

Vibrational and Normal Coordinate Analysis of 1-Methyl-2,6-Diphenylpiperidone

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Normal coordinate analysis of the fundamental vibrations of the title compound has been carried out by assuming C_{2v} point group symmetry. The observed FTIR vibrations have been interpreted and assigned based on the normal coordinate analysis. The potential energy distribution analysis also confirms the present assignments.

INTRODUCTION

Piperidone and its derivatives are widely used in the pharmacological industry due to their biological activities. The actual pharmacological activity of the compound is determined by the nature, size and the position of the side groups attached to the ring. Piperidone derivatives have many medical properties such as anti-hypoxic, anti-mycotic, psycotropic activities. Some of these derivatives also have herbicidal, bactericidal and mutagenetic activities¹. The study of intermolecular interaction, vibrations and forces between the atoms in the molecules are very much useful for the better understanding of the title compound. Consideration of these factors leads us to undertake the detailed spectral investigation of 1-methyl-2,6-diphenyl piperidone.

EXPERIMENTAL

Preparation of the Compound

The compound 1-methyl-2,6-diphenylpiperidone has been prepared and purified by the procedure outlined by Selvaraj *et al.*² Sodium hydroxide (5 g) was dissolved in water (20 mL) and alcohol (20 mL). To this solution, add a mixture of acetone (1.5 mL) and benzaldehyde (6 mL). Stirred the mixture for 1 h and kept it for one day. Dichalcone was formed. The dichalcone (1 g) was dissolved in N,N-dimethyl-formamide (10 mL) and then methyl amine (2 mL) was added. Stirred well and kept it again for one day. Then a small piece of ice was taken, into which the above solution was poured and stirred well. Kept it for overnight to get the polycrystalline sample of the title compound.

The FTIR spectrum of this compound was recorded in KBr disc on Perkin-

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Elmer Model-1600 multiple internal reflection spectrophotometer in the mid-region. The frequencies of all sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$.

Molecular Structure and Symmetry

The molecular structure of 1-methyl-2,6-diphenyl piperidone and its FTIR spectrum are shown in Fig. 1. The molecule is assumed to have C_{2v} symmetry by treating the methyl group as point mass. The 42 fundamental modes of vibrations of this molecule are classified into

$$\Gamma_{\text{vib}}(C_{2v}) = 16A_1 + 6A_2 + 8B_1 + 12B_2.$$

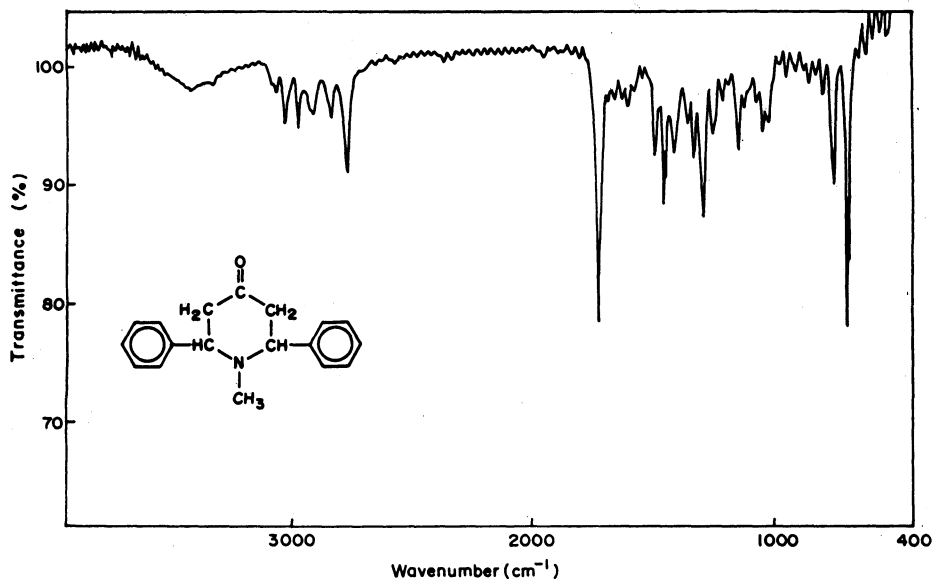


Fig. 1. Molecular structure and FTIR spectrum of 1-methyl-2,6-diphenyl piperidone

