A Method of Analysis of the Rotational Strength in Terms of the Contributions from Molecular Fragments in the CNDO/2 Approximation

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Abstract: In order to investigate the contribution of a substituent in a molecule to the rotational strength, a method was proposed to analyze the rotational strength by dividing the molecule into two molecular fragments. This method was applied to (3*R*)-methylcyclohexanone (axial form) and (3*S*)-methylcyclohexanone (equatorial form), leading to the finding that different signs of rotational strengths of these two molecules are due to the difference in the magnitudes of the overlap integrals between the carbonyl lone pair orbitals and the C–C bond localized orbitals of the methyl groups. Moreover, this method was also applied to (1*R*)-3-ketopiperidine (axial form) and (1*S*)-3-ketopiperidine (equatorial form) in comparison with (3*R*)-methylcyclohexanone (axial form) and (3*S*)-methylcyclohexanone (equatorial form). It is concluded that the lone pair orbitals of the nitrogen atoms in 3-ketopiperidines have a similar effect on the rotational strengths of the molecules in question as the methyl groups of 3-methylcyclohexanones. The method proposed in this paper may reasonably be expected to be very useful to investigate the contribution of a substituent to the rotational strength.

Optical rotatory dispersions or circular dichroisms of various molecules have been measured, and their conformations, also, have been studied.[2,3] Following the accumulation of these experimental data, molecular orbital calculations on rotational strengths have been developed and found to be in satisfactory agreement with the experimental data.[4–8] However, the number of molecules calculated is very small in comparison with the number of molecules of which the optical rotatory dispersions or circular dichroisms were measured. Therefore, the correspondence between the observed values of rotational strengths and configurations in and conformations of molecules was usually determined by investigating the similarity between the observed data of similar but slightly different molecules.[9] Although this procedure has proved to be very useful in predicting the conformation of the molecule in question, the correspondence has not always been determined unambiguously. Hence, it is desirable to be able to relate the conformation of the molecule with its rotational strength from a theoretical point of view.

There have been many theoretical approaches to relate molecular structures with their rotational strengths by the perturbation method. Moscowitz, *et al.*,[10] calculated the rotational strength of methylenebicycloheptene and bicyclooctenone on the basis of the method of molecules in molecules[11] by using the Pariser–Parr approximation.[12] That is, the interaction between two π-electron systems of ethylenic or carbonyl groups in the above-mentioned molecules was regarded as perturbation to calculate the rotational strengths of the molecules. The obtained results were in good agreement with the experimental data and were subjected to analysis in terms of local excitation and charge-transfer excitation. Höhn and Weigang[13] also developed the perturbation method for the rotational strength with emphasis on electron correlation, and applied it, in connection with the octant rule, to a carbonyl group interacting with a perturber. More recently, Bayley, *et al.*,[14] applied the perturbation method to molecules containing two peptide groups, and the rotational strengths of the molecules were obtained as the function of two dihedral angles. All these studies[10,13,14] employed the wave functions of the two isolated chromophores as the zeroth-order wave function, and the rotational strength of the molecule in question was calculated by regarding the interaction between the two chromophores as perturbation. Recently, however, the rotational strength was obtained by straightforward and unambiguous calculations[4–8] with the molecular orbitals of the whole system of the molecule, as is written in the previous paragraph, although this approach did not give any information on the contribution of the group in the molecule to the rotational

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[1] (a) National Cancer Center; (b) The University of Tokyo; (c) Shionogi Research Laboratory.

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strength. Under these circumstances, it should be desired that the rotational strength thus obtained can be explained in terms of contributions of parts of the molecule.

Our purpose is to calculate the contribution of molecular fragments to the rotational strength in order to relate the conformation of molecules with their rotational strength. In other words, the calculated rotational strength is divided into the contributions of the molecular fragments, hence the effect of the substituent or the chromophore on the rotational strength can be systematically evaluated. Therefore, our method opens the way to interpret the theoretically calculated rotational strength in terms of the concepts generally used in organic chemistry, such as the substituent effect, and may give the theoretical base for many empirical rules, such as the octant rule, the sector rule, and so on.

Cyclohexanone methyl derivatives are the most suitable for our investigation, since the calculated rotational strengths of this series of molecules were in good agreement with the experimental data,[4] and since these molecules have been well known to obey the octant rule which describes the effect of the methyl substituent. The CNDO/2 molecular orbital method[15] was used in our calculation since this method is known to be reliable[16] and the neglect of overlap integral in the CNDO/2 method makes the analysis of the rotational strength feasible. Consequently, the contributions of a methyl group, carbonyl group, etc., to the total rotational strength of n–π* transition of 3-methylcyclohexanone were evaluated, and hence the relation between the position of a substituent group in the molecule and its contribution to rotational strength was clarified.

