648 cm^{-1} for the C=O stretch and

TABLE 2: Experimental and Calculated Structural Data[a]

	gas-phase					crystal	
feature	VWN r_e	BLYP r_e	MP2 r_e	MP2 r_g[b]	MM3+ ($\epsilon = 1.5$)	expt X-ray	MM3+ ($\epsilon = 4.0$)
C1−C2	1.398	1.416	1.407	1.412	1.400	1.38(1)	1.400
C2−C3	1.489	1.516	1.502	1.507	1.500	1.50(1)	1.500
C2−C7	1.400	1.417	1.409	1.414	1.400	1.39(2)	1.400
O4−C3	1.238	1.250	1.239	1.229	1.225	1.23(1)	1.241
C3−N5	1.363	1.387	1.374	1.380	1.382	1.34(2)	1.340
N5−C6	1.435	1.467	1.456	1.462	1.455	1.46(2)	1.454
C1−C2−C3	116.5	117.7	117.8		116.5	118(1)	116.2
C3−C2−C7	123.8	123.0	122.4		123.8	123(1)	124.3
C2−C3−O4	121.5	121.9	122.5		120.4	121(1)	120.3
C2−C3−N5	116.0	115.7	115.2		117.0	117(1)	117.2
O4−C3−N5	122.4	122.5	122.3		122.3	122(1)	122.4
C3−N5−C6	120.9	121.9	119.7		121.0	122(2)	121.3
C1−C2−C3−O4 (Φ)	16.3	28.6	28.3		24.4	22(12)	16.6
C7−C2−C3−N5	17.4	30.6	29.3		30.5	22(11)	20.7
C2−C3−N5−C6	178.4	177.7	174.7		179.0	175(4)	179.4
O4−C3−N5−C6	−0.9	−2.3	−5.7		−3.0	−5(4)	−1.9
γ	359.3	358.6	355.3		359.7		359.9
α	7.6	12.2	21.6		4.7		2.5

[a] Bond lengths are in angstroms, and bond angles are in degrees. Pyramidalization of the amide nitrogen is expressed in terms of γ, the sum of the three bond angles subtended at nitrogen, and α, the angle between the N−H bond and the C−N−C plane. [b] MP2 r_g values were estimated from computed r_e values based on past performance.[27]

3559 cm^{-1} for the N−H stretch are consistent with the experimental ranges of 1630−1690 cm^{-1} for C=O and 3400−3500 cm^{-1} for N−H.[25] A table of all frequencies is given as Supporting Information.

The fully optimized MP2/DZP geometry for the minimum energy structure is shown in Figure 3, and important geometry parameters at all levels of electronic structure theory are given in Table 2. The coordinates for the optimized structures are given as Supporting Information. All levels of theory predict that the phenyl ring rotates out of the plane of the amide group. The degree of rotation, as measured by the C1−C2−C3−O4 dihedral angle Φ, is 16.3 at SVWN/DZVP2/A2, 28.6 at BLYP/DZVP2/A2, and 28.3° at MP2/DZP. The deviation from planarity results from steric repulsion between the arene ortho hydrogen atoms and the amide N−H and O atoms. For example, in the MP2/DZP structure, the N−H$\cdots$H$_{\mathrm{arene}}$ distance is 2.256 Å and the O$\cdots$H$_{\mathrm{arene}}$ distance is 2.590 Å. The former interaction is consistent with pyramidalization of the amide nitrogen, as is shown by the parameters α and γ in Table 2. The O$\cdots$H$_{\mathrm{arene}}$ distance falls within the range of values expected for C−H$\cdots$O hydrogen bonds.[26] However, the weak acidity of the arene hydrogen coupled with unfavorable geometric features, a C=O$\cdots$H angle of 79.3° (ideal angle = 120°) and a C−H$\cdots$O angle of 94.5° (ideal angle = 180°),[7] suggests this interaction to be repulsive rather than attractive. Consistent with this hypothesis, an examination of the MM3 energy reveals this interaction to be repulsive, 0.35 kcal/mol, even when the C−H$\cdots$O interaction is included in the force field (see Theoretical Details section).

