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# AN ANALYSIS OF THE THROUGH BOND INTERACTION USING THE LOCALISED MOLECULAR ORBITALS—III

## LONG RANGE EFFECT OF LONE PAIR ORBITAL TO THE OPTICAL ROTATORY STRENGTH OF THE CARBONYL n–$\pi^*$ TRANSITION IN 3-KETOPIPERIDINES

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**Abstract**—The optical rotatory strengths of the carbonyl n–$\pi^*$ transitions of (1*R*)-3-ketopiperidine and (1*S*)-3-ketopiperidine were subjected to the analysis in terms of the through-space and the through-bond interactions according to the procedure using localised molecular orbitals we proposed in the preceding papers. As a result of the present analysis, the optical rotatory strengths of the molecules were found to be influenced by the direction of the remote nitrogen lone pair orbital. This influence was found to be illustrated by the coupling between the CO group and the nitrogen lone pair orbital as well as the N–H bond localized orbital via a path containing the through-bond and the through-space interactions. That is, the positive coupling and the negative coupling paths were determined by the present analysis and the sign of the optical rotatory strength was found to correspond to the sum of the contributions of both coupling paths.

THEORETICAL and experimental data on optical rotatory strengths of organic and inorganic molecules have accumulated. Rotatory strengths of the CO n–$\pi^*$ transition have been extensively studied in relation to the octant rule.[1–8] Many efforts have been made to illustrate the observed rotatory strength in terms of structural factors of the molecule by theoretical analysis with various molecular orbital methods.[5–8] One of the present authors also attempted the theoretical analysis of the rotatory strength in terms of the contributions from molecular fragments.[5] In this study, it was found that the direction of the remote lone pair orbital on the N atom in 3-ketopiperidine determines the sign of the rotatory strengths of the CO n–$\pi^*$ transition of the molecule: that is, (1*R*)-3-ketopiperidine having the nitrogen lone pair orbital in the equatorial direction (Fig. 1) has negative rotatory strength while (1*S*)-3-ketopiperidine having the nitrogen lone pair orbital in the axial direction (Fig. 1) has positive rotatory strength. It was found that the signs of the rotatory strength was determined by the interaction between the CO lone pair orbital and the N lone pair orbital from the analysis of the calculated rotatory strengths. However, the detailed analysis for the interaction has not been carried out.

Recently, we proposed the method which analyses the through-space and the through-bond interactions[9,10] by using localised molecular orbitals.[11–13] This method has been applied to the interaction between two nitrogen lone pair orbitals in azines[11,13] and to the long range hyperfine coupling in bicycloalkyl radicals.[12] From these studies, the interaction or the coupling was divided into the contribution of individual through-bond and through-space interactions. In the calculation of the rotatory strength, this method should shed light on the detailed mechanism of the interaction between the chromophore and the other parts of the molecule. The important role of the through-bond and the through-space interactions for the optical rotatory strength has already been pointed out although methods for the numerical evaluations of these interactions have not been established.[7,8] Recently, a perturbational approach to this problem was published to interpret the octant rule in terms of the through-bond and the through-space interactions by using relevant molecular orbitals.[8]

In the present paper, we applied the above-mentioned method[11–13] to the rotatory strengths of (1*S*)- and (1*R*)-3-ketopiperidine in order to see the reason why the direction of the remote nitrogen lone pair orbital controls the signs of the rotatory strengths of the CO n–$\pi^*$ transition. As a result of the analysis, the specific through-space and the through-bond interactions were found to be responsible for the sign of the rotatory strength.

### METHOD OF ANALYSIS

The reduced rotatory strength $[R_{i\rightarrow j}]$ was calculated by using the equation:[4]

$$[R_{i\rightarrow j}] = -7313 < \psi_i|\nabla|\psi_j > \cdot < \psi_j|r \times \nabla|\psi_i > /\Delta E_{ji} \tag{1}$$

where $\psi_i$ is the ith molecular orbital and $\Delta E_{ji}$ the transition energy from the ith to the jth molecular orbitals.

