Quadrupole and Octopole Moments of Heteroaromatic Rings

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Ab initio, second-order, Møller−Plesset perturbation theory calculations of quadrupole and octopole moments are reported for 36 different 6π-electron monocycles: benzene, 12 azines, pyrrole, 9 azoles, furan, 9 oxazoles, borazine, boroxine, and 1,2,4,3,5-trioxadiborole. Agreement with the limited experimental and computational data available is generally good.

1. Introduction

Electric multipole moments measure the departure from spherical symmetry of a charge distribution.[1−3] They are required for the description of the long-range interactions between two molecules and between a molecule and an incoming electron. Dipole moments can be measured precisely by a variety of experimental methods and are available for many molecules.[3−5] However, experimental values of quadrupole moments are comparatively scarce. Quadrupole moments for highly symmetric molecules can be obtained from the electric field gradient induced birefringence experiment.[6−8] Measurements of the Zeeman splitting of the rotational spectra of dipolar molecules lead to anisotropies of the magnetizability tensor χ and the gyromagnetic $\mathbf{g}$ tensor, which can be combined with the moment of inertia tensor $\mathbf{I}$ to obtain the quadrupole moment tensor $\boldsymbol{\Theta}$ in the inertial axis system.[4,9,10] Unfortunately, the combination of the data often leads to large error bars for Θ. Quadrupole moments are also becoming available through X-ray diffraction experiments using rigid pseudoatom refinement of the electron density.[11] Indirect methods for estimating multipole moments, such as collision-induced spectroscopy,[12] depend on the intermolecular potential model used to analyze the data. Experimental values of octopole moments are available only for a handful of molecules, most of which have vanishing dipole and quadrupole moments. Thus, high-quality ab initio calculations[13,14] are probably the most reliable way to obtain quadrupole and octopole moments.

We report systematic ab initio second-order Møller−Plesset (MP2) calculations of the quadrupole and octopole moments of 36 planar heteroaromatic monocycles: benzene, 12 azines, pyrrole, 9 azoles, furan, 9 oxazoles, borazine, boroxine, and 1,2,4,3,5-trioxadiborole ($B_2H_2O_3$). Experimental measurements and/or electron-correlated calculations of quadrupole moments have been reported previously for only 15 of these important molecules,[11,15−51] and we are unaware of any such work for octopole moments of these heterocycles.

2. Computations

The multipole moment computations were carried out with the HONDO program[52] at MP2(full)/6-31G(d) equilibrium geometries. We have reported these geometries previously[53−56] for all the molecules except boroxine and 1,2,4,3,5-trioxadiborole (referred to as trioxadiborole hereafter) for which the necessary computations were performed with Gaussian 90.[57]

TABLE 1: Comparison of MP2/6-31G(d) and Experimental Bond Lengths (Å) and Angles (deg)

parameter	MP2[a]	CBSQ[b]	expt[c]
	Trioxadiborole		
OO bond	148.5		147.0 ± 0.2
O2B3 bond	137.6		136.5 ± 0.4
B3O4 bond	138.1		138.0 ± 0.3
BH bond	118.3		118.2 ± 0.3
OOB angle	104.5		105.0 ± 0.3
OBO angle	113.5		113.1 ± 0.3
O2B3H angle	120.0		120.7 ± 0.3
	Boroxine		
OB bond	138.1	138.2	137.6 ± 0.2
BH bond	118.7	119.3	119.2 ± 1.7
OBO angle	120.2	121.	120.0 ± 0.6

[a] This work. [b] Reference 65. [c] Microwave spectroscopy[63] for trioxadiborole and electron diffraction[64] for boroxine.

We calculated multipole moments at the MP2(full) level using a [5s3p2d/3s2p] basis set, denoted C in refs 53−56, which was specifically optimized for polarizabilities and should give good results for multipole moments as well. This basis set consists of a double-ζ substrate[58] augmented by [1s1p/1s] diffuse GTF, [1d/1p] polarization functions optimized for polarizabilities,[53−56] and another [1d/1p] set optimized for electron correlation.[59]

Both unabridged[3,60] and traceless[1,2,61,62] multipole moments were computed with the center of mass as the origin. The coordinates specifying the equilibrium geometries of these molecules are available on the Internet at http://www.unb.ca/chem/ajit/download.htm. Inertial axes were calculated with standard, isotopically averaged atomic masses. The quadrupole moment tensor was then rotated to the inertial frame.

