Effect of Intermolecular Hydrogen Bonding on the Nuclear Quadrupole Interaction in Imidazole and its Derivatives as Studied by *ab initio* Molecular Orbital Calculations

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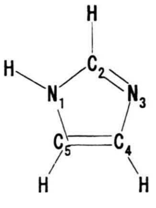
Ab initio Hartree-Fock molecular orbital calculations were applied to the crystalline imidazole and its derivatives in order to examine systematically the effect of possible N–H···N type hydrogen bonding on the nuclear quadrupole interaction parameters in these materials. The nitrogen quadrupole coupling constant (QCC) and the asymmetry parameter (η) of the electric field gradient (EFG) were found to depend strongly on the size of the molecular clusters, from single molecule, to dimer, trimer and to the infinite molecular chain, i.e., crystalline state, implying that the intermolecular N–H···N hydrogen bond affects significantly the electronic structure of imidazole molecule. A certain correlation between the QCC of ^{14}N and the N–H bond distance R was also found and interpreted on the basis of the molecular orbital theory. However, we found that the value of the calculated EFG at the hydrogen position of the N–H group, or the corresponding QCC value of ^{2}H, increases drastically as R^{-3} when R is shorter than about 0.1 nm, due probably to the inapplicability of the Gaussian basis sets to the very short chemical bond as revealed in the actual imidazole derivatives. We suggested that the observed N–H distances in imidazole derivatives should be re-examined.

Key words: Hydrogen Bond; Nuclear Quadrupole Interaction; Molecular Orbital; Imidazole.

1. Introduction

Hydrogen bonding of the type N–H···N plays an important role in biological systems and has been studied extensively by means of a variety of spectroscopic methods as well as diffraction experiments [1, 2]. Very recently, the usefulness of solid state NMR for studies of hydrogen bonding was pointed out [2].

Imidazole (**I**) and its derivatives are showing various biological activities. The important properties of the imidazole originate from the N–H···N hydrogen bonding, which therefore has been studied in a number of works [3–5]. Structural studies on crystals of the imidazole family have been done in [6–12].



I

Nuclear magnetic resonance of ^{15}N as well as ^{1}H and ^{13}C, and also nuclear quadrupole resonance of ^{2}H and ^{14}N are very useful for the study of N–H···N hydrogen bonding, as pointed out in [2], and a number of experimental and theoretical studies were conducted on the imidazole family and related materials in solution [13, 14] and in the solid state [12, 15–28].

Garcia et al. measured the ^{14}N and ^{2}H quadrupole interaction parameters in a variety of substituted imidazoles by means of double resonance techniques [27]. They found that the quadrupole parameters of the amino nitrogen >N– are sensitive to the molecular structure, whereas those of the imino nitrogen =N– are less sensitive. Although intermolecular hydrogen bonding is considered to contribute to the quadrupole parameters in the imidazole family, it seems difficult to derive quantitative conclusions from their experimental works.

We determined the crystal structure of 4,5-dichloroimidazole and 4,5-dicyanoimidazole by X-ray diffraction in order to confirm the existence of intermolecular hydrogen bonding in these di-substituted compounds [12]; we found a very short N–H bond length in the former compound and a bifurcated hydrogen bond of a type

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Table 1. Nuclear Quadrupole Interaction Parameters in Imidazole and Its Derivatives.[a]