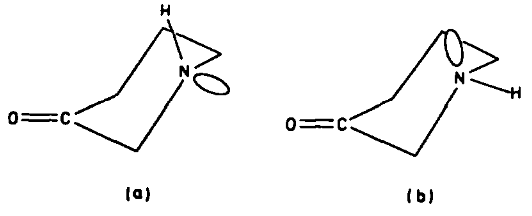


Fig. 1. Molecular structures of 3-ketopiperidines: (a) (1R)-3-ketopiperidine (axial form); (b) (1S)-3-ketopiperidine (equatorial form).

Although eqn (1) is obtained by using single Slater determinant without configuration interactions, the rotatory strength by eqn (1) is fairly reliable as far as qualitative predictions such as signs of the rotatory strength are concerned. When we need quantitative predictions, the treatment with configuration interactions should be indispensable. The extension of eqn (1) for the calculation with configuration interactions is straightforward. In eqn (1), the matrix element of the gradient operator ($\nabla$) was calculated in units of Å, and the transition energy in units of eV. The molecular orbitals $\psi_k$, $\psi_l$ in the equation were obtained by the CNDO/2 method;[14,15] these molecular orbitals gave good results for the calculation of the rotatory strength of 3-ketopiperidines.[5]

For the analysis of the rotatory strength, the concepts of the through-space and the through-bond interactions should be very fruitful because the theoretically calculated value should be related to the molecular structures in terms of the through-space and the through-bond interactions. As to the through-space interaction, the magnitude of the interaction has been evaluated by the calculations after zero is set to the relevant core resonance integrals or the relevant Fock matrix elements. However, the through-bond interaction can not be evaluated directly, and the difference between total energies with and without the through-space interaction has been assigned to the through-bond interaction. In the preceding series of papers,[11,13] we proposed a method to evaluate directly the through-bond interaction by using the localised molecular orbitals as is mentioned in the previous section. In the present article, this method is applied to the analysis of the optical rotatory strength of the n-$\pi^*$ transition in 3-ketopiperidines.

The method for the analysis has been described[11] so that we briefly illustrate the method in the following. The occupied molecular orbitals are transformed into localised molecular orbitals according to the procedure by Edmiston–Ruedenberg.[16] By using localised molecular orbitals thus obtained, we can represent a core resonance integral between atomic orbitals, $\chi_r$ and $\chi_s$, as the summation of the core resonance integrals between localised molecular orbitals, $\psi_k^{(L)}$ and $\psi_l^{(L)}$,

$$I_{rs}^0 = \sum_k \sum_l C_{kr} C_{ls} I_{kl}^{0(L)} \tag{2}$$

where $I_{rs}^0$ and $I_{kl}^{0(L)}$ are the core resonance integral between the atomic orbitals, $\chi_r$ and $\chi_s$, and that between localised molecular orbitals, $\psi_k^{(L)}$ and $\psi_l^{(L)}$, respectively. $C_{kr}$ is the coefficient of the atomic orbital $\chi_r$ in the k th localised molecular orbital. Making use of eqn (2), we can evaluate the through-space and the through-bond interaction energies. A procedure for the analysis is dropping the interactions between specified localised molecular orbitals. In order to drop the interactions, the core resonance integral between atomic orbitals should be modified as given by eqn (3).

$$I_{rs} = I_{rs}^0 - \sum_{(k_1-l_1)} (C_{k_1r} C_{l_1s} + C_{k_1s} C_{l_1r})\, I_{k_1l_1}^{0(L)} \tag{3}$$

where $(k_1 - l_1)$ means that the summation should cover over only definite pairs of specified localised molecular orbitals ($k_1$ and $l_1$) and $I_{rs}^0$ is an unmodified core resonance integral given by eqn (2) and $I_{rs}$ is a modified one. It is easily proved that the core resonance integrals between atomic orbitals, $I_{rs}$, by eqn (3) gives zero for the core resonance integrals between specified localised molecular orbitals, $I_{k_1l_1}^{(L)}$, and the correct values for the others. That is,