Table 2 provides a comparison of bond lengths and bond angles obtained at the various electronic structure levels, at the MM3 level in the gas phase ($\epsilon = 1.5$) and in the condensed phase ($\epsilon = 4.0$), and experimental averages from X-ray diffraction data. Comparison of bond lengths obtained with electronic structure calculations reveals that, with respect to the MP2/DZP method, the SVWN/DZVP2/A2 method underestimates bond lengths (low by 0.011 Å on average), whereas the BLYP/DZVP2/A2 calculation overestimates bond lengths (high by 0.011 Å on average). Bond lengths from electronic structure calculations (r_e) tend to be shorter than those of experimental values (r_g). The r_e values from MP2/DZP have been corrected to r_g values by a set of empirical parameters to allow a more meaningful comparison against the MM3.[27] The agreement between MP2/DZP and MM3 ($\epsilon = 1.5$) bond lengths is good, with an average absolute deviation of 0.008 Å. Similarly, there is good agreement between MM3 ($\epsilon = 4.0$) and X-ray bond lengths, with an average absolute deviation of 0.008 Å. The average deviations between the theoretical and experimental bond angles are as follows: VWN/DZVP2/A2, 0.88°; BLYP/DZVP2/A2, 0.52°; MP2/DZP, 1.11°; MM3 ($\epsilon = 1.5$), 0.70°; MM3 ($\epsilon = 4.0$), 0.85°.

Figure 2 compares the distribution of Φ observed in 170 X-ray crystal structures, plotted as a histogram of the number of occurrences versus the absolute value of Φ, against the PES obtained at the MP2/aug-cc-pVTZ level and reproduced with our modified version of MM3. Fully consistent with the theoretical results, the experimental data shows that Φ is populated predominantly in the region where the energy is less than 1 kcal/mol above the minimum, i.e., 0 ± 55°. The average experimental value, 22 ± 11°, is close to the predicted minimum energy values, and Φ is more heavily populated in the range of 11−33° than it is near 0°, which is in agreement with the presence of a small barrier at 0°.

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Supporting Information Available: Cartesian coordinates of optimized structures in angstroms and frequencies in inverse centimeters. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Zabicky, J. *The Chemistry of Amides*; Wiley-Interscience: New York, 1970. (b) Solomons, G.; Fryhle, C. *Organic Chemistry*; John Wiley: New York, 2000.

(2) (a) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385. (b) Clement, O.; Rapko, B. M.; Hay, B. P. *Coord. Chem. Rev.* **1998**, *170*, 230.

(3) Hay, B. P.; Clement, O.; Sandrone, G.; Dixon, D. A. *Inorg. Chem.* **1998**, *37*, 5887 and references therein.

(4) Sandrone, G.; Dixon, D. A.; Hay, B. P. *J. Phys. Chem. A* **1999**, *103*, 893.

(5) Sandrone, G.; Dixon, D. A.; Hay, B. P. *J. Phys. Chem. A* **1999**, *103*, 3554.

(6) Vargas, R.; Garza, J.; Dixon, D. A.; Hay, B. P. *J. Phys. Chem. A* **2000**, *104*, 5115.

(7) Vargas, R.; Garza, J.; Dixon, D. A.; Hay, B. P. *J. Am. Chem. Soc.* **2000**, *122*, 4750.

(8) (a) Harris, W. R.; Raymond, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 6534. (b) Harris, W. R.; Raymond, K. N.; Weitl, F. L. *J. Am. Chem. Soc.* **1981**, *103*, 2667. (c) Pecoraro, V. L.; Weitl, F. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5133. (d) Kappel, M. J.; Pecoraro, V. L.; Raymond, K. N. *Inorg. Chem.* **1985**, *24*, 2447. (e) Rodgers, S. J.; Lee, C.-W.; Ng, C. Y.; Raymond, K. N. *Inorg. Chem.* **1987**, *26*, 1622. (f) Scrarrow, R. C.; Ecker, D. J.; Ng, C.; Liu, S.; Raymond, K. N. *Inorg. Chem.* **1991**, *30*, 900. (g) Loomis, L. D.; Raymond, K. N. *Inorg. Chem.* **1991**, *30*, 906. (h) Stack, T. D. P.; Karpishin, T. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1512. (i) Karpishin, T. B.; Raymond, K. N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 466. (j) Stack, T. D. P.; Hou, Z.; Raymond, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 6466.

