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AN ANALYSIS OF THE THROUGH-BOND INTERACTION USING THE LOCALIZED MOLECULAR ORBITALS WITH *AB INITIO* CALCULATIONS—II

LONE-PAIR ORBITAL ENERGIES IN BICYCLO COMPOUNDS: 7-AZABICYCLO[2.2.1]HEPTANE AND 2-AZABICYCLO[2.2.2]OCTANE, AND THEIR N-METHYL DERIVATIVES

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Abstract—*Ab initio* SCF MO calculations using STO-3G basis set were performed on 7-azabicyclo[2.2.1]heptane, N-methyl-7-azabicyclo[2.2.1]heptane, 2-azabicyclo[2.2.2]octane, N-methyl-2-azabicyclo[2.2.2]octane, and their model molecules. The orbital energies obtained by these calculations were compared with the experimental ionization potentials. The canonical MOs obtained for the model molecules were then transformed into the localized Mos. With the use of the localized MOs thus obtained, the lone-pair orbital energies were pursued in the light of the through-space and/or the through-bond interactions between thw specified localized MOs. As a result of this analysis, it was found that the effects of the inner shell orbitals, ls electrons of the N atom, and of the neighbouring N-C bonds of the skeleton (through-bond interaction) play a dominant role in the interaction with the lone-pair orbitals. It was also found that the effect of the N-Me group on the lone-pair orbital energy is considerably important.

The concept of the through-space and the through-bond interactions was first introduced by Hoffmann *et al.* to explain the energy levels of the lone-pair orbitals (LPOs).[1,2] This concept has been applied to many fields in chemistry. Heilbronner *et al.* developed a method for the quantitative calculation of the through-space and the through-bond interactions by using the symmetry adapted localized LMOs and applied to varieties of molecules.[3-10] We have previously developed a method[11] to evaluate semi-empirically the through-space and the through-bond interactions by using the LMOs and this procedure has been successfully applied to explain the long-range hyperfine spin coupling constants in alkyl radicals,[12,13] to explain LPO interactions in azines,[11,14] and to explain the long-range effect of the LPO to optical rotatory strength of the carbonyl $n \rightarrow \pi^*$ transition in ketopiperidines.[15] Very recently we have proposed a procedure to evaluate the through-space/bond interactions based on an *ab initio* calculation and applied to the analysis of the LPO interactions in hydrazines.[16]

In the present work, in order to extend the applicability of the previous procedure, we have applied the method to an analysis of the lone-pair orbital energy (LPOE) on the N atom in bicyclo compounds now of interest.

METHOD OF CALCULATION

The original canonical MOs were obtained from the ab initio SCF calculations. The basis set used was the STO-3G and the program GAUSSIAN 70[17] was used. The LMOs were obtained from the CMOs by the procedure of Edmiston-Ruedenberg.[18] In order to evaluate the various types of the through-space/bond interactions, the SCF calculations were carried out on the basis of the LMOs.

The detailed procedure of the analysis to estimate the effect of a particular through-bond or a through-space interaction has been described in the previous paper.[16] Therefore, the method is not reviewed in the present article.

Molecular geometries used for 7-azabicyclo[2.2.1]heptane (**1**) and N-methyl-7-azabicyclo[2.2.1]heptane (**2**) were those reported[19] except the N atom and the H atom or the Me group bonded to the nitrogen (Fig. 1.). The position of the N atom was determined so as to give the N-C bond lengths of 1.47 Å on condition that the other atoms in the bicyclo- part were fixed. As to the H atom or the Me group bonded to the N atom, the positions of the atoms were determined by using the N-C bond length of 1.47 Å, the C-H bond length of 1.09 Å, and the N-H bond length of 1.01 Å. Molecular geometries for 2-azabicyclo[2.2.2]octane (**3**) and N-methyl-2-azabicyclo[2.2.2]octane (**4**) (Fig. 1.) were also calculated in the similar manner as those of **1** and **2**, that is, the geometry for bicyclo[2.2.2]octane were determined by using all C-H bond lengths of 1.09 Å, all C-C bond lengths of 1.54 Å, and all bond angles of 109°28′. The modification by inclusion of the N atom were evaluated in the same manner as that in bicyclo[2.2.1]heptane. In the present work, **1**, **2**, **3** and **4** were treated. However, it takes a lot of computation times to obtain LMOs of these molecules in questions. Therefore, in order to analyze the through-space/bond interactions of these molecules, the model