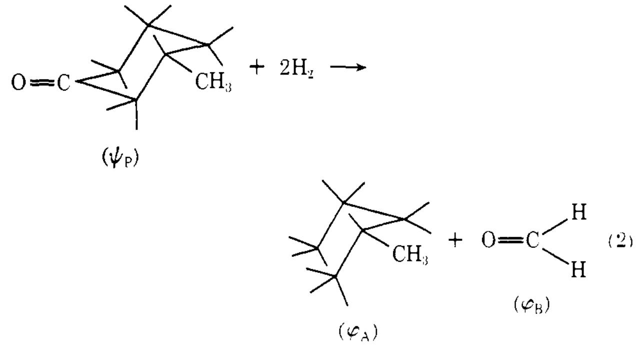
Furthermore, the rotational strength of 3-ketopiperidine subjected to our method of analysis led to the finding that the relative orientation of the nitrogen lone pair is critical to the optical rotational strength. This is of interest in connection with some striking conformationally dependent spectroscopic anomalies recently noted for the α- and β-amino ketones.[17] Although the method might be a first approximation, it should provide valuable insight into the structural origins of the molecular optical rotatory properties.

Method of Calculation

The reduced rotational strength $[R_{i-j}]$ was calculated by using the equation

$$[R_{i-j}] = -7313\langle\psi_i|\nabla|\psi_j\rangle\langle\psi_j|\mathbf{r}\times\nabla|\psi_i\rangle/\Delta E_{ji} \qquad (1)$$

where ψ_i is the ith molecular orbital and ΔE_{ji} the transition energy from the ith to the jth molecular orbitals. As is well known, the dipole velocity formalism in this equation gives the rotational strength which is not dependent on the position of the origin.[3] The molecular orbitals ψ_i, ψ_j in the equation were obtained by the CNDO/2 method; these molecular orbitals gave good results for the calculation of the rotational strength of cyclohexanone methyl derivatives.[4] In eq 1, the matrix element of the gradient operator (∇) was calculated in units of Å, and the transition energy in units of eV. The molecular orbital ψ_i can be represented by the linear combination of the molecular orbitals belonging to the molecular fragments.[18] For example, the following virtual reaction was considered. Here two hydrogen molecules in the left side of eq 2 were added so as to make equal the numbers of the atomic orbitals in both sides of the reaction. Then, the ith molecular orbital of the parent molecule (ψ_{Pi}) can be represented by the linear combination of the molecular orbitals for molecular fragment A (φ_A) and for molecular fragment B (φ_B) as



$$\psi_{Pi} = \sum_k C_{Ak}^{\,i}\varphi_{Ak} + \sum_l C_{Bl}^{\,i}\varphi_{Bl} \qquad (3)$$

where, in the expansion of the ith molecular orbital ψ_{Pi} of the parent molecule, φ_{Ak} is the kth molecular orbital of the molecular fragment A and $C_{Ak}^{\,i}$ is its coefficient and φ_{Bl} and $C_{Bl}^{\,i}$ are for the molecular fragment B. It should be emphasized that the neglect of the overlap integrals makes possible the decomposition of the molecular orbitals into molecular fragments as shown in eq 3. Therefore, the molecular orbitals obtained by the CNDO/2 method are suitable for the analysis of contributions of molecular fragments. The same equation as eq 3 can be derived for the jth molecular orbital. The matrix element of gradient operator between the ith and the jth molecular orbitals can be expanded into those of the molecular fragments as

$$\begin{aligned}\langle\psi_i|\nabla|\psi_j\rangle &= \sum_k\sum_{k'} C_{Ak}^{\,i}C_{Ak'}^{\,j}\langle\varphi_{Ak}|\nabla|\varphi_{Ak'}\rangle + \\ &\sum_k\sum_l C_{Ak}^{\,i}C_{Bl}^{\,j}\langle\varphi_{Ak}|\nabla|\varphi_{Bl}\rangle + \sum_l\sum_k C_{Bl}^{\,i}C_{Ak}^{\,j}\langle\varphi_{Bl}|\nabla|\varphi_{Ak}\rangle + \\ &\sum_l\sum_{l'} C_{Bl}^{\,i}C_{Bl'}^{\,j}\langle\varphi_{Bl}|\nabla|\varphi_{Bl'}\rangle \qquad (4)\end{aligned}$$

where the first term in the right-hand side of eq 4 is the contribution of the local excitation in the molecular fragment A, the second term the charge transfer from the molecular fragment A to B, the third term the charge transfer from the molecular fragment B to A, and the fourth term the local excitation in the molecular fragment B. Hereafter, these terms are designated as A → A, A → B, B → A, and B → B. The matrix element of the magnetic moment operator $\mathbf{r}\times\nabla$ can also be represented as a summation of the A → A, A → B, B → A, and B → B contributions. Since the rotational strength is calculated by the scalar product of the matrix elements of the gradient and the magnetic moment operators, the rotational strength may be decomposed into the contributions of molecular fragments written in a 4 by 4 matrix,[19] the row and column of which corre-

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(19) A 4 by 4 matrix can directly be calculated from the molecular orbitals ψ_i and ψ_j by dividing these orbitals into two parts corresponding to the molecular fragments. However, this direct division of

spond to the A → A, A → B, B → A, and B → B components of the gradient and the magnetic moment operators. Thus, the rotational strength of a molecule is equal to the sum of all the matrix elements. Moreover, each matrix element is also the sum of many terms corresponding to the excitation of the molecular fragments concerned. When some terms in the summation for a matrix element are more dominant than the other terms, the matrix element can be characterized by the excitations of the molecular fragment corresponding to the dominant terms involved. For instance, when 3-methylcyclohexanone is subjected to analysis by dividing the parent molecule into the carbonyl group and the remaining part, the matrix element of the magnetic moment operator of the parent molecule is characterized by the n–π^* transition of the carbonyl group.