$$\begin{aligned}
I_{kl}^{(L)} &= \sum_r \sum_s C_{kr} C_{ls} I_{rs} = \sum_r \sum_s C_{kr} C_{ls} \\
&\quad \times \Big(I_{rs}^0 - \sum_{(k_1-l_1)} (C_{k_1r} C_{l_1s} + C_{k_1s} C_{l_1r})\, I_{k_1l_1}^{0(L)}\Big) \\
&= I_{kl}^{0(L)} - \sum_{(k_1-l_1)} I_{k_1l_1}^{0(L)} \Big(\sum_r C_{kr} C_{k_1r}\Big)\Big(\sum_s C_{ls} C_{l_1s}\Big) \\
&\quad - \sum_{(k_1-l_1)} I_{k_1l_1}^{0(L)} \Big(\sum_r C_{kr} C_{l_1r}\Big)\Big(\sum_s C_{ls} C_{k_1s}\Big) \\
&= I_{kl}^{0(L)} - \sum_{(k_1-l_1)} I_{k_1l_1}^{0(L)} (\delta_{kk_1}\delta_{ll_1} + \delta_{kl_1}\delta_{lk_1}) \\
&= \begin{cases} 0 & (k = k_1, l = l_1) \text{ or } (k = l_1, l = k_1) \\ I_{kl}^{0(L)} & (\text{Otherwise}) \end{cases}
\end{aligned} \tag{4}$$

Consequently, when the localised molecular orbitals, $\psi_k^{(L)}$ and $\psi_l^{(L)}$, which specified the bonds k and l, are picked up in eqn (3) for example, the core resonance integral between $\psi_k^{(L)}$ and $\psi_l^{(L)}$ should be cut off, that is, the through-bond interaction between $\psi_k^{(L)}$ and $\psi_l^{(L)}$ can be considered to be cut off. Thus, the SCF calculations by using the core resonance integrals in eqn (3) give the molecular orbitals without the relevant through-bond interaction.

In the previous paragraph, the through-bond or the through-space interaction is obtained by dropping the relevant core resonance integrals. Another approach to the analysis is the SCF calculations involving the specific through-bond or the through-space interaction. In this case, first, the molecular orbital calculations should be carried out after dropping the core resonance integrals between two parts of the molecule, so that the molecular orbitals have to be localised in a part of the molecule. In other words, the molecular orbitals should be classified into two groups. In the case of 3-ketopiperidine, for example, the pure CO $\pi$ and $\pi^*$ molecular orbitals are separated from other $\sigma$ orbitals by the SCF calculations with dropping the core resonance integrals between $2p\pi$ atomic orbitals on CO group and other atomic orbitals on the piperdine moiety as shown in Fig. 2. Next, the canonical molecular orbitals are transformed into localised molecular orbitals for each group. By using the localised molecular orbitals, the specified through-bond or the through-space interaction can be evaluated; that is, the specified through-bond or the through-space interaction can be obtained by the SCF calculations using

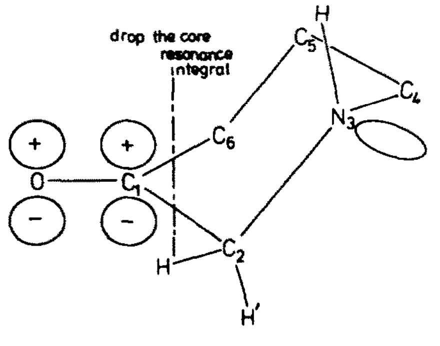


Fig. 2. The numbering of atoms in the molecule.

Table 1. Observed and calculated optical rotatory strengths of 3-ketopiperidine

| Molecule | Rotatory strength | |
|---|---|---|
| | Calcd[a] | Obsd[b] |
| 1(a)-Ketopiperidine | -42.9<br>(-171.5) | -11.2 |
| 1(e)-Ketopiperidine | 16.6<br>(66.3) | 8.9 |

[a] The value divided by the excitation energy (4.0 eV). The undivided value is given in parentheses for comparison with those in Tables 2-4.

[b] From reference 5.

the modified core resonance integrals between the atomic orbitals, $I_{rs}$, given by eqn (5).

$$I_{rs} = \sum_{(k_l - l_l)} C_{k_l r} C_{l_l s} I^{0(L)}_{k_l l_l} \tag{5}$$

where the meanings of the notations in eqn (5) are the same as those in eqn (3). It is easily proved in a similar manner as in eqn (4) that eqn (5) gives the correct value for the core resonance integrals between the specified localised molecular orbitals and zero for other core resonance integrals. In eqn (5), when $k_l$ designates CO $\pi$ molecular orbitals, and $l_l$ $\sigma$ orbital localised in a specified bond in piperidine moiety, the SCF calculations give the through-space interaction between CO $\pi$ group and $\sigma$ specified bond.