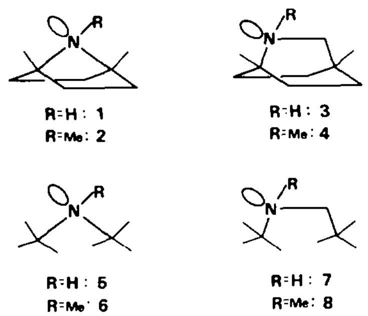

Fig. 1. Schematic structures of 7-azabicyclo[2.2.1]heptane (**1**), N-methyl-7-azabicyclo[2.2.1]heptane (**2**), 2-azabicyclo[2.2.2]-octane (**3**), and N-methyl-2-azabicyclo[2.2.2]octane (**4**), and their model molecules, **5**, **6**, **7** and **8**.

molecules as shown in Fig. 1 were treated for convenience sake. The geometries for the model molecules were assumed that the two hydrogens at the both-side Me groups are located on the C–C bonds of the parent molecules, and that the bond length of the C–H bond was appropriately assumed: r(C–H) = 1.09 Å.

RESULTS AND DISCUSSION

First of all, we discuss the validity of the model molecules taken up instead of the parent molecules. The orbital energies of the parent molecules and their model molecules are summarized in Table 1 together with the observed ionization potentials (IPs)[20] in relation to the LPO on the N atom. As we have no experimental data on the IPs of **1** and **2**, the observed values for 7-azabenzobibicyclo[2.2.1]heptane and its N-Me derivative were used for the comparison. From this, we can see that the calculated values correspond very well to those observed. To examine in more details, the relations of the observed IPs existing between **1** and **2**, and between **3** and **4** are well explained by the relations existing in the calculated LPOEs, that is, the molecule **1** has smaller IP than that of the molecule **2**, which corresponds to the values of the orbital energies concerned, and the same is true for the molecules **3** and **4**. Moreover the tendencies of the calculated LPOEs between **1** and **3**, and **2** and **4** also correspond with those of the observed IPs.

We then make comparison between the results of the parent molecules and the model molecules. The tendencies of the calculated LPOEs in the parent molecules are well reproduced by those in the model molecules. The fact that the ionization energies of the parent molecules become smaller by the methylation is also reproduced reasonably by those of the model molecules.

From these results, the model molecules now considered are suitable to analyze the orbital interactions of the parent molecules. Therefore, hereafter the analyses of the through-space/bond interactions in relation to the parent molecules were made on the basis of the LMOs of these model molecules.

Model molecules 5 *and* 6

Figures 2 and 3 show the typical interaction diagrams for **5** and **6**. The orbital energies and the difference are summarized in Table 2. First we analyze the model molecule **5** by using Fig. 2. The LPOE is raised up

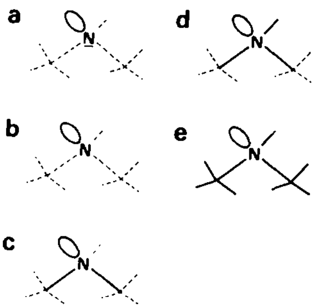

Fig. 2. Typical LPO interaction diagrams for **5**. Broad line part shows the interaction allowed part. $\underline{\mathrm{N}}$: ls electrons of N atom are not included in the interaction, and $\overline{\mathrm{N}}$: they are included **a**: LPO is cut off from all type of interaction, **b**: interaction between the LPO and ls electrons of the N atom alone is allowed, **c**: in addition to the diagram **b**, the neighbouring N–C bonds are included in the interaction, **d**: in addition to the diagram **c**, the N-H bond is included in the interaction, **e**: full interaction case.

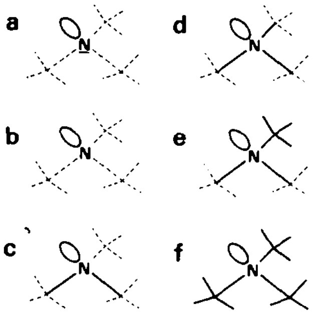

Fig. 3. Typical interaction diagrams for **6**. Notations: see Fig. 2. **a**, **b**, **c**: see **a**, **b**, **c** of Fig. 2. **d**: in addition to the diagram **c**, the N–C bond in the N-methyl group is included in the interaction, **e**: in addition to the diagram **d**, the C-H bonds in the N-methyl group are included in the interaction **f**: see **e** of Fig. 2.