The practical procedure for our analysis is as follows. First of all, the molecular orbitals of a parent molecule concerned are computed by the CNDO/2 method. Molecular fragments are also similarly calculated. For example, for the analysis of the virtual reaction given by eq 2, 3-methylcyclohexanone along with two hydrogen molecules are treated as a composite molecular system in a single computation by the CNDO/2 method to obtain individual molecular orbitals for each molecule under the assumption that they are separated far enough from each other. Therefore, we can get a set of molecular orbitals, *i.e.*, those of 3-methylcyclohexanone, of one hydrogen molecule and of another hydrogen molecule.

Next, a similar computation for the right side of the virtual reaction is carried out for two molecular fragments A and B to obtain molecular orbitals of formaldehyde and the remaining part of the parent molecule (isohexane). Here, ψ_i is designated for the *i*th molecular orbital of methylcyclohexanone, φ_{Ak} for the *k*th molecular orbital of isohexane, and φ_{Bl} for the *l*th molecular orbital of formaldehyde. From eq 3

$$\int \varphi_{Ak'}\psi_i \mathrm{d}\tau = \sum_k C_{Ak}{}^i \int \varphi_{Ak'}\varphi_{Ak}\mathrm{d}\tau + \sum_l C_{Bl}{}^i \int \varphi_{Ak'}\varphi_{Bl}\mathrm{d}\tau \qquad (5)$$

Since a set of φ_{Ak}'s are orthonormal

$$\int \varphi_{Ak'}\varphi_{Ak}\mathrm{d}\tau = \delta_{kk'} \qquad (6)$$

The molecular orbitals φ_{Ak}'s have no common atomic orbitals with the molecular orbital φ_{Bl} and the differential overlap integrals are completely neglected; hence

$$\int \varphi_{Ak'}\varphi_{Bl}\mathrm{d}\tau = 0 \qquad (7)$$

Substituting eq 6 and 7 into eq 5, the coefficient $C_{Ak}{}^i$ can be obtained by

$$C_{Ak}{}^i = \int \varphi_{Ak}\psi_i \mathrm{d}\tau \qquad (8)$$

The right-hand side of eq 8 can easily be calculated by expanding the molecular orbitals φ_{Ak} and ψ_i into atomic orbitals. The coefficient $C_{Bl}{}^i$ can be calculated in the same manner.

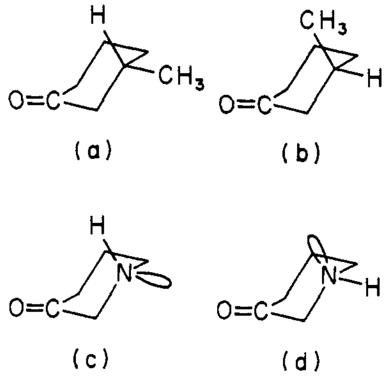

Figure 1. Molecular structures of 3-methylcyclohexanones and 3-ketopiperidines: (a) (3*S*)-methylcyclohexanone (equatorial form); (b) (3*R*)-methylcyclohexanone (axial form); (c) (1*R*)-3-ketopiperidine (axial form); (d) (1*S*)-3-ketopiperidine (equatorial form).

Obtaining the value of the coefficients $C_{Ak}{}^i$ and $C_{Bl}{}^i$, we are now in a position to calculate matrix elements of the gradient operator given by eq 4 as well as those of the magnetic moment operator. Since the above-mentioned matrix elements are represented in terms of molecular orbitals concerned, the expansion of these matrix elements leads to the summation of the matrix elements between atomic orbitals. The matrix elements in terms of atomic orbitals can be calculated in the same manner as was described in our previous paper.[4] It should be noticed that matrix elements between atomic orbitals have to be calculated by using coordinates of atoms of the parent molecule.

There are many options for the division of a molecule into molecular fragments. In other words, we can analyze the rotational strength of the molecule from various points of views. Information can be obtained on the effect of a certain chromophore or the effect of a substituent, and so on, depending on the method of division of a molecule into parts. For instance, when 3-methylcyclohexanone is divided into the carbonyl group and the remaining parts, the information given by the analysis should concern the contribution of the carbonyl chromophore group, especially those of n–π^* and π–π^* transitions, to the rotational strength of 3-methylcyclohexanone. On the other hand, when 3-methylcyclohexanone is divided into the methyl group and the remaining parts, then the substituent effect should be the object of the analysis. Therefore, our present method can give the correspondence between the substituent effect for the rotational strength calculated theoretically and that used generally in organic chemistry. Furthermore, our analysis described in this article can lead to the decision whether or not two different types of substituent have similar effects on the rotational strength. In the following section, we show how the analysis can be carried out by using 3-methylcyclohexanones and 3-ketopiperidines as examples.