3. Results

The MP2/6-31G(d) equilibrium geometries and dipole moments of 34 of the 36 molecules were presented and discussed earlier.[53−56] Only the other two molecules are considered here. Table 1 shows that the MP2/6-31G(d) geometry of trioxadiborole agrees with the microwave geometry[63] to better than 1% except for the OO bond length for which the discrepancy is 1.5 pm. The MP2/6-31G(d) geometry of boroxine is within the uncertainties of the electron diffraction geometry[64] and in

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TABLE 2: MP2/C Quadrupole Moments (in au) at MP2/6-31G(d) Geometries (1 au ≈ 4.4866 × 10^{-40} C m^2 ≈ 1.3450 buckingham)

molecule	symmetry	Θ_{aa}	Θ_{ab}	Θ_{bb}	Θ_{cc}
benzene	D_{6h}	2.97	0	2.97	−5.94
pyridine	C_{2v}	−2.18	0	5.93	−3.75
pyridazine	C_{2v}	−3.66	0	5.57	−1.91
pyrazine	D_{2h}	−7.68	0	9.12	−1.44
pyrimidine[a]	C_{2v}	−3.12	0	4.70	−1.58
1,2,3-triazine	C_{2v}	−0.47	0	0.59	−0.12
1,2,4-triazine	C_s	−7.83	0.23	7.39	0.43
s-triazine	D_{3h}	−0.34	0	−0.34	0.67
1,2,3,4-tetrazine[a]	C_{2v}	−5.25	0	3.35	1.89
s-tetrazine	D_{2h}	−10.43	0	7.96	2.47
1,2,3,5-tetrazine	C_{2v}	−5.89	0	3.60	2.29
pentazine[a]	C_{2v}	−6.66	0	2.71	3.96
hexazine	D_{6h}	−2.81	0	−2.81	5.63
pyrrole	C_{2v}	5.11	0	1.47	−6.57
pyrazole	C_s	−2.51	1.91	7.11	−4.60
imidazole	C_s	−0.48	2.58	4.90	−4.42
1,2,3-triazole	C_s	1.24	−4.07	1.58	−2.82
1,2,5-triazole[a,b]	C_{2v}	−5.96	0	8.53	−2.58
1,2,4-triazole	C_s	−5.61	2.16	7.95	−2.34
1,3,4-triazole[b]	C_{2v}	−0.23	0	2.79	−2.56
1,2,3,4-tetrazole	C_s	−1.84	−1.70	2.72	−0.89
1,2,3,5-tetrazole[b]	C_s	−7.08	2.54	7.72	−0.64
pentazole[a]	C_{2v}	−5.78	0	4.85	0.93
furan	C_{2v}	0.13	0	4.36	−4.49
isoxazole	C_s	−0.11	−2.85	2.84	−2.72
oxazole	C_s	−3.96	−0.34	6.22	−2.26
1,2,3-oxadiazole	C_s	−0.46	−0.56	1.41	−0.95
1,2,5-oxadiazole[a]	C_{2v}	−2.41	0	3.32	−0.91
1,2,4-oxadiazole	C_s	−6.29	−2.94	6.66	−0.36
1,3,4-oxadiazole	C_{2v}	−5.61	0	5.88	−0.27
1,2,3,4-oxatriazole	C_s	−4.90	1.10	3.85	1.06
1,2,3,5-oxatriazole	C_s	2.95	2.12	−4.13	1.18
oxatetrazole[a]	C_{2v}	−1.79	0	−1.00	2.79
borazine	D_{3h}	1.56	0	1.56	−3.11
boroxine	D_{3h}	−2.08	0	−2.08	4.15
trioxadiborole	C_{2v}	−4.62	0	2.82	1.81

[a] I_a perpendicular to the C_2 axis. [b] Numbered with NH as first locant.

excellent agreement with the density functional theory (DFT) and ab initio CBS-Q computations of Politzer et al.[65] The MP2/C dipole moment (0.95 D with O−O end negative) of trioxadiborole agrees perfectly with the experimental value[63] of 0.95 ± 0.01 D.

The supplementary tables S1−S4 in Supporting Information list the calculated MP2/C dipole moments, $\langle r^2 \rangle$, and the unabridged and traceless forms of the quadrupole and octopole moment tensors in the coordinate system referred to above. The rest of this paper deals exclusively with traceless quadrupole moments in the inertial frame because they can be compared directly with experimental work.