Substance	State	Method[b]	Energy/Molecule a.u.	Nitrogen	e^2Qq/h of ^{14}N			η of ^{14}N	
					Exptl./MHz	V_{zz}/a.u.	Calc./MHz[c]	Exptl.	Calc.
Imidazole	Molecule	Gaussian Optimized	–224.879856	>N–	1.391	0.626	1.408	0.930	0.109
				=N–	3.220	1.047	2.355	0.119	0.201
		Gaussian	–224.876512	>N–		0.603	1.356		0.275
				=N–		1.035	2.327		0.161
		Crystal95	–224.660148	>N–		–0.557	1.496		0.335
				=N–		–0.878	2.357		0.167
	Dimer	Gaussian	–224.882764	>N–		0.403	0.906		0.568
				=N–		0.901	2.027		0.059
		Crystal95	–224.668134	>N–		–0.390	1.046		0.369
				=N–		–0.731	1.963		0.046
	Trimer	Gaussian	–224.886106	>N–		0.377	0.848		0.684
				=N–		0.890	2.001		0.032
		Crystal95	–224.672135	>N–		–0.364	0.977		0.459
				=N–		–0.721	1.936		0.011
	Crystal	Crystal95	–224.686653	>N–		–0.319	0.856		0.635
				=N–		–0.671	1.801		0.039
4,5-Dichloro-imidazole	Molecule	Gaussian	–1142.649559	>N–		0.482	1.084		0.703
				=N–		1.037	2.332		0.108
	Dimer	Gaussian	–1142.654312	>N–		–0.458	1.030		0.663
				=N–		0.949	2.135		0.084
4,5-Dicyano-imidazole	Molecule	Gaussian	–408.365133	>N–		–0.507	1.362		0.297
				=N–		–0.884	2.373		0.130
				–CN		–0.968	2.599		0.114
				–CN		–0.977	2.624		0.249
4-Nitro-imidazole	Molecule	Gaussian Optimized	–428.408581	>N–	1.377	0.575	1.292	0.786	0.084
				=N–	3.249	1.067	2.400	0.277	0.196
				–NO$_2$		–0.679	1.528		0.216
		Gaussian	–428.365190	>N–		0.512	1.152		0.219
				=N–		1.064	2.393		0.175
				–NO$_2$		–0.691	1.554		0.267
		Gaussian	–428.328796	>N–		0.428	0.962		0.688
				=N–		1.077	2.421		0.154
				–NO$_2$		–0.689	1.549		0.257
		Crystal95	–427.847333	>N–		–0.252	0.677		0.505
				=N–		–0.442	1.186		0.301
				–NO$_2$		0.542	1.455		0.290
	Dimer	Gaussian	–428.335626	>N–		–0.402	0.904		0.625
				=N–		0.996	2.240		0.075
				–NO$_2$		–0.710	1.597		0.304
				–NO$_2$		–0.691	1.554		0.267
	Crystal	Crystal95	–427.891083	>N–		–0.307	0.824		0.987
				=N–		–0.772	2.073		0.018
				–NO$_2$		0.615	1.650		0.468
4-Bromo-imidazole	Molecule	Gaussian	–2796.604422	>N–	1.377	0.436	0.978	0.949	0.408
				=N–	3.174	1.075	2.418	0.265	0.119
				–Br		–7.830	582	–	0.025
	Dimer	Gaussian	–2796.608523	>N–		–0.354	0.797		0.864
				=N–		0.994	2.234		0.069
				–Br		–7.991	595		0.014
4-Chloro-imidazole	Molecule	Gaussian	–683.764247	>N–	1.483	0.516	1.061	0.890	0.242
					1.440			0.943	
				=N–	3.145	1.030	2.316	0.261	0.080
					3.123			0.284	
				–Cl	70.800	–3.531	67.30		0.039
	Molecule	Crystal95	–683.509938	>N–		–0.499	1.340		0.111
				=N–		–0.876	2.352		0.092
				–Cl		3.732	70.830		0.030
	Dimer	Gaussian	–683.769170	>N–		0.394	0.886		0.894
				=N–		0.923	2.076		0.043
				–Cl		–3.623	69.05		0.037
4-Methyl-imidazole	Molecule	Gaussian	–263.926014	>N–	1.364	0.614	1.381	0.977	0.278
					1.326			0.992	
				=N–	3.127	0.997	2.242	0.161	0.121
	Dimer	Gaussian	–263.921784	>N–					
				=N–					
1-Methyl-imidazole	Molecule	Gaussian	–263.916190	>N–		0.594	1.336		0.290
				=N–		1.051	2.363		0.160