Results and Discussion

In our present study, the n–π^* transition of carbonyl groups was subjected to the analysis for (3*R*)-methylcyclohexanone (axial form) and (3*S*)-methylcyclohexanone (equatorial form) (subsequently referred to as 3(a) and 3(e)-methylcyclohexanones, respectively), and (1*R*)-3-ketopiperidine (axial form) and (1*S*)-3-

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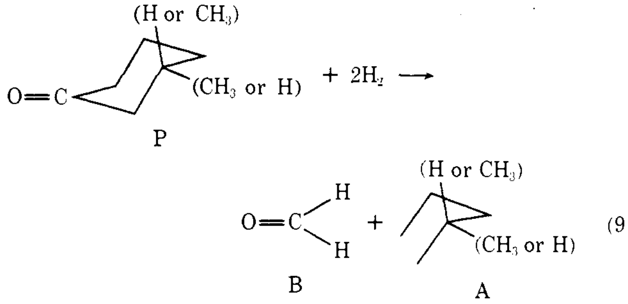
molecular orbitals cannot give any information on the nature of the local transition in molecular fragments which is included in the molecular orbital of the parent molecule. As stated below, our procedure of the calculation makes it possible to characterize the transition of the parent molecule in terms of the nature of the transitions of molecular fragments.

ketopiperidine (equatorial form) (subsequently referred to as 1(a)- and 1(e)-ketopiperidines, respectively). The structures of all these molecules are shown in Figure 1.

Methylcyclohexanones are suitable for our analysis since the calculated rotational strengths of these molecules have been well known to be in excellent agreement with the observed values. The n–π^* transition of these cyclohexanones is the lowest transition; that is, the transition from the highest occupied to the lowest vacant orbitals.

(A) 3-Methylcyclohexanones. First, the following virtual reaction was assumed in order to characterize the contribution of the carbonyl group to the rotational strength. The results for the above virtual reaction are given in Table I.



(9)

Table I. Matrix for the Analysis of 3(e)-Methylcyclohexanone for the Virtual Reaction Given by Eq 9

∇	$\mathbf{r} \times \nabla$: A → A	A → B	B → A	B → B	Total
A → A	0.64	−4.29	0.09	−6.86	−10.43
A → B	−0.47	−1.62	0.05	−4.10	−6.15
B → A	0.84	0.31	−0.02	2.50	3.63
B → B	−1.42	−1.53	0.06	−6.11	−9.00
Total	−0.41	−7.13	0.18	−14.58	−21.94

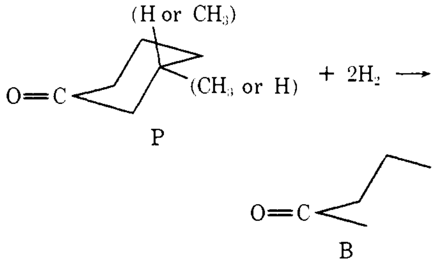
The values in the table are the scalar products of the vectors of each molecular fragment corresponding to the gradient and the magnetic moment operators, multiplied by the appropriate coefficient appearing in eq 1, without dividing by the n–π^* excitation energy. Therefore, the reduced rotational strength can be obtained from the values in the table after dividing by the excitation energy ($\approx$4 eV). For relative comparison of reduced rotational strengths, values obtained without being divided by the excitation energy can be used with ease and hence will be listed in the tables, unless otherwise stated. From Table I, it is obvious that the negative value in the reduced rotational strength is primarily due to the large contribution of the magnetic moment of the carbonyl group coupled with the gradient term of A → A, B → B, local excitations, as well as the A → B charge-transfer excitation. The n–π^* excitation in the carbonyl group is undoubtedly responsible for the large contribution of the magnetic moment term to the reduced rotational strength.

The matrices of the analysis for 3(a)- and 3(e)-methylcyclohexanones are given in Table II. The signs of the rotational strength differ from each other for both methylcyclohexanones. It is obvious from Table II that the magnetic moment term of the carbonyl group couples with the gradient terms of the A → A, A → B, and B → B types, giving rise to the different signs for the rotational strengths; that is, the large negative values were found in the B → B type magnetic moment term for 3(e)-methylcyclohexanone, in contrast to the large positive values in the same term for 3(a)-methylcyclohexanone.