Table 1. Calculated LPOEs (a.u.) and observed IPs (a.u.) in **1**, **2**, **3** and **4**, and in their model molecules, **5**, **6**, **7** and **8**

	LPOE	IP[a]		LPOE
1	-0.286	-0.310	**5**	-0.291
2	-0.274	-0.306	**6**	-0.281
3	-0.274	-0.302	**7**	-0.284
4	-0.263	-0.286	**8**	-0.271

[a] From Ref. 20.

considerably by interacting with ls electrons of the N atom (**b**) and with the neighbouring N–C bonds (**c**) as shown in Table 2. These are the through-bond interactions. The importance of the ls electrons in the N atom had been already discussed in relation to the interaction with LPO previously.[16] The LPOE is also raised up by the interaction with the methyl groups in the both-side, which correspond to the bridgehead parts of the parent molecules (**e**). This change includes both the through-space and the through-bond interactions.

The N-Me species is then discussed using Fig. 3. In this species also the LPOE is raised upward considerably by interacting with the ls electrons of the N atom (**b**) and with the neighbouring N–C bonds (**c**). Next largest contribution is the interaction with the Me groups in the both-side (**f**). The interaction with the N-Me group (**e**) is also remarkably large and plays an important role for the determination of the relative heights of the LPOEs in the series of the molecules **5**–**8**.

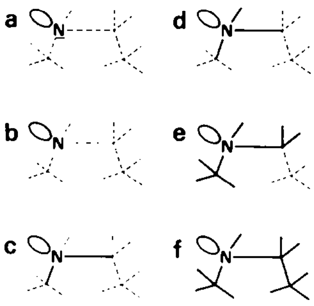

Fig. 4. Typical interaction diagrams for **7**. Notations: see Fig. 2. **a**, **b**, **c**, **d**: see **a**, **b**, **c**, **d** of Fig. 2, **e**: in addition to the diagram **d**, the C–H bonds of the methylene group as well as the methyl group of the left-hand side are included in the interaction, **f**: see **e** of Fig. 2.

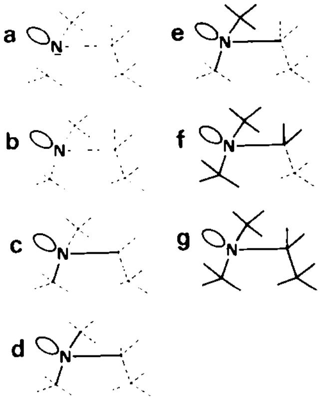

Fig. 5. Typical interaction diagrams for **8**. Notations: see Fig. 2. **a**, **b**, **c**: see **a**, **b**, **c** of Fig. 2. **d**, **e**: see **d**, **e** of Fig. 3. **f**: see **e** of Fig. 4. **g**: see **e** of Fig. 2.

Model molecules **7** *and* **8**

Figures 4 and 5 show the typical interaction diagrams for the model molecules **7** and **8**. In these species, the variation in the LPOE is fairly large by the interactions with ls electrons of the N atom and with the neighbouring N–C bonds (**b** and **c** of Figs. 4 and 5). The same was also shown in The case of **5** and **6**. However the interactions with the N–H group (**d**) are not so large (Fig. 4).

The interaction with both the neighbouring Me and methylene groups is considerably large, which corresponds well with the cases of **5** and **6** (**e** in **5** and **7**. **f** in **6** and **8**). The neighbouring Me group corresponds to the bridgehead part of the parent molecules. The effect of the N-Me group in **8** is quite similar to that in **6**, that is, the LPOE is raised up considerably by the presence of the N-Me group.

GENERAL DISCUSSION

Effect of ls electrons

Let us examine again the diagrams **a** of Fig. 2–5 (Table 2). Here we examine the magnitude of the coefficient of the N inner shell ls atomic orbital in the localized LPO on the N, since the mixing of the ls atomic orbital is expected to give the remarkable effect to the LPOE. The values of the coefficients for **5**, **6**, **7** and **8** are −0.070, −0.071, −0.067 and −0.068, respectively. The LPOE of **a** in **5**, **6**, **7** and **8** are −0.527, −0.536, −0.521 and

Table 2 The changes in the LPOEs (a.u.) by various types of interactions in the model molecules, **5**, **6**, **7** and **8**