In the following section, the rotatory strength of the CO n–$\pi^*$ transition in 3-ketopiperidines was subjected to the analysis in terms of the through-space and the through-bond interactions by combinations of the SCF calculations using the core resonance integrals given by eqn (3) (cutting off the interaction) and by eqn (5) (inclusion of the interaction).

## RESULTS AND DISCUSSION

In the present article, the CO n-$\pi^*$ transition was studied for (1*R*)-3-ketopiperidine (axial form) and (1*S*)-3-ketopiperidine (equatorial form). Subsequently, these molecules are referred to as 1(a)- and 1(e)-ketopiperidines in the present paper. The structures of these molecules are shown in Fig. 1. 1(a)-Ketopiperidine has a nitrogen lone pair orbital in the equatorial direction, while 1(e)-ketopiperidine has one in the axial direction. As described in the previous section, this difference in the direction of the remote nitrogen lone pair orbitals leads to the difference in sign of the optical rotatory strength. The observed and the calculated rotatory strengths are given in Table 1 indicating that theoretical prediction in sign of the optical rotatory strength is in good agreement with experimental data, which was already published in our previous paper.[5]

***The through-space interaction between carbonyl $\pi$ group and the piperidine moiety.*** First of all, the carbonyl $\pi$ orbitals were separated from the remaining $\sigma$ type orbitals by the SCF calculations with dropping the core resonance integrals between CO $\pi$ atomic orbitals and the atomic orbitals on the piperidine moiety as shown in Fig. 2. By using molecular orbitals thus obtained, the rotatory strengths for the CO n–$\pi^*$ transition were calculated and listed in the 3rd line of Table 2. The values in the Table are the scalar products of the vectors corresponding to the gradient and the magnetic moment operator, multiplied by the appropriate coefficient appearing in eqn (1), without dividing by the n–$\pi^*$ transition energy. Therefore, the reduced rotatory strength can be obtained from the values in the Table after dividing by the transition energy ($\simeq$ 4 eV). For relative comparison of reduced rotatory strengths, values obtained wothout being divided by the transition energy can be used with ease and hence will be listed in the Tables, unless otherwise stated. From the values in the 3rd line of Table 2, it is obvious that 1(e)-ketopiperidine has a positive rotatory strength while 1(a)-ketopiperidine has negative one without interactions between $\sigma$ molecular orbitals and CO $\pi$ orbitals. In the same Table, the rotatory strengths by canonical molecular orbitals are listed in the 1st line. Comparing the values in the 3rd line with those in the 1st line, we can say that the signs of the rotatory strengths in both calculations agree with each other but the absolute magnitudes don't. Consequently, dropping of the core resonance integrals between CO $\pi$ atomic orbitals and the remaining atomic orbital of

Table 2. Calculated optical rotatory strengths of 3-ketopiperidines with various types of localized molecular orbitals

| | Equatorial[a] | Axial[a] |
|---|---|---|
| Calculations with canonical molecular orbitals | 62.75 | -171.25 |
| Calculations with oxygen localized molecular orbitals | -9.40 | -13.11 |
| Calculations with dropping the interaction between $\sigma$ and carbonyl $\pi$ orbitals | 38.45 | -25.31 |

[a] The value of the numerator in Eq. 1.

piperidine moiety leads to the small difference in the rotatory strengths between two molecules in question. In other words, the through-space interaction between CO $\pi$ orbitals and piperidine $\sigma$ type orbitals should be responsible for the remarkable difference in the optical rotatory strength.

Next, the $\sigma$ type molecular orbitals from the SCF calculations with dropping the above-mentioned core resonance integrals were transformed into localised molecular orbitals. These orbitals are localised in the specified bonds, the nitrogen lone pair and the oxygen lone pair. The optical rotatory strengths were calculated for the transition in which the excitation occurs from the above-mentioned oxygen lone pair orbital to CO $\pi^*$ orbital, namely, pure $n$–$\pi^*$ transition. The values are collected in the 2nd line of Table 2, indicating that two molecules have nearly equal optical rotatory strength as is expected from the nature of so-called pure $n$–$\pi^*$ transition.