Table II. Matrix for the Analysis of 3(a)- and 3(e)-Methylcyclohexanones for the Virtual Reaction Given by Eq 9

∇	$\mathbf{r} \times \nabla$: A → A	A → B	B → A	B → B	Total
	3(e)-Methylcyclohexanone				
A → A	0.64	−4.29	0.09	−6.86	−10.43
A → B	−0.47	−1.62	0.05	−4.10	−6.15
B → A	0.84	0.31	−0.02	2.50	3.63
B → B	−1.42	−1.53	0.06	−6.11	−9.00
Total	−0.41	−7.13	0.18	−14.58	−21.94
	3(a)-Methylcyclohexanone				
A → A	5.49	3.46	−0.07	16.24	25.12
A → B	2.45	2.01	−0.07	8.42	12.82
B → A	0.08	−0.27	0.01	−0.88	−1.05
B → B	4.40	5.13	−0.15	21.17	30.54
Total	12.43	10.33	−0.28	44.95	67.42

Next, the contributions of an asymmetric carbon as well as a methyl substituent to the rotational strength were investigated by using the following virtual reaction. The results of the analysis listed in Table III indicate that the signs in each matrix element are coincident with each other. The opposite signs of the total rotational strength come from the fact that the absolute magnitude of the B → B type term in 3(a)-methylcyclohexanone is much larger than that in 3(e)-methylcyclohexanone. In this virtual reaction, both the asymmetric carbon and the methyl group are removed as ethane from the cyclohexanone ring frame. Therefore, the large difference in the B → B term for the methylcyclohexanones should be ascribed to either the asymmetric carbon itself or the methyl group attached to the asymmetric carbon.

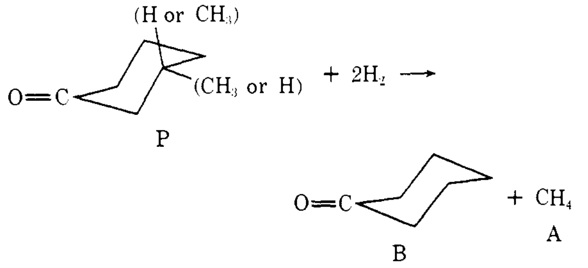


(10)

Table III. Matrix for the Analysis of 3(a)- and 3(e)-Methylcyclohexanones for the Virtual Reaction Given by Eq 10

∇	$\mathbf{r} \times \nabla$: A → A	A → B	B → A	B → B	Total
	3(e)-Methylcyclohexanone				
A → A	0.94	−2.39	−1.45	−73.06	−75.96
A → B	0.04	0.77	−1.88	−46.00	−47.07
B → A	−0.61	2.94	1.33	43.25	46.91
B → B	1.70	−9.59	4.84	57.20	54.15
Total	2.07	−8.26	2.83	−18.61	−21.97
	3(a)-Methylcyclohexanone				
A → A	0.56	−1.35	−1.14	−69.44	−71.37
A → B	−0.09	0.47	−1.49	−24.66	−25.78
B → A	−0.53	1.76	0.95	46.58	48.77
B → B	1.45	−8.53	4.68	118.18	115.78
Total	1.39	−7.65	3.01	70.66	67.40

In order to determine whether the asymmetric carbon or the methyl group is responsible for the difference in the rotational strength, the following virtual reaction was considered to analyze the effect of the methyl



(11)

group. The results of the analysis are given in Table IV. The most striking aspect observed for this virtual reaction is the negative values in the matrix elements between either A → A or A → B or B → A gradient terms and the B → B magnetic moment operator term for 3(e)-methylcyclohexanone, in contrast to the positive values in the corresponding matrix elements for 3(a)-methylcyclohexanone. This characteristic is undoubtedly responsible for the different signs of the total rotational strength. In other words, the stereoisomerism of the methyl substituent decides the sign of the rotational strength not through indirect interaction with the carbonyl group but through direct contribution of the methyl group to the rotational strength.

Table IV. Matrix for the Analysis of 3(a)- and 3(e)-Methylcyclohexanones for the Virtual Reaction Given by Eq 11

∇	$\mathbf{r} \times \nabla$				
	A → A	A → B	B → A	B → B	Total
	3(e)-Methylcyclohexanone				
A → A	0.06	0.02	0.02	−12.65	−12.55
A → B	0.14	−0.04	0.09	−34.64	−34.45
B → A	−0.01	−0.10	0.02	−3.63	−3.73
B → B	0.07	0.97	−1.20	28.94	28.77
Total	0.25	0.86	−1.08	−21.99	−21.96
	3(a)-Methylcyclohexanone				
A → A	0.00	−0.07	−0.09	2.93	2.78
A → B	0.01	0.05	0.11	7.17	7.33
B → A	0.07	−0.04	0.00	4.02	4.05
B → B	1.51	0.07	1.43	50.24	53.25
Total	1.59	0.01	1.46	64.36	67.42