Table 2 lists components of the traceless, MP2/C quadrupole moment tensor $\boldsymbol{\Theta}$ in the inertial frame. Only two of the diagonal elements are unique because

$$\Theta_{aa} + \Theta_{bb} + \Theta_{cc} = 0 \tag{1}$$

where the principal axes of inertia follow the usual spectroscopic convention

$$I_a \le I_b \le I_c \tag{2}$$

I_c is perpendicular to the molecular plane, and the quadrupole moment tensor is block diagonal for the planar molecules considered in this work:

$$\Theta_{ac} = \Theta_{ca} = \Theta_{bc} = \Theta_{cb} = 0 \tag{3}$$

TABLE 3: Comparison of Quadrupole Moments (in au) for Symmetric Tops

molecule	method	$\Theta_{cc} = -2\Theta_{aa}$
benzene	MP2//MP2[a]	−5.94
	CISD//HF[b]	−6.35
	CISD//expt[c]	−6.52
	MP2/DZ//expt[d]	−6.40
	MP2/DZ+2P (on C only)//expt[d]	−7.11
	MP2//expt[e]	−6.03
	X-ray[f]	−6.40 ± 0.78
	Zeeman (from fluorobenzene)[g]	−6.50 ± 0.67
	Zeeman (adjusted)[g]	−6.32 ± 1.04
	birefringence in CCl_4[h]	−7.42 ± 0.47
	birefringence in CCl_4[i]	−6.31 ± 0.27
	birefringence in C_6H_{12}[i]	−6.02 ± 0.25
	gas-phase birefringence[j]	−6.46 ± 0.38
s-triazine	MP2//MP2[a]	0.67
	CISD//SCF[k]	0.79
	X-ray[f]	−0.78 ± 0.13
	birefringence in C_6H_{12}[l]	−0.62 ± 0.69
borazine	MP2//MP2[a]	−3.11
	MP2//MP2[m]	−3.28
	birefringence in C_6H_{12}[n]	−2.36 ± 0.29

[a] This work. [b] Reference 39. [c] Reference 36. [d] Reference 25. [e] Reference 50. [f] Reference 11. [g] Reference 31. [h] Reference 16. [i] Reference 19. [j] Reference 22. [k] Reference 44. [l] Reference 51. [m] Keir and Spackman as cited in ref 20. [n] Reference 20.

The $\boldsymbol{\Theta}$ tensor is symmetric, $\Theta_{ab} = \Theta_{ba}$, and so $\boldsymbol{\Theta}$ has at most three independent components. Θ_{ab} is nonzero for the 13 C_s symmetry monocycles shown in Figure 1, which indicates the direction chosen for the coordinate axes in the inertial frame; the sign of Θ_{ab} changes if the direction of one of these axes is reversed. Figure 1 also shows the principal axis of the $\boldsymbol{\Theta}$ tensor corresponding to the in-plane component of largest magnitude. In the remaining 23 molecules, symmetry ensures that the principal axes of the quadrupole moment tensor are aligned with the inertial axes, and hence, $\Theta_{ab} = 0$. The I_a axis is perpendicular to the C_2 axis in 7 of the 16 C_{2v} molecules indicated in Table 2, whereas I_a coincides with the C_2 axis in the rest. I_a is perpendicular to N···N in D_{2h} pyrazine, but I_a is parallel to the N−N bonds in D_{2h} *s*-tetrazine. Benzene, *s*-triazine, hexazine, borazine, and boroxine are oblate symmetric tops for which the in-plane components of $\boldsymbol{\Theta}$ are equal ($\Theta_{aa} = \Theta_{bb}$); often, only Θ_{cc} is reported for these molecules.

4. Comparison with Previous Work

Our MP2/C quadrupole moments ought to be compared with previous experimental estimates and electron-correlated computations available for 15 of the 36 molecules.