Table 1. (Continued)

e^2Qq/h of ^{2}H			η of ^{2}N		R(N−H···N) nm	R(N−H) nm	R(H···N) nm	Structure data	H-bond energy kJ/mol
Exptl./kHz	V_{zz}/a.u.	Calc./MHz^d	Exptl.	Calc.					
157.0	−0.4507	236.7	0.167	0.1507	–	0.099	–	–	
	−0.3287	172.8		0.1719					
	0.3487	193.7		0.1686					
	−0.2632	138.4		0.1987					
	0.2762	153.4		0.1922	0.286	0.104	0.183	Ref. [8]	25.2 (69.6)
	−0.2595	136.4		0.1984					
	0.2718	151.0		0.1953					
	0.2644	146.9		0.2080					
	−1.4848	780.5		0.0782	0.286	0.082	0.200	Ref. [12]	12.4
	−1.4383	756.1		0.0786	0.280	0.080	0.202		
	−0.5401	283.9		0.1361	0.305	0.096	0.224	Ref. [12]	
160.9	−0.4404	231.5	0.160	0.1501	–	0.0992	–		
	−0.6519	342.7		0.1189	0.286	0.093	0.186	Ref. [10]	
	−1.3124	689.9		0.0797					
	1.3231	735.2		0.0837					
	−1.2733	669.4		0.0751	0.287	0.082	0.206	Ref. [9]	17.9 (114.9)
	1.2654	703.1		0.0760					
159.4	−1.1109	584.0	0.157	0.0862	0.283	0.085	0.204	[e]	10.8
	−1.0686	561.8		0.0879					
165.8 163.7 or 164.5 144.9	−0.7927	416.7	0.160 0.170 or 0.185 0.146	0.1069					
	0.7988	443.8		0.1109	0.285 0.288	0.090 0.090	0.199 0.197	[e]	12.9
	−0.7441	391.1		0.1130					
158.5 155.8	−0.3293	173.1	0.182 0.171	0.1764	0.282	0.1015	0.1805	[f]	–
	−0.3147	165.4		0.1744					
	–				–	–	–		

** Footnotes a–f on page 318

>N–H···N=/ N–H···(NC)– with reasonable N–H and N···N lengths in the latter compound. We also conducted a ^{15}N CP/MAS (cross-polarization/magic angle spinning) NMR study on these compounds and found that the isotropic chemical shifts of ^{15}N of the amino and imino nitrogens are much different from each other in the crystalline state. Recently, we determined the ^{15}N isotropic chemical shifts of ring nitrogens of several 4-substituted imidazoles by CP/MAS NMR and, after applying *ab initio* molecular orbital computations of the chemical shielding to these materials, we concluded that the values of the chemical shielding are closely related to the hydrogen bond distances [29].

Very recently we conducted a ^{15}N line shape measurement of the amino and imino nitrogens in crystalline imidazole and found that the chemical shielding anisotropy of the imino nitrogen is more than twice as large as that of the amino nitrogen; we applied also an *ab initio* molecular orbital computation to the chemical shift anisotropy in imidazole and pointed out that the degree of the anisotropies in the chemical shifts can only be understood by taking into account the significant effect of the intermolecular hydrogen bonding [30].

The present paper concerns the structure and the properties of the N–H···N type hydrogen bond in crystals of several 4-substituted and two 4,5-disubstituted imidazoles (see Table 1) by *ab initio* molecular orbital calculations.

2. Computational Methods

The nuclear quadrupole interaction parameters in each of the compounds were computed by the conventional Hartree-Fock SCF method for clusters of molecules at their actual crystallographic configurations using the available structural data (see references in Table 1). The calculations were carried out by the use of the GAUSSIAN 94 program package [31] with the 6-311G(*df,p*) basis set [32] and CRYSTAL95 program package [33] with the 6-21G* basis set [34]; both have been installed on a DEC Alpha-Station 500 work station. The size of the molecular cluster was limited by the memory size of the work station to three for imidazole and to two for other larger molecular systems in the case of computation by GAUSSIAN 94: The computation on the actual crystalline states by means of CRYSTAL95 was successfully applied to imidazole and 4-nitroimidazole. We calculated the values (in a.u.) of the electric field gradient components at the nitrogen site in nitromethane molecule, and, by referring to its experimental e^2Qq/h value, 1.6946 MHz [35], determined the conversion factors to the quadrupole coupling constant as –2.2487 MHz/a.u. for GAUSSIAN 94 results and 2.6846 MHz/a.u. for CRYSTAL95 results. The electric field gradients at the proton or deuteron position in the N–H(D)···N system were converted by multiplying by conversion factors of 525.7 kHz/a.u. and 555.6 kHz/a.u. for GAUSSIAN 94 and CRYSTAL95 computational results, respectively, by referring to the average experimental values of the quadrupole coupling constant (176.9 kHz) and the asymmetry parameter (0.068) for C–H in crystalline imidazole [27]. Although the absolute values of the experimental and the calculated QCC's do not agree, we never applied any other scaling to the computed QCC values, as we are concerned with the systematic trends among the computational results.