For the detailed analysis of the effect of the methyl substituent on the carbonyl chromophore, the rotational strengths of both 3(a)- and 3(e)-methylcyclohexanones are examined more precisely in terms of the molecular orbital which gives dominant terms in the summation in eq 4. The virtual reaction most suitable for this purpose is the decomposition of the 3-methylcyclohexanones into formaldehyde and isohexane as is shown in eq 2. The weight of the lone pair orbital of formaldehyde for the highest occupied molecular orbitals of 3(a)- and 3(e)-methylcyclohexanones is listed in Table V, as well as that of π^* orbital for the lowest vacant molecular orbitals of methylcyclohexanones. It is clear from this table that the weight of the lone pair orbital in 3(e)-methylcyclohexanone is considerably smaller than 1.0, in contrast to the weight for 3(a)-methylcyclohexanone which is close to 1.0. The weights for π^* orbitals in both molecules are close to 1.0. Consequently, the highest occupied molecular orbital of 3(e)-methylcyclohexanone consists of a lone pair orbital of the carbonyl group, mixed to a considerable extent with other types of orbitals mainly localized in the $\mathrm{C^*{-}CH_3}$ bond, *i.e.*, the bond between the asymmetric carbon and the methyl group. Further inspection of the molecular orbitals led to the conclusion that the above-mentioned mixing of the orbitals is primarily due to the fact that the lone pair orbital lies almost parallel in the direction of the $\mathrm{C^*{-}CH_3}$ bond in question, and hence the lone pair orbital has a large overlap with the $\mathrm{C^*{-}CH_3}$ bond localized orbital. It is obvious from the geometrical point of view that the corresponding overlap should be relatively small for 3(a)-methylcyclohexanone as it is in fact the case in the calculation. The conclusion of our analysis is, therefore, the difference in the signs of the rotational strengths of 3(a)- and 3(e)-methylcyclohexanones can be explained by the difference in the magnitudes of the overlap integrals between the carbonyl lone pair orbital and the $\mathrm{C^*{-}CH_3}$ bond localized orbital, leading to the difference in nature of the highest occupied orbitals of methylcyclohexanones.

Table V. Weight of the Lone Pair Orbital and π^* Orbital of the Carbonyl Group for the Highest Occupied and the Lowest Vacant Molecular Orbitals of 3-Methylcyclohexanones

	n	π^*
3(e)-Methylcyclohexanone	0.897	0.987
3(a)-Methylcyclohexanone	0.985	0.994

(B) 3-Ketopiperidines in Comparison with 3-Methylcyclohexanones. The analysis described in the preceding paragraphs is mainly concerned with the reason for the difference in the signs of the rotational strengths of a series of molecules with regard to their molecular structures. Through application of this analysis, an analogy between two different molecules can also be derived, by comparing the corresponding matrix elements with each other. In our present study, we attempted to compare 3(a)- and 3(e)-methylcyclohexanones with 1(e)- and (1a)-ketopiperidines, respectively.

The calculated rotational strengths are listed for these molecules in Table VI, together with the observed values of the rotational strengths. As far as the signs are concerned, complete agreement was found between theoretical and experimental results. The absolute magnitude of the rotational strength is difficult to compare, since these molecules themselves have no fixed conformations but exist in interconvertible conformations (*i.e.*, different conformations); hence the observed values of these molecules are inferred from other molecules whose fragments are coincident with the molecules in question.[17,20–23] The molecular orbitals used in our analysis can be expected to be adequately reliable, although we cannot compare the magnitude of the calculated rotational strength with the observed value because of the lack of the observed value of the molecule itself.

In Table VII, the matrices for the analysis of 3(e)-

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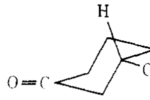
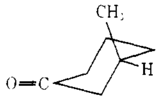
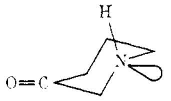
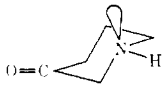
(20) G. Snatzke and G. Eckhardt, *Tetrahedron*, **24**, 4543 (1968).

(21) G. Snatzke, B. Ehrig, and H. Klein, *ibid.*, **25**, 5601 (1969).

(22) G. Snatzke and G. Eckhardt, *ibid.*, **26**, 1143 (1970).

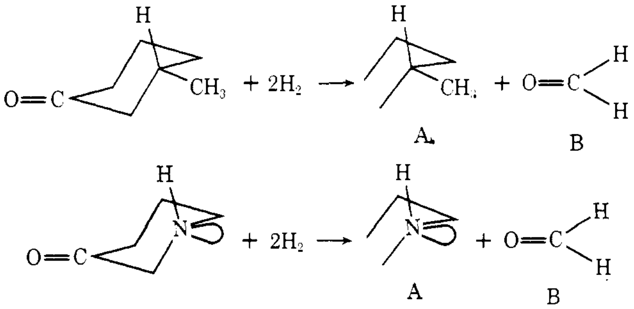
(23) (a) S. Yamada and K. Kunieda, *Chem. Pharm. Bull.*, **15**, 490 (1967); (b) S. F. Mason, K. Schofield, and R. J. Wells, *J. Chem. Soc. C*, 626 (1967).