(9) (a) Kiefl, C.; Zinner, H.; Burgemeister, T.; Mannschreck, A. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 125. (b) Ahmed, A.; Bragg, R. A.; Clayden, J.; Lai, L. W.; McCarthy, C.; Pink, J. H.; Westlund, N.; Yasin, S. A. *Tetrahedron* **1998**, *54*, 13277.

(10) Hummel, J. P.; Flory, P. J. *Macromolecules* **1980**, *13*, 479.

(11) Irwin, R. S.; Vorpagel, E. R. *Macromolecules* **1993**, *26*, 3391.

(12) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

(13) DGauss is a program that is part of UniChem and is available from Oxford Molecular. (a) Andzelm, J.; Wimmer, E.; Salahub, D. R. In *The Challenge of d and f Electrons: Theory and Computations*; Salahub, D. R., Zerner, M. C., Eds.; ACS Symposium Series 394; American Chemical Society: Washington, DC, 1989; p 228. (b) Andzelm, J. In *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer-Verlag: New York, 1991. (c) Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 1280.

(14) Vosko, S. J.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(15) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(16) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.4; Gaussian, Inc.: Pittsburgh, PA, 1998.

(18) (a) Dunning, T. H., Jr. *J. Chem. Phys*. **1970**, *53*, 2823. (b) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3.

(19) Bernholdt, D. E.; Apra, E.; Fruchtl, H. A.; Guest, M. F.; Harrison, R. J.; Kendall, R. A.; Kutteh, R. A.; Long, X.; Nicholas, J. B.; Nichols, J. A.; Taylor, H. L.; Wong, A. T.; Fann, G. I.; Littlefield, R. J.; Nieplocha, J. *Int. J. Quantum Chem.*, *Quantum Chem. Symp.* **1995**, *29*, 475.

(20) (a) Dunning, T. H., Jr. *J. Chem. Phys*. **1989**, *90*, 1007. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys*. **1992**, *96*, 6769.

(21) *Cambridge Structural Database System*, version V5.18, Oct 1999 Release. Allen, F. H.; Bellard, S. A.; Brice, B. A.; Cartwright, A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr.*, *Sect. B* **1979**, *35*, 2331.

(22) *MM3*(*96*). The program may be obtained from Tripos Associates, 1699 S. Hanley Road, St. Louis, MO 63144, for commercial users, and it may be obtained from the Quantum Chemistry Program Exchange, Mr. Richard Counts, QCPE, Indiana University, Bloomington, IN 47405, for noncommercial users.

(23) (a) Lii, J.-H.; Gallion, S.; Bender, C.; Wikstrom, H.; Allinger, N. L.; Flurchick, K. M.; Teeter, M. M. *J. Comput. Chem.* **1989**, *10*, 503. (b) Lii, J.-H.; Allinger, N. L. *J. Comput. Chem.* **1991**, *12*, 186.

(24) Vargas, R.; Garza, J.; Dixon, D. A.; Hay, B. P. *THEOCHEM* **2000**, in press.

(25) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley-Interscience: New York, 1974.

(26) (a) Green, R. D. *Hydrogen Bonding by C−H Groups*; Macmillan: London, 1974. (b) Berkovich-Yellin, Z.; Leiserowitz, L. *Acta Crystallogr.*, *Sect. B* **1984**, *40*, 159. (c) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441. (d) Steiner, T. *Crystallogr. Rev.* **1996**, *6*, 1. (e) Allen, F. J. P.; Lommerse, M.; Hoy, V. J.; Howard, J. A. K.; Desiraju, G. R. *Acta Crystallogr.*, *Sect. B* **1996**, *52*, 734. (f) Steiner, T. *Chem. Commun.* **1997**, 727. (g) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, U.K., 1997. (h) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, U.K., 1999.

(27) Ma, B.; Lii, J.-H.; Schaefer, H. F.; Allinger, N. L. *J. Phys. Chem.* **1996**, *100*, 8763,