We are now in a position to study what types of interactions between a CO $\pi$ part and piperidine moiety are responsible for the difference in the optical rotatory strength by the change in the direction of the nitrogen lone pair orbital. By using the $\sigma$ type localised orbitals and eqn (5), we can evaluate any specific through-space interactions between the CO $\pi$ group and any specific bonds or the lone pair in the piperidine moiety. First of all, the direct through-space interaction between the CO $\pi$ orbitals and the nitrogen lone pair orbitals was included in the calculations. The result is given in the 2nd line of Table 3, indicating that the contribution of this direct through-space interaction to the rotatory strength is relatively small and hence this interaction is not responsible for the difference in the rotatory strength between two molecules. Next, the rotatory strengths were calculated with the direct through-space interactions between the CO $\pi$ orbitals and the $N_3$–H bond localised orbitals. The values are shown in the 3rd line of Table 3, indicating that this through-space interaction contributes only partially to the difference in the rotatory strength. From these results, it should be the indirect interactions between the CO $\pi$ orbitals and the nitrogen lone pair or the $N_3$–H bond localised orbitals that is responsible for the difference in the optical rotatory strength in both molecules. Accordingly, our attention was drawn to the indirect interaction between the CO $\pi$ group and nitrogen lone pair or $N_3$–H bond. In the 4th line in Table 3, the rotatory strength is given in the case that the through-space interaction between the CO $\pi$ orbitals and the $C_2$–$N_3$ bond localised orbital is involved. It should be noteworthy that the above-mentioned through-space interaction gives the very large difference in the rotatory strength between both molecules, and that the calculated rotatory strengths are very close near in the absolute magnitude to the values calculated by using canonical molecular orbitals and listed in the 1st line of Table 3. This result is particularly surprising in view of the fact that it is not the nitrogen lone pair orbital or the $N_3$–H bond localised orbital but the $C_2$–$N_3$ bond localised orbital that results in the large difference in the rotatory strength, since the geometrical situations of $C_2$–$N_3$ bond in both molecules are quite similar and the nitrogen lone pair and $N_3$–H bond in both molecules have very different steric situations. In the same Table, the rotatory strengths given in the last line were calculated with the through-space interaction between the $C_2$–$N_3$ as well as the $C_5$–$C_6$ bond localised orbitals. It is obvious from these values that the above-mentioned through-space interactions give the values for the rotatory strength which are nearly equal to those obtained by using canonical molecular orbitals, that is, the above-mentioned interactions determine the signs and the magnitudes of the optical rotatory strengths of 1(a)- and 1(e)-ketopiperidines. The next problem is how the nitrogen lone pair orbital or the $N_3$–H bond localized orbital is concerned with the difference in the rotatory strength. For this purpose, the through-bond or the through-space interaction which is followed by the above-mentioned through-space interaction should be subjected to analysis.

*The through-bond and/or the through-space interactions concerning the nitrogen atom.* The interactions via the nitrogen lone pair orbital and/or the $N_3$–H bond localised orbital should be analysed in order to understand the mechanism of the remote interaction in the $n$–$\pi^*$ transition between the CO group and the remote N

Table 3. Calculated optical rotatory strengths of 3-ketopiperidines including various types of the through-space interactions

| Type of interaction[b,c] | Equatorial[a] | Axial[a] |
|---|---|---|
| Calculations with canonical MO | 62.75 | -171.25 |
| Calculations including the interaction between $\pi$ MOs and the nitrogen LP | -17.73 | -51.77 |
| Calculations including the interaction between $\pi$ MOs and $N_3$-H bond LMO | 12.30 | -69.12 |
| Calculations including the interaction between $\pi$ MOs and $C_2$-$N_3$ bond LMO | 50.81 | -119.69 |
| Calculations including the interaction between $\pi$ MOs and $C_2$-$N_3$ as well as $C_5$-$C_6$ bond LMOs | 67.40 | -157.21 |

[a] The value of the numerator in Eq. 1.