Table VI. Calculated Rotational Strengths of 3-Methylcyclohexanones and 3-Ketopiperidines

Molecule	Rotational strength (Calcd)[a]	Rotational strength Obsd
	−5.5 (−21.9)	−2.23[b]
	16.9 (67.4)	+0.04[c]
	−42.9 (−171.5)	−11.2[d]
	16.6 (66.3)	+8.9[e]

[a] The value divided by the excitation energy (4.0 eV). The undivided value is given in parentheses for comparison with those in Tables VII and VIII. [b] Reference 20. [c] Reference 21. [d] Estimated from CD data[17] of tropin-2-one and (+)-bicyclo[3.2.1]-octanone-2. [e] Estimated from CD data[17] of (−)-1-oxoquinolizidine and (+)-*trans*-1-decalone.

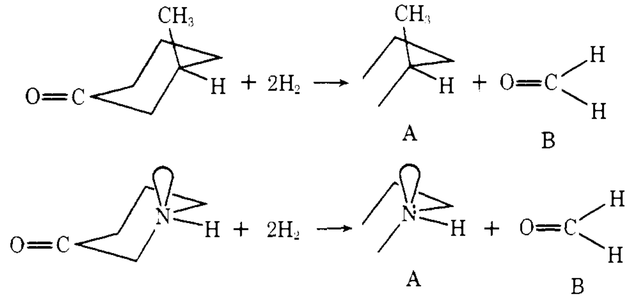
Table VII. Comparison of the Matrices of the Analysis for 3(e)-Methylcyclohexanone and 1(a)-Ketopiperidine for the Virtual Reaction Given Below



∇	$r \times \nabla$ A → A	A → B	B → A	B → B	Total
			3(e)-Methylcyclohexanone		
A → A	0.64	−4.29	0.09	−6.86	−10.43
A → B	−0.47	−1.62	0.05	−4.10	−6.15
B → A	0.84	0.31	−0.02	2.50	3.63
B → B	−1.42	−1.53	0.06	−6.11	−9.00
Total	−0.41	−7.13	0.18	−14.58	−21.94
			1(a)-Ketopiperidine		
A → A	−8.18	−24.48	0.92	−70.91	−102.64
A → B	−1.17	−5.68	0.45	−14.85	−21.25
B → A	−0.26	−1.50	0.06	−3.72	−5.43
B → B	−5.93	−6.78	0.32	−29.77	−42.16
Total	−15.54	−38.45	1.75	−119.24	−171.48

methylcyclohexanone and 1(a)-ketopiperidine are listed in comparison with each other. The similarity between two molecules can be noticed from this table. That is, almost all the matrix elements have the same signs, and a relatively large matrix element in a molecule corresponds to the relatively large matrix element in another molecule, although the absolute magnitudes are considerably different from each other for the corresponding matrix elements. Thus, this similarity leads to the conclusion that the lone pair orbital of the nitrogen atom in 1(a)-ketopiperidine may play a similar role as the methyl group in 3(e)-methylcyclohexanone for the determination of the signs of the rotational strengths. The same conclusion can be derived for the analysis of 3(a)-methylcyclohexanone and 1(e)-ketopiperidine; that is, as the matrices for the analysis given in Table VIII indicate, there is a similarity in the signs and the relative magnitudes. Therefore, the lone pair orbital in both 3-ketopiperidines has the similar effect as the methyl group in both methylcyclohexanones on the rotational strength of n–π^* transition.

Table VIII. Comparison of the Matrices of the Analysis for 3(a)-Methylcyclohexanone and 1(e)-Ketopiperidine for the Virtual Reaction Given Below



∇	$r \times \nabla$ A → A	A → B	B → A	B → B	Total
			3(a)-Methylcyclohexanone		
A → A	5.49	3.46	−0.07	16.24	25.12
A → B	2.45	2.01	−0.07	8.42	12.82
B → A	0.08	−0.27	0.01	−0.88	−1.05
B → B	4.40	5.13	−0.15	21.17	30.54
Total	12.43	10.33	−0.28	44.95	67.42
			1(e)-Ketopiperidine		
A → A	0.99	2.63	0.15	8.82	12.59
A → B	1.03	5.04	0.06	20.82	26.95
B → A	−4.36	−3.94	0.23	−16.07	−24.14
B → B	4.53	9.11	−0.09	37.36	50.91
Total	2.20	12.85	0.34	50.94	66.32

(C) Concluding Remarks. The present method of analysis for the rotational strength was applied to 3-methylcyclohexanones and 3-ketopiperidines, leading to the finding that the overlap interaction between the carbonyl lone pair and the methyl group or the nitrogen lone pair is critical to the sign of the rotational strength of these molecules. Therefore, it may be reasonably expected that the present method of analysis is very useful in investigating factors to determine the sign and magnitude of the rotational strength of various series of molecules.