3. Results and Discussion

Table 1 records the total energies and the QCC and η for ^{14}N and ^{2}H by *ab initio* computations for molecular clusters of imidazole and its derivatives, together with the observed QCC and η [27] and reported hydrogen bond geometries. The orientation of the principal components of the ^{14}N EFG tensor ($V_{zz} = \partial^2 V/\partial z^2$ etc., where V is the electrostatic potential, and defined according to the convention that $|V_{xx}| \leqq |V_{yy}| \leqq |V_{zz}|$) with respect to the molecular geometry in imidazole is as follows:

** Footnotes for Table 1

[a] Observed values of the QCC and η of ^{14}N and ^{2}H are taken from [27].

[b] Method/GAUSSIAN: Calculation carried out using GAUSSIAN 94 program package with the basis set RHF/6-311G(*df,p*) [31]; for 4-bromoimidazole STO-3G basis set was used. Method/CRYSTAL95: Calculation carried out using CRYSTAL95 program package with the basis set RHF/6-21G* [33].

[c] Values of QCC of ^{14}N referred to the experimental QCC = 1.6946 MHz for ^{14}N in nitromethane [35]: Conversion factors from V_{zz} to QCC are –2.2487 (MHz/a.u.) for GAUSSIAN and +2.6846 (MHz/a.u.) for CRYSTAL95; Values of QCC of ^{35}Cl referred to the experimental QCC = 108.95 MHz for ^{35}Cl in solid Cl_2^+: Conversion factors from V_{zz} to QCC are 19.06 (MHz/a.u.) for GAUSSIAN and 18.98 (MHz/a.u.) for CRYSTAL95; Values of QCC of ^{79}Br referred to the experimental QCC = 765 MHz for ^{79}Br in solid Br_2^+: Conversion factor from V_{zz} to QCC is 74.4 (MHz/a.u.) for GAUSSIAN.

[+] See in W. Gordy, R. L. Cook, Microwave Molecular Spectra, 3rd ed., John Wiley & Sons, Inc., New York 1984.

[d] Values of QCC of ^{2}H referred to the experimental QCC = 176.9 kHz for ^{2}H in crystalline imidazole [27]: Conversion factors from V_{zz} to QCC are 525.7 (kHz/a.u.) for GAUSSIAN and 555.6 (kHz/a.u.) for CRYSTAL95.

[e] S. Nagatomo, unpublished results.

[f] Structure of the dimer derived from imidazole dimer using a program package MOLDA [I. Yoshida and H. Matsuura, Molda for Windows, 1998], and the optimized structure is generated by the use of MOPAC/PM3 program [J. J. P. Stewart, MOPAC6, QCPE #455].

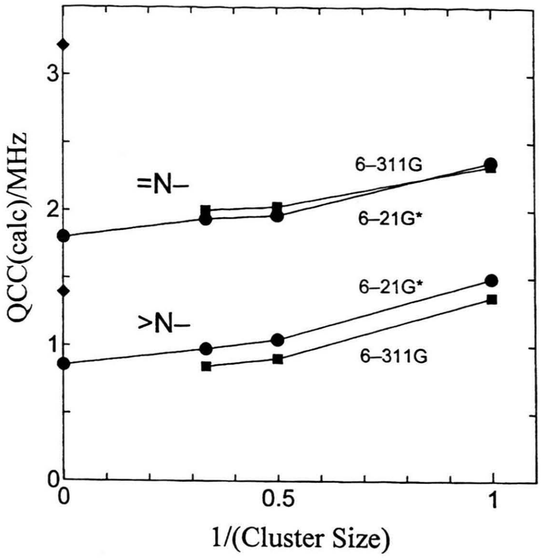

Fig. 1. Dependence of the Calculated ^{14}N quadrupole coupling constant on the reciprocal of the molecular cluster size (1, 2, 3, and ∞) in imidazole. ◆'s denote the observed QCC.