Benzene. Consider the experimental values listed in Table 3. Shoemaker and Flygare[34] derived an approximate value for the quadrupole moment of benzene from the fluorobenzene $\boldsymbol{\Theta}$ obtained from Zeeman effect experiments. Prompted by suggestions[16,22] that the estimate was much too low, Stolze et al.[31] made a better one by performing improved Zeeman effect experiments on fluorobenzene and using an extrapolation to benzene based on semiempirical CNDO calculations. Ritchie et al. published three values[16,17,19] of $\boldsymbol{\Theta}$ for benzene from field-gradient-induced birefringence measurements. Their best result, in the nonquadrupolar solvent CCl_4, is in excellent agreement with the value of Stolze et al.[31] and is a little higher than their own value in the quadrupolar solvent C_6H_{12}. Battaglia et al.[22] studied the temperature dependence of field-gradient-induced birefringence in the gas-phase. Their value of $\boldsymbol{\Theta}$ depends on the value they measured for the polarizability anisotropy, and the mean polarizability they took from previous work.[66] Their

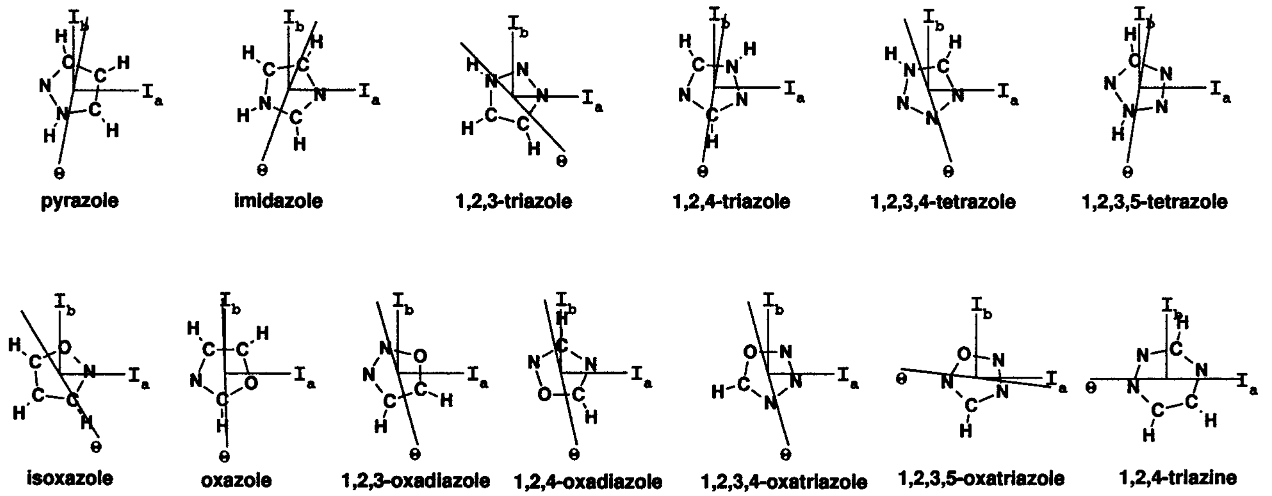

Figure 1. C_s symmetry monocycles, their in-plane principal axes of inertia (I_a and I_b), and the principal axis of the quadrupole moment (**Θ**) tensor corresponding to the in-plane component of largest magnitude.

gas-phase value of **Θ** is reasonably close to the best results of the other methods. Spackman[11] obtained the quadrupole moment from various model fits to X-ray data[67] for benzene; his best monopole model gave a **Θ** that is close to the result of Battaglia et al.[22] The experimental values for benzene listed in Table 3 range from −6.02 to −7.42 au; the most accurate value is probably −6.46 ± 0.38 au from Battaglia et al.[22]

Published calculations of **Θ** for benzene show that improving the basis set and increasing the C−C bond length both make Θ_{cc} more negative, whereas electron correlation makes Θ_{cc} more positive. The correlated values in Table 3 range from −5.94 to −7.11 au. The DFT values[50] of **Θ** are quite sensitive to the functional used. We estimate that, in a complete basis set, the MP2 $\Theta_{cc} \approx -6.2$ au, well within the uncertainty of the best experimental estimate[22] of −6.46 ± 0.38 au.

***s*-Triazine.** Dennis[51] reported a small, negative Θ_{cc} from birefringence experiments on a dilute solution of *s*-triazine in cyclohexane (see Table 3). Spackman[11] reported a similar value from a monopole fit to X-ray data.[68] However, the configuration interaction (CI) calculation of Walker et al.[44] and our MP2/C calculation both yield small, positive values of Θ_{cc}.