[b] The following abbreviations are used : MO...Molecular orbital, LP...Lone pair, LMO...Localised molecular orbital.

[c] For the $N_3$-H, $C_2$-$N_3$ and $C_5$-$C_6$ bonds, see Fig. 2.

atom. The interactions between the CO $\pi$ orbital and the $C_2$–$N_3$ bond as well as $C_5$–$C_6$ bond localised orbitals play an essential role in the determination of the rotatory strength. Therefore, the CO $\pi$ molecular orbitals were allowed to interact with all other parts of the molecules, and the specific through-bond and/or the specific through-space interactions were cut off by means of eqn (3) using canonical molecular orbitals. It should be noticed that the canonical molecular orbitals are the molecular orbitals obtained in the condition that the CO $\pi$ molecular orbitals were allowed to interact with all other parts of the molecules.

First of all, in 1(a)- and 1(e)-ketopiperidines the nitrogen lone pair orbital as well as the $N_3$–H bond localised orbital were cut off from the remaining part of the molecules and the rotatory strengths were calculated. These values are shown in the 2nd line of Table 4, indicating that two molecules have nearly equal values of rotatory strengths. This result is to be expected since the remaining part of two molecules are identical. Next, as the $C_2$–$N_3$ bond localised orbital was known to play an important role, the interaction only between the nitrogen lone pair orbital and the $C_2$–$N_3$ bond localised orbital was allowed to calculate the rotatory strength. The result is shown in the 3rd line of Table 4, indicating the increases for both molecules, so that this type of interaction can not explain the difference in the rotatory strength. Consequently, the coupling of two types of interactions were taken into account, that is, the nitrogen lone pair orbital interacted with the $C_2$–$N_3$ bond localised orbital as well as with the $C_2$–$C_1$ bond, $C_2$–H bond, and $C_2$–H′ bond localised orbitals. The former is the through-bond interaction, while the latter the through-space interactions. With these interactions, the rotatory strengths were calculated. The result shows in the 4th line of Table 4, that these interactions increase the rotatory strength in 1(e)-ketopiperidine, and decrease the rotatory strength in 1(a)-ketopiperidine.

In the preceding paragraph, the interactions including the nitrogen lone pair orbital were subjected to analysis. Next, we will analyse in the same manner the interactions including the $N_3$–H bond localized orbital. When the $N_3$–H bond localised orbital interacts with the $C_2$–$N_3$ bond localised orbital, the rotatory strengths have similar characteristics as in the case of the interaction with the nitrogen lone pair orbital (5th line of Table 4), that is, the above-mentioned interaction increases the rotatory strength although the absolute values of increment are not as large as those in the case of the lone pair orbital. It should be stressed that the increment in 1(e)-ketopiperidine is larger than that in 1(a)-ketopiperidine. This corresponds with the result concerning the nitrogen lone pair orbital which indicates that the rotatory strength in 1(a)-ketopiperidine is larger than that in 1(e)-ketopiperidine, since the former has the lone pair orbital in the equatorial direction and the latter has one in the axial direction.

Next, the $N_3$–H bond localised orbital were allowed to interact with the $C_2$–$N_3$ bond, the $C_1$–$C_2$ bond, the $C_2$–H bond, and the $C_2$–H′ bond localised orbitals. This type of the coupling of the interactions is the same as that considered for the nitrogen lone pair orbital. The rotatory strengths with these interactions are indicated in the 6th line of Table 4. From the results it is obvious that the coupling of the interactions increases the rotatory strength in 1(a)-ketopiperidine and decreases in 1(e)-ketopiperidine. This tendency for the change of the rotatory strength is also in accordance with that shown in the 4th line of Table 4, that is, the $N_3$–H bond localised orbital in the axial direction behaves in a similar manner as the nitrogen lone pair orbital in the axial direction and, this is also true for the $N_3$–H bond localised orbital in the equatorial direction. The absolute magnitudes in the change of the rotatory strength for the $N_3$–H bond localised orbital (the 6th line of Table 4) is considerably smaller than those for the nitrogen lone pair orbital (the 4th line of Table 4). This result also corresponds with the values shown in the 3rd and the 5th lines of Table 4.