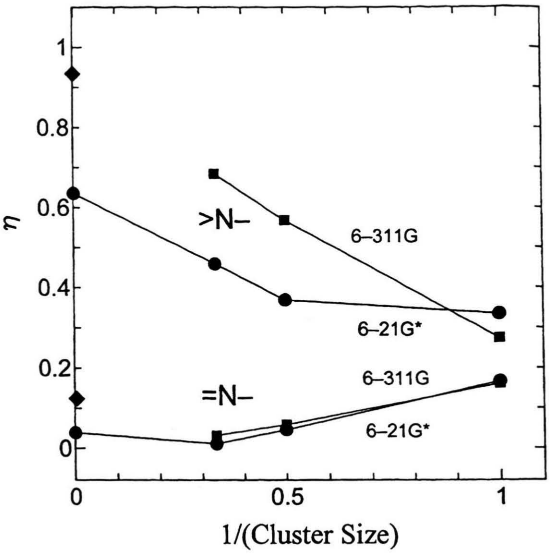

Fig. 2. Dependence of the Calculated ^{14}N asymmetry parameter, η, on the reciprocal of the molecular cluster size (1, 2, 3, and ∞) in imidazole. ◆'s denote the observed η.

i) The principal z axis for $e\,q = e\,V_{zz}$ is perpendicular to the molecular plane, and the y axis is nearly parallel to the N–H bond in the >N–H group.

ii) The z axis is parallel to and the y axis is perpendicular to the molecular plane in the =N– group.

These findings are consistent with the reported situation for gaseous imidazole [36].

1) ^{14}N Quadrupole Interaction

As we mentioned above, the nuclear quadrupole interaction in the imidazole family depends on the type, number, and position of substituent(s), and the strength of possible intermolecular hydrogen bonding. Therefore we examined first the existence of any significant effect of the hydrogen bonding on the nuclear quadrupole interaction at the ^{14}N sites in the imidazole molecular species. Figures 1 and 2 are the plot of the calculated QCC and η, respectively, against the reciprocal of the cluster size of imidazole. Here the cluster size denotes the inverse of the number of molecules (1, 2, 3, and ∞ for imidazole) used in an ab initio molecular orbital calculation. We see in Fig. 1 that the QCC's of ^{14}N of both the amino (>N–) and the imino (=N–) nitrogens decrease steadily with increase in the cluster size, and the total change on the crystallization amounts to about 43% for the amino nitrogen (>N–) and 24% for the imino nitrogen (=N–). Note that the difference in the QCC of a single molecule and a dimer is the largest compared with the differences between clusters, and that the calculations with the basis sets 6-311G(*df,p*) by GAUSSIAN 94 and with 6-21G* by CRYSTAL95 give similar results.

The variation of η with change in the cluster size is quite remarkable, as can be seen in Figure 2. A large discrepancy is found between the results calculated by GAUSSIAN 94 and CRYSTAL95 for the amino nitrogen. This fact suggests that η at the amino nitrogen site is very sensitive to the choice of the basis set. The QCC's of the amino and imino nitrogens change nearly parallel with each other as the cluster size changes, but that the difference between η's of these nitrogens increases dramatically with an increase in the cluster size. Note also that there are significant disagreements between the experimental and the calculated QCC's as well as η's.

As to the QCC and η of the amino and imino nitrogens in 4-nitroimidazole, we saw a similar trend to the case of imidazole except that the difference between the η's of the amino and imino nitrogens in 4-nitroimidazole is much larger than in imidazole.