Borazine. Table 3 shows that our MP2/C result is close to the MP2/6-31G(+sd,+sp)//MP2/6-31G(d) Θ_{cc} of Keir and Spackman cited by Dennis and Ritchie.[20] Both calculated values are more negative than and outside the error bars of the value deduced by Dennis and Ritchie from induced birefringence of borazine in cyclohexane. In benzene, the birefringence Θ_{cc} becomes increasingly negative in the sequence cyclohexane solvent, CCl_4 solvent, gas phase. If a similar trend holds for borazine, then the gas-phase measurement would be closer to the ab initio values.

Pyridine. Table 4 lists three Zeeman derived **Θ** tensors for pyridine. The older Zeeman experiment on pyridine[35] was less accurate and does not agree with all components of the ^{15}N-pyridine data.[30] Our MP2/C results are within the error bars of the ^{15}N-pyridine and 4-D-pyridine results of Hamer and Sutter.[30] Our MP2 results are virtually the same as the MP2 results of Palmer et al.[46] and the nonlocal DFT results[37] obtained with a triple-ζ basis set. The CI results of Walker et al.[40] are only slightly different. Palmer et al.[46] have noted that their CI values[40,42] of **Θ** suffer from the use of inadequate Hartree−Fock (HF) geometries.

Pyridazine. There are no experimental values. Our MP2 result is almost identical to the CI calculations of Palmer and Walker.[43]

Pyrazine. deLuca et al.'s DFT results[37] differ from our MP2 values by a greater amount for pyrazine than for pyridine. Similarly, the agreement among our MP2 results, the MP2 results of Palmer et al.,[46] and the CI values of Walker and Palmer[42] is not quite as good as for pyridine. The **Θ** tensor derived by Moss and Feil[69] from a multipole fit to X-ray data does not agree with any of the five calculations listed in Table 4 within the ±0.7 au error bars estimated by Spackman.[11] However, the trend in the X-ray **Θ** components does agree with the correlated calculations.

Pyrimidine. Our MP2 results are closer to the CI values of Palmer et al.[41] than to those of Malmqvist et al.[38] There are no experimental values.

1,2,3-Triazine. There are no experimental values. Table 4 shows that all the calculated components of the **Θ** tensor are small in magnitude. Our MP2 results differ by as much as 0.51 au from the MP2 results of Palmer et al.[46]

***s*-Tetrazine.** The DFT results of deLuca et al.[37] and the MP2 values of Palmer et al.[45] are similar, but not very close, to ours. There are no experimental values.

Pyrrole. Table 4, which lists the MP2 quadrupole moment tensors computed by Palmer et al.[48] and by us, indicates that even the fairly large error bars on the Zeeman derived values of Sutter and Flygare[28] are not large enough, except for Θ_{aa}.

Furan. Sutter and Flygare[27] determined the quadrupole moment of furan with respect to the center of mass using the microwave Zeeman effect. Subsequently, Bak et al.[29] performed a Zeeman study of 2,5-D_2-furan obtaining the components of the **Θ** tensor of furan with error bars larger than in the previous work. The two sets of results do overlap within the error bars of the two experiments. Judging by the error bars, we expect that the older experiment[27] is the more accurate one. Dennis et al.[18] determined the out-of-plane component Θ_{cc} at the effective quadrupole center for furan from infinite-dilution molar field-gradient birefringence, Kerr, and Cotton−Mouton constants of furan dissolved in cyclohexane. This value is difficult to compare with the others that are relative to the center of mass; we note that this value was ignored in a later discussion of the quadrupole moment of furan by the same group.[15] Table 4 shows that our MP2 results are in nearly perfect agreement with the Zeeman values of Sutter and Flygare.[27] The MP2 values reported by Coonan et al.[15] and the CI values of Palmer et al.[47] are further from the Zeeman values.

Pyrazole. Sutter and co-workers[32,33] published two Zeeman determinations of the diagonal elements of the **Θ** tensor of