	5		**6**		**7**		**8**	
a	LPOE	Δ[b]	LPOE	Δ	LPOE	Δ	LPOE	Δ
a	-0.527	0.	-0.536	0.	-0.521	0.	-0.529	0.
b	-0.430	0.097	-0.438	0.098	-0.431	0.090	-0.437	0.092
c	-0.356	*0.074* 0.171	-0.362	*0.076* 0.174	-0.353	*0.078* 0.168	-0.357	*0.080* 0.172
d	-0.342	*0.014* 0.185	-0.349	*0.013* 0.187	-0.343	*0.010* 0.178	-0.347	*0.010* 0.182
e	-0.291	*0.051* 0.236	-0.320	*0.029* 0.216	-0.294	*0.049* 0.227	-0.317	*0.030* 0.212
f			-0.281	*0.039* 0.255	-0.284	*0.010* 0.237	-0.281	*0.036* 0.248
g							-0.271	*0.010* 0.258

[a] See also Figs. 2 - 5. [b] Difference: figures in italics show the difference between a certain diagram and a neibouring upper diagram to know easily a definite interaction effect, and figures in roman show the difference between a certain diagram and the diagram **a**.

−0.529 (a.u.). There is a clear parallelism between the coefficients of the ls atomic orbital and the LPOE. In comparison of **5** with **7**, the effect of the interaction with ls electrons on the LPO of the N atom is in proportion to the magnitude of the total interactions (see **a** and **e** in **5**, and **a** and **f** in **7** in Table 2). The same is true for **6** and **8**. However, the presence of the N-Me group reverses the order between **5** and **6** and between **7** and **8**. That is, the molecule **6** with the N-Me group has lower LPOE in **a** than the molecule **5** without the N-Me group, while **6** has higher LPOE in **f** than **5** has in **e**. The same situation is found for **7** and **8**. This result should be noteworthy.

Through-bond interaction.

Next we examine the diagrams **b** of Fig. 2–5. In these diagrams, the interaction between the localized LPO and the localized N inner shell ls orbital is allowed. The LPOEs in **5** and **7** are nearly equal after this interaction, and the LPOEs in **6** and **8** are also nearly equal with each other. Accordingly, the difference between **5** and **7** (or **6** and **8**) in the geometry around the N atom gives quite small effect to the LPOE; in other words, the strain in the ring part of the molecules gives little difference in the LPOE. The LPOE of the N-Me species (**6** and **8**) is smaller than the others (**5** and **7**).

By using the diagrams **c** and **d** of Figs. 2–5, we explain the effect of the N–C, and N–C and N–H bonds. From these diagrams we can deduce that the effects in relation to these bonds are not so different in each model molecules.

Combinative effect of the through-space and through-bond interactions.

Next we discuss the effects of the N-Me group using diagrams **d** (**5** and **7**) and **e** (**6** and **8**) of Figs. 2–5. The effect of the N-Me group on the LPOE is fairly large as was already shown in the preceding section in the present paper. By this effect the order of the LPOE is reversed between **d** and **e** in both species. Accordingly, the relative height of the LPOE for **5** and **6** was determined by the presence of the N-Me group primarily, and this conclusion is true for the LPOE of **7** and **8**.

We disucss the effect of the remote Me group in the ethyl group of **7** and **8**, which corresponds to the remote bridgehead part of the parent molecules. The molecules **5** and **6** lack in this Me group. In Table 2, the LPOE of **e** in **5** (−0.291 a.u.) is nearly equal to that of **e** in **7** (−0.294 a.u.) and the LPOE of **f** in **6** (−0.281 a.u.) is nearly equal to that of **f** in **8** (−0.281 a.u.). From this result, we can expect that without the remote Me group, the LPOE of **5** should be nearly equal to the LPOE of **7**, and the LPOE of **6** to the LPOE of **8**; in other words, it is the remote Me group that is responsible for the difference in the LPOE between **5** and **7**, and also between **6** and **8**.

In conclusion, the LPOE, i.e. the IPs of **1**, **2**, **3**, **4**, and their model molecules are governed largely by the interaction with the (i) ls electrons of the N atom and (ii) the neighbouring N–C skeletal bonds. The other effect is governed by the rest of the bicyclo part. The differences in the LPOE between **5** and **6**, and between **7** and **8** are found to be attributed to the effect of the N-Me group, while the differences in the LPOE between **5** and **7**, and between **6** and **8** are reasonably explained by the contribution of the remote Me group, which corresponds to the remote bridgehead of the bicyclo part. Moreover it is recognized that to the analysis of the LPOE of the fairly complicated molecules under study, the analysis on the appropriate model molecules is very useful, convenient, and indispensible.

The present procedure will also be used for the analysis of the other chemical phenomena.

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