RESULTS AND DISCUSSION

The normal coordinate analysis has been carried out using General Valence Force Field (GVFF) based on Wilson's GF Matrix method³. The computations of normal coordinate analysis are performed on a personal computer using CART, GMAT and FPERT programmes⁴. The cartesian coordinates obtained for the optimized structure using CART were given as input to GMAT to get the elements of G matrix. The number of internal coordinates exceeds that of the normal modes and redundant coordinates were eliminated during the normalization by GMAT programme. The initial values of the force constants obtained from the related molecules^{5,6} are refined using FPERT programme by applying least square fit algorithm. The final values of force constants are given in Table-1.

TABLE-1
 VALENCE FORCE CONSTANTS OF 1-METHYL-2,6-DIPHENYL PIPERIDONE
 (In the units mdyne \AA^{-1} ; mdyne rad^{-1} and mdyne $\text{\AA}^{-1} \text{rad}^{-2}$)

Types of constants	Parameters	Coordinates	Values	
Diagonal Constants				
Stretching	f_D	C—H	4.55	
	f_d	C—N	5.66	
	f_Q	C=O	10.65	
	f_p	C—C	4.03	
	f_r	N—C	3.56	
	f_R	C—H	4.72	
Bending	f_α	CCC	1.01	
	f_β	CNC	1.07	
	f_θ	CHC	0.88	
	f_r	CCN	1.47	
	f_δ	CCO	1.56	
	f_ϕ	CCH	0.60	
	f_ψ	NCH	0.60	
	Stretch-Stretch	f_{dp}	CN CC	0.298
f_{dr}		CN NC	0.417	
f_{pp}		CC CC	0.101	
f_{Dp}		CH CC	0.338	
f_{pQ}		CC CO	0.751	
f_{pD}		CC CH	0.513	
Interaction Constants				
Stretch-Bend	$f_{D\alpha}$	CH CCC	0.181	
	$f_{D\beta}$	CH CNC	0.101	
	$f_{d\alpha}$	CN CCC	0.417	
	$f_{d\beta}$	CN CNC	0.425	
	f_{Dr}	CH CCN	0.273	
	$f_{Q\alpha}$	CO CCC	0.513	
	$f_{p\phi}$	CC CCH	0.338	
	f_{pr}	CC CCN	-0.098	
	$f_{p\psi}$	CC NCH	0.233	
	$f_{r\psi}$	NC NCH	-0.182	
	$f_{p\delta}$	CC CCO	0.225	
	Bend-Bend	$f_{\alpha\beta}$	CCC CNC	-0.098
		$f_{\beta\beta}$	CNC CNC	0.051
$f_{\beta\sigma}$		CNC CCH	0.164	
$f_{\alpha\delta}$		CCC CCO	0.138	
$f_{\alpha\alpha}$		CCC CCC	0.830	

Force Constants

The calculated value of the carbonyl force constant $f_Q(\text{C}=\text{O})$ is found to be $10.65 \text{ mdyne } \text{\AA}^{-1}$ which is in close agreement with the values reported by Fan *et al.*⁷ The values of other stretching force constants $f_D(\text{C}-\text{H})$, $f_d(\text{C}-\text{N})$, $f_p(\text{C}-\text{C})$ and $f_r(\text{N}-\text{C})$ are found to be 4.55, 5.66, 4.03 and $3.56 \text{ mdyne } \text{\AA}^{-1}$ respectively. These values are in good agreement with their characteristic values. The value of the force constant between the nitrogen and the carbon atoms attached with the first substituted position of the title compound is found to be $3.56 \text{ mdyne } \text{\AA}^{-1}$ which is in agreement with the electron-donor acceptor (EDA) theory of Milliken⁸. The negative values of interaction force constants f_{pr} , f_{rp} and $f_{\alpha\beta}$ indicate that the electrons are highly delocalized near their bonds. The interaction force constants are slowly introduced in the force constant refinement process in order to minimise the difference between the observed and calculated frequencies. In general the values of principal and interaction force constants obtained in the present investigation are fairly in good agreement with the literature values reported by the earlier workers^{5,9} on some similar types of molecules. The set of force constants reported here reproduces the observed frequencies fairly well.