TABLE 4: Comparison of Quadrupole Moments (in au) for C_{2v} and D_{2h} Molecules

molecule	method	Θ_{aa}	Θ_{bb}	Θ_{cc}
pyridine	MP2//MP2[a]	−2.18	5.93	−3.75
	DFT(NLSD)//DFT[b]	−2.10	5.83	−3.72
	CISD//HF[c]	−1.91	5.91	−4.00
	MP2//MP2[d]	−2.22	5.91	−3.69
	Zeeman[e]	−2.60 ± 0.67	7.21 ± 0.74	−4.61 ± 1.12
	Zeeman[f]	−1.71 ± 0.89	6.91 ± 1.12	−5.13 ± 1.64
	Zeeman[g]	−1.93 ± 0.30	5.95 ± 0.30	−4.01 ± 0.45
pyridazine	MP2//MP2[a]	−3.66	5.57	−1.91
	CISD//HF[h]	−3.64	5.55	−1.92
pyrazine	MP2//MP2[a]	−7.68	9.12	−1.44
	DFT(NLSD)//DFT[b]	−7.58	8.85	−1.25
	MRCI//HF[i]	−7.58	9.22	−1.64
	CISD//HF[j]	−7.42	8.91	−1.48
	MP2//MP2[d]	−7.82	8.98	−1.16
	X-ray[k]	−6.17	8.36	−2.18
pyrimidine	MP2//MP2[a]	−3.12	4.70	−1.58
	CISD//HF[l]	−2.92	4.44	−1.52
	MRCI//expt[m]	−2.71	4.79	−2.07
1,2,3-triazine	MP2//MP2[a]	−0.47	0.59	−0.12
	MP2//MP2[d]	−0.74	0.36	0.39
s-tetrazine	MP2//MP2[a]	−10.43	7.96	2.47
	DFT(NLSD)//DFT[b]	−10.39	7.58	2.80
	MP2//MP2[n]	−10.74	7.63	3.11
pyrrole	MP2//MP2[a]	5.11	1.47	−6.57
	MP2//MP2[o]	5.26	1.43	−6.69
	Zeeman[p]	4.91 ± 0.89	4.31 ± 1.19	−9.22 ± 1.71
furan	MP2//MP2[a]	0.13	4.36	−4.49
	CISD//HF[q]	−0.02	4.76	−4.73
	MP2//MP2[r]	−0.31	4.37	−4.06
	birefringence[s]			−6.06 ± 1.20
	Zeeman[t]	−0.15 ± 0.37	4.76 ± 0.45	−4.61 ± 0.67
	Zeeman[u]	0.15 ± 0.30	4.39 ± 0.22	−4.54 ± 0.30

[a] This work. [b] Reference 37. [c] Reference 40. [d] Reference 46. [e] Reference 35. [f] Reference 30, 4-D-pyridine. [g] Reference 30, ^{15}N-pyridine. [h] Reference 43. [i] Reference 49. [j] Reference 42. [k] Reference 11. [l] Reference 41. [m] Reference 38. [n] Reference 45. [o] Reference 48. [p] Reference 28. [q] Reference 47. [r] Reference 15. [s] At effective quadrupole center in C_6H_{12}, ref 18. [t] Reference 29. [u] Reference 27.

TABLE 5: Comparison of Quadrupole Moments (in au) for C_s Molecules

molecule	method	Θ_{aa}	Θ_{ab}	Θ_{bb}	Θ_{cc}
pyrazole	MP2//MP2[a]	−2.51	1.91	7.11	−4.60
	Zeeman[b]	−2.64 ± 0.16		7.28 ± 0.15	−4.64 ± 0.26
	Zeeman[c]	−2.65 ± 0.12	0.06 ± 0.13	7.28 ± 0.10	−4.65 ± 0.20
imidazole	MP2//MP2[a]	−0.48	2.58	4.90	−4.42
	X-ray[d]	4.32	−4.32	0.74	−5.06
	Zeeman[b]	−0.68 ± 0.20		5.05 ± 0.25	−4.36 ± 0.39
isoxazole	MP2//MP2[a]	−0.11	−2.85	2.84	−2.72
	MP2//expt[e]	0.92	−3.40	1.43	−2.36
	MP2//MP2[e]	−0.10	−3.12	2.88	−2.79
	Zeeman[f]	0.07 ± 0.82		2.23 ± 0.97	−2.30 ± 1.19
oxazole	MP2//MP2[a]	−3.96	−0.34	6.22	−2.26
	MP2//expt[g]	−4.44	−0.16	6.37	−1.93
	MP2//MP2[g]	−4.10	−3.04	7.11	−3.00
	Zeeman[f]	−3.64 ± 2.16		7.06 ± 2.30	−3.42 ± 3.64

[a] This work. [b] Reference 32. [c] 1-D-Pyrazole, ref 33. [d] Reference 11. [e] Reference 23 (Θ_{aa} and Θ_{bb} interchanged). [f] Reference 26. [g] Reference 24.

pyrazole. Table 5 shows that our MP2 results are in fine agreement with theirs. Böttcher and Sutter[33] used Zeeman data on the 1-D-pyrazole isotopomer to obtain a value for the off-diagonal component Θ_{ab}. However, their $\Theta_{ab} = 0.06 \pm 0.13$ au is probably incorrect in light of our MP2 calculation, which predicts $\Theta_{ab} = 1.91$ au.