The fact that the calculated QCC and η of nitrogens vary with the cluster size in imidazole and 4-nitroimidazole implies that the formation of the intermolecular hydrogen bond affects significantly the electronic structure

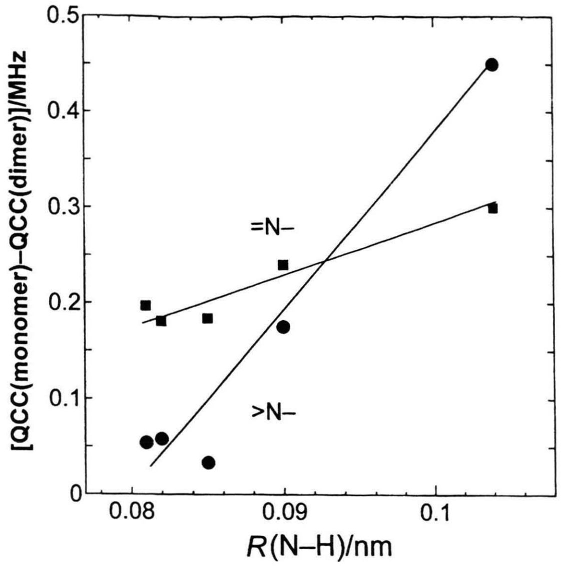

Fig. 3. Difference between the calculated ^{14}N quadrupole coupling constants of the single molecule and of the molecular dimer plotted against R(N–H) in substituted imidazoles.

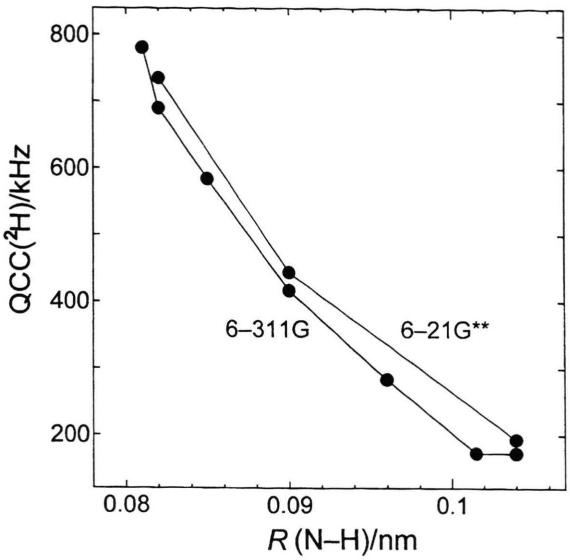

Fig. 4. Dependence of the calculated ^{2}H quadrupole coupling constant on R(N–H) in substituted imidazoles.

of these molecules. Therefore, it provides us with a way to extract the contribution of the hydrogen bond to QCC and η by taking the difference between these parameters of monomers and clusters.

Since the N–H bond distance, R(N–H), and the N–H···N distance, R(N···N), have been regarded as important quantities for evaluating the nature of the hydrogen bond of the N–H···N type and are usually considered to be a measure of the strength of the hydrogen bond [1, 37], we attempted to relate the QCC, η and some other properties with these interatomic distances. We found, however, that both the observed and calculated QCC and η do not have any systematic correlation with R(N···N) as well as R(N–H) distances. We also examined the existence of any correlation between a computed quantity, δ QCC = [QCC of monomer–QCC of dimer], which is expected to represent the extent of the effect of hydrogen bond, with the above distances; δ QCC has no significant correlation with R(N···N) but increases nearly linearly with increase in R(N–H), as shown in Figure 3. The variation of δ QCC with R(N–H) is reasonable, but it is interesting that δ QCC of nitrogens of both >N= and =N– have positive slopes and the slope for >N– is four times as large as that for =N–. This fact implies that the electronic state of >N– is more influenced by the formation of the hyrogen bond than that of =N–.