In our analysis, rotational strengths were calculated without taking configuration interactions into account. However, when the configuration interaction has a large effect on the rotational strength of a molecule in question, the analysis should be modified so as to include the effect of the configuration interaction. This extension of our method of analysis can be carried out directly by using the configuration analysis developed by Baba, *et al.*,[24] which has proved to be useful in correlating transitions of any substituted molecule with those of nonsubstituted molecules. Although the practical procedure for the calculation of matrix elements of this kind of analysis becomes rather com-

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(24) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, 50, 2078 (1969).

plicated and troublesome, development toward this direction should be made in the future because of the importance of the configuration interaction in the calculation of the rotational strength of many molecules. Another possible development of this analysis is to increase the number of the molecular fragments for analysis by more than two. For example, methylcyclohexanone can be divided into the methyl group, the carbonyl group, and the remaining part. In this case, the contribution of each part cannot be represented in matrix form, although the results may sometimes be very convenient in order to see the effect of a substituent on a chromophore. But development toward this direction would be rather trivial, since the precedure of calculation would be quite similar to that described in this paper and the obtained results may be expected to be essentially similar to those given here.

Finally, it should be noted that the method presented here can also be applied by using the molecular orbitals obtained by INDO approximation.

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Interaction between Closed-Shell and Open-Shell Molecules.[1] Nuclear Magnetic Resonance Contact Shift Studies on the π-Hydrogen Bonding Involving Stable Hydrocarbon π Radicals

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Abstract: ^{1}H and ^{13}C nmr shifts induced by the π-hydrogen bond between the BDPA radical (stable hydrocarbon π radical) and various proton donor molecules have been studied. The preferential upfield ^{1}H shift of the XH proton, as compared with the shift induced by BDPP (the corresponding closed-shell hydrocarbon molecule), was attributed to the contact shift characteristic of negative spin density on the XH proton. The experimental results were also substantiated by MO theoretical calculation.

We are currently interested in the use of a stable free radical induced nmr contact shift as a potential probe for studying weak molecular interactions involving free radicals. Our recent studies[2] on the ^{1}H and ^{13}C nmr contact shifts have shown that nitroxide radical (di-*tert*-butyl nitroxide, DTBN) can be used to probe chemical phenomena associated with molecular interactions such as hydrogen bond and charge-transfer interactions involving free radicals. We have also been studying the features and mechanism of intermolecular electron spin transmission associated with these interactions in the light of elucidating the intrinsic nature of the interaction between closed- and open-shell molecules.[2,3]

Concerning the hydrogen bond involving free radicals, we have observed nmr contact shifts for a variety of the proton donor molecules, XH, induced by the presence of DTBN radical which serves as a proton acceptor. It was found that the X–H···DTBN hydrogen bond produces quite sensitively upfield contact shift for the X–H proton. MO (molecular orbital) theoretical studies have also been performed for the H-bonding in the protic molecule–nitroxide radical bimolecular system.[3] MO calculations (UHF-INDO method) have shown that in the H-bonding between XH and DTBN, the observed *upfield* contact shift (characteristic of negative spin density) of the XH proton is reproduced only for the π model in which the XH proton is directly over the oxygen or nitrogen pπ orbital (the π-hydrogen bonding), while the σ model fails to explain the observed DTBN-induced ^{1}H and ^{13}C contact shifts (Figure 1).

In order to obtain more confirmative evidence for the π model responsible for DTBN-induced negative spin density on the XH proton and to get further insight into the π-hydrogen bond involving free radicals, we used here the stable hydrocarbon π radical, α,γ-bisdiphenylene-β-phenylallyl (BDPA) (Figure 2), as a proton acceptor (the π base) in the π-hydrogen bonding and followed the ^{1}H and ^{13}C contact shifts for various proton donor molecules, XH, induced by the presence of BDPA. This contact shift would serve as a sensitive probe for elucidating the chemical phenomena involved in the very weak interaction of the π-hydrogen bonding.[4]

Experimental Section

Materials. We tried to observe the ^{1}H shifts of various XH molecules caused by the addition of varying amounts of BDPA

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[1] Part IX in this series. Part VIII, see I. Morishima, *et al.*, *J. Amer. Chem. Soc.*, **94**, 6555 (1972).

[2] I. Morishima, K. Endo, and T. Yonezawa, *ibid.*, **93**, 2408 (1971); *Chem. Phys. Lett.*, **9**, 203 (1971); I. Morishima, T. Inubushi, K. Endo, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, **94**, 4812 (1972); *Chem. Phys. Lett.*, **14**, 372 (1972); I. Morishima, T. Matsui, T. Yonezawa, and K. Goto, *J. Chem. Soc., Perkin, Trans. 2*, 633 (1972).

[3] I. Morishima, K. Endo, and T. Yonezawa, *Chem. Phys. Lett.*, **9**, 143 (1971); *J. Chem. Phys.*, **58**, 3146 (1973).

[4] The study of intermolecular hydrogen bonding involving a π base as the proton acceptor has been most extensively carried out by the ir method; see R. West, *J. Amer. Chem. Soc.*, **81**, 1614 (1959); Z. Yoshida and E. Osawa, *ibid.*, **87**, 1467 (1965); **88**, 4019 (1966).

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