Imidazole. Our MP2 results for the diagonal components of the $\boldsymbol{\Theta}$ tensor are well within the error limits of the experimental Zeeman values of Stolze and Sutter.[32] The X-ray results of Epstein et al.[70] in Table 5 are drastically different probably because of the strong hydrogen bonding in crystalline imidazole; a similar drastic difference was noted by Spackman[11] in a comparison with HF calculations.

Isoxazole. Davidson et al.[26] obtained the diagonal elements of the $\boldsymbol{\Theta}$ tensor from microwave Zeeman effect experiments. Table 5 shows that our MP2 components are well within their large error limits. Spoerel et al.[23] calculated MP2/6-31G(+sd,+sp) quadrupole moments at both the experimental and MP2 geometries. After we interchange their Θ_{aa} and Θ_{bb} values, we see that their results at the MP2 geometry agree with ours and with the Zeeman values, unlike their calculations at the experimental geometry.

Oxazole. Table 5 shows that our MP2 components of $\boldsymbol{\Theta}$ are well within the large error limits of Davidson et al.'s Zeeman effect values;[26] perhaps their error bars are overly pessimistic. Kraka et al.[24] calculated MP2/6-31G(+sd,+sp) $\boldsymbol{\Theta}$ tensors at both the experimental and MP2 geometries. Apart from Θ_{aa}, their results at the experimental geometry give the closest agreement with ours. Their MP2//MP2 off-diagonal element differs from ours by 2.7 au. These discrepancies are largely due to the poor geometries predicted by their MP2/6-31G(+sd,+sp) calculations. The Kraka et al. and Spoerel et al. results show that the quadrupole moment is very sensitive to changes in the geometry.

We are unaware of any experimental measurements or electron-correlated ab initio computations of the quadrupole moments of the remaining molecules. Thus, our MP2 results in Table 2 are the first ones available for these 21 important heteroaromatic monocycles. Similarly, our octopole moments listed in the Supporting Information are the first ones reported for the molecules considered in this work. It would be useful to assess the MP2 results presented in this work by performing detailed basis set, molecular geometry, and electron correlation studies on the quadrupole moment tensors of a few molecules such as benzene, pyridine, and furan for which there is ample experimental data.

Uniform quality data for a series of related molecules helps to bring out trends. Table 2 reveals that the out-of-plane component Θ_{cc} shows strong and clear trends. Note that Θ_{cc} increases with increasing aza substitution in each of the benzene to hexazine, pyrrole to pentazole, and furan to oxatetrazole sequences. Each aza substitution (N for C−H substitution) leads to a flattening of the electron distribution because (a) the N brings with it a lone pair centered in the molecular plane and outside the ring and (b) the N holds its π electron more tightly than the C it replaced did. Moreover, the aza substitution makes the nuclear contribution to Θ_{cc} less negative because the added N atom is closer to its bonding partners than the replaced CH was to its bond partners. These arguments do not depend on the location in the ring at which the aza substitution takes place, suggesting that isomers such as the three triazines should have similar values of Θ_{cc}, as indeed they do. An exactly analogous rationalization explains why an O for N−H substitution increases Θ_{cc} as seen in Table 2 by comparing pyrrole with furan, each azole with its oxazole counterpart, and borazine with boroxine. Trends for the individual in-plane components Θ_{aa} and Θ_{bb} are not easy to detect. However, the in-plane quantity $\Theta_{aa} + \Theta_{bb}$ exhibits trends that are precisely opposite to those for Θ_{cc} and can be rationalized in exactly the same manner because of eq 1.

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Supporting Information Available: Tables S1−S4 contain MP2/C dipole, quadrupole and octopole moments, and $\langle r^2 \rangle$ for the 36 molecules. This material is available free of charge via the Internet at http://pubs.acs.org and at http://www.unb.ca/chem/ajit/download.htm.

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