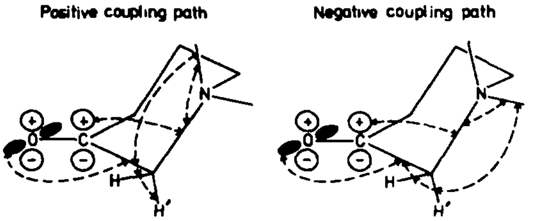
Table 4. Calculated optical rotatory strengths of 3-ketopiperidines cutting off the various types of the through-bond and or the through-space interactions

| Type of interaction included[b,c] | Equatorial[a] | Axial[a] |
|---|---|---|
| Calculations with canonical MO | 62.75 | -171.25 |
| Calculations cutting off the interactions between $[N_{LP}, N_3H]$ and all other parts of the molecule | 290.05 | 291.44 |
| Calculations including only the interaction between $N_{LP}$ and $(C_2-N_3)$ | 396.84 | 512.44 |
| Calculations including only the interaction between $N_{LP}$ and $[(C_2-N_3), (C_1-C_2), (C_2-H), (C_2-H')]$ | 500.05 | -266.60 |
| Calculations including only the interaction between $N_3H$ and $(C_2-N_3)$ | 369.86 | 340.82 |
| Calculations including only the interaction between $N_3H$ and $[(C_2-N_3), (C_1-C_2), (C_2-H), (C_2-H')]$ | -19.13 | 429.80 |
| Sum of the contributions of $N_{LP}$ and $N_3$-H LMOs | 190.87 | -128.24 |

[a] The value of the numerator in Eq. 1.

[b] The following abbreviations are used(see Fig. 2) : $N_{LP}$...nitrogen lone pair orbital, $N_3H$...$N_3$-H bond LMO, $(C_2-N_3)$...$C_2-N_3$ bond LMO, etc.

[c] $[N_{LP}, N_3H]$ means the group consisting of $N_{LP}$ and $N_3H$.


Positive coupling path

Negative coupling path

Fig. 3. Schematic diagrams for the positive and the negative coupling paths. The broken lines with arrows show the interaction between the localised molecular orbitals.

In the last line of Table 4, the sum of the contributions of the nitrogen lone pair orbital and the $N_3$–H bond localised orbital to the rotatory strength is listed. For example of 1(e)-ketopiperidine, the expected value for the rotatory strength, 190.87, is obtained by the following calculation:

$$290.05 + (500.05 - 290.05) + (-19.13 - 290.05) = 190.87$$

where 290.05 can be considered to be the standard value without the interactions. From the values in the last line of Table 4, the coupling of the interactions stated-above can explain why 1(e)-ketopiperidine has a positive rotatory strength and 1(a)-ketopiperidine has a negative one for the CO $n$–$\pi^*$ transition, although the absolute magnitudes in the last line of Table 4 are different from the values obtained by using canonical molecular orbitals (1st line of Table 4). In other words, the most important type of the through-space and/or the through-bond interactions which are responsible for the determination of the signs of the rotatory strength could be clarified by the present procedure of the analysis.

*Coupling paths in ketopiperidines.* When we summarized the result of the analysis, we could depict the coupling paths which are responsible for the determination of the sign of the CO $n$–$\pi^*$ transition. In Fig. 3, one coupling path is positive and another is negative. Via the positive coupling path, the $n$–$\pi^*$ transition has positive rotatory strength and *vice versa*. By making use of the coupling path models in Fig. 3, we can explain the sign of the rotatory strength for ketopiperidines as follows: For 1(e)-ketopiperidine, the positive coupling overcomes the negative coupling, since the nitrogen lone pair orbital in the axial direction is concerned with the positive coupling while the $N_3$–H bond localized orbital in the equatorial direction is in the path of the negative coupling. For 1(a)-ketopiperidine, the reverse is true.

In conclusion, the optical rotatory strengths of the ketopiperidines could be analysed in terms of the through-space and the through-bond interactions by using localised molecular orbitals. This method can easily be applied to other organic as well as inorganic molecules to shed light on the relation between the optical rotatory strength and the molecular structure. Moreover, the present procedure can easily be extended to calculations with configuration interactions.

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