2) ^{2}H *Quadrupole Interaction*

As mentioned in the preceding section, the observed QCC's do not show any systematic trend with R(N···N) or R(N–H) as is usually expected [36]. In order to throw light on this point, we examined the observed [27] and the calculated QCC of ^{2}H in a similar way to the case of ^{14}N. The calculated QCC and η of ^{2}H in imidazole show similar dependences on the size of clusters to those for ^{14}N. The amount of decrease in the QCC on crystallization is 24%, which is comparable with that for the amino nitrogen. So we can understand that the hydrogen bonding affects significantly the ^{2}H quadrupole parameters in the N–H···N system.

The observed QCC and η of ^{2}H do not show any meaningful correlation with either R(N···N) or R(N–H), suggesting that it is impossible to extract experimentally the net contribution of hydrogen bonding to the QCC and η. On the other hand, the calculated QCC for single molecules increases by an unrealistically large amount with decrease in the R(N–H) distance, as is shown in Figure 4. It depends on R roughly as $1/R^3$(N–H) and is larger for the 6-21G* basis set than for 6-311G. Such an observation suggests that the electronic distribution at the amino nitrogen site contributes directly to the EFG at the deuterium site. We then examined the extent of the electronic wave functions of the 6-311G and 6-21G* basis

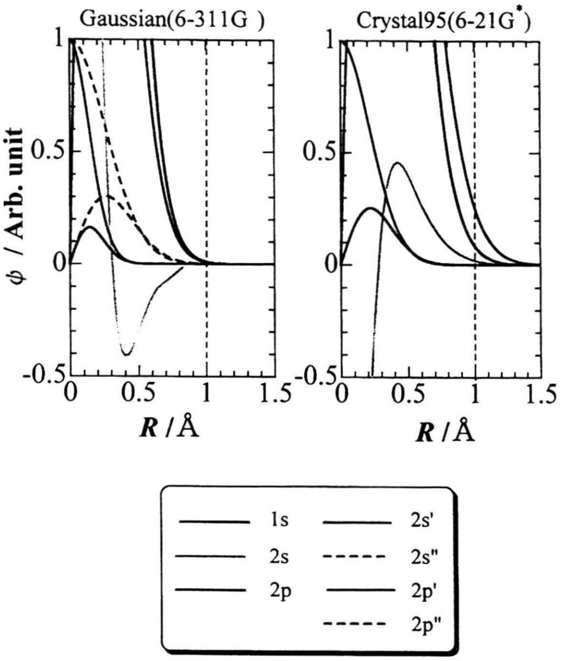

Fig. 5. Shape of the wave functions of the nitrogen atom adopted for the 6-311G and 6-21G basis sets.

sets. The results are shown in Figure 5. It can be seen that the deuteron is buried under the nitrogen molecular orbitals when R(N–H) is shorter than about 0.1 nm for the 6-311G basis set and 0.13 nm for 6-21G*. The reported R(N–H) ranges from 0.080 nm to 0.096 nm in 4-substituted imidazoles, and obviously the electrons in the nitrogen molecular orbitals contribute directly to the EFG at the deuterium site in each of these materials; hence the molecular orbital calculation does not apply to the EFG at the hydrogen of N–H group in the imidazole family.

It is interesting to see that the observed R(N–H) in 4-substituted imidazoles are very short compared with other compounds [37]. In order to examine the applicability of the *ab initio* molecular orbital calculation to such short bond lengths, we generated the optimized molecular structure of imidazole and 4-nitroimidazole by the use of the GAUSSIAN 94 program. The total molecular energies and the value of R(N–H) in each optimized molecule are listed in Table 1. We see that the optimized R(N–H) in imidazole, 0.099 nm, is shorter than the observed bond length in the crystalline state, implying that R(N–H) is reasonably lengthened when an intermolecular hydrogen bond is formed. On the other hand, the optimized R(N–H), 0.099 nm is significantly longer than the observed one, 0.093 nm or 0.082 nm in 4-nitroimidazole, which may not be interpreted as due to the hydrogen bond formation. A similar situation may happen in other 4-substituted imidazoles in which unusually short R(N–H)'s have been reported. Though we pointed out that our molecular orbital computation may not apply to the nuclear quadrupole interaction in the present materials, reexamination of the R(N–H) in them may also be required.

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