Vibrational Assignment

The vibrational spectra of the title compound were analysed with the help of normal coordinate calculations. The observed and calculated frequencies along with the percentage of potential energy distribution are given in Table-2. The calculated fundamental frequencies agree well with the observed frequencies.

C—H Vibrations

The compound under investigation contains CH_3 , CH_2 groups, apart from C—H group present in the system. Hence it may give rise to C—H valence oscillations. Accordingly in the title compound, the FTIR bands observed at 3190 and 3125 cm^{-1} are assigned to C—H asymmetric stretching and C—H symmetric stretching respectively in CH_3 group. The other C—H stretching vibrations are given in Table-2. These assignments are supported by the literature values¹⁰. The C—H in-plane and out-of-plane bending vibrations of 1-methyl-2-6-diphenyl piperidone have been identified at 985 , 948 , 789 and 751 cm^{-1} respectively. These assignments are in good agreement with the assignments proposed by Yadav *et al.*¹¹.

C—N Vibrations

The identification of C—N bands is highly complex since it is very difficult to distinguish these vibrations from other vibrations. In this study the bands observed at 1510 , 1294 and 1265 cm^{-1} have been designated to C—N stretching vibrations. These assignments are also supported by the literature¹². The C—N in-plane and out-of-plane bending vibrations reported in Table-2 are made in accordance with the characteristic values.

TABLE-2
VIBRATIONAL ASSIGNMENTS OF 1-METHYL-2,6-DIPHENYLPYPERIDONE

Species	Observed frequency (in cm^{-1}) FTIR	Calculated frequency (in cm^{-1})	assignments (% PED)
A ₁	3190 w	3174	C—H asymmetric stretching (98)
B ₂	3125 w	3118	C—H symmetric stretching (97)
B ₂	3105 w	3101	C—H stretching (99)
A ₁	3034 w	3048	C—H stretching (93)
A ₁	2971 w	2986	C—H stretching (96)
A ₁	2928 w	2941	CH ₂ stretching (94)
B ₂	2860 w	2876	CH ₂ stretching (92)
A ₁	2804 w	2819	CH ₂ stretching (96)
B ₂	2765 w	2774	CH ₂ stretching (92)
A ₁	1810 w	1826	C=O stretching (91)
B ₂	1732 s	1744	C=O stretching (87)
A ₁	1640 w	1631	C=C stretching (88)
B ₂	1564 w	1558	C=C stretching (84)
A ₁	1510 w	1522	C—N stretching (88)
A ₁	1470 m	1484	CH ₃ deformation (86)
B ₂	1456 ms	1472	CH ₂ scissoring (89)
B ₂	1423 w	1411	CH ₂ scissoring (91)
B ₁	1380 w	1389	CH ₂ deformation (82)
B ₁	1368 w	1372	CH ₂ deformation (84)
A ₁	1317 w	1327	C—N stretching (81)
A ₁	1294 ms	1300	C—N stretching (86)
B ₂	1265 w	1289	C—N stretching (84)
A ₁	1156 w	1170	C—C stretching (89)
B ₂	1136 w	1144	C—C stretching (82)
A ₁	1121 w	1134	C—C stretching (74)
B ₁	1102 w	1113	CH ₃ rocking (78)
B ₂	1037 uw	1049	C—C—C trigonal bending (72)
A ₁	985 w	971	C—H in-plane bending (79)
A ₁	948 w	932	C—H in-plane bending (78)
B ₂	876 w	866	C—N in-plane bending (71)
A ₁	828 w	839	C—N in-plane bending (68)
A ₂	798 w	812	C—H out-of-plane bending (76)
B ₁	751 m	769	C—H out-of-plane bending (64)
B ₁	743 m	736	C—C—C out-of-plane bending (62)
A ₂	698 s	712	C—N out-of-plane bending (68)
B ₁	650 w	663	C—N out-of-plane bending (64)
A ₂	601 w	614	C—C—N out-of-plane bending (62)
B ₁	570 w	584	C—N—C out-of-plane bending (66)
A ₂	515 w	502	N—C—H out-of-plane bending (62)
B ₁	435 w	448	C—C—H out-of-plane bending (65)
A ₂	421 w	421	C—H—C out-of-plane bending (66)
A ₂	405 w	411	C—C—O out-of-plane bending (64)

Abbreviations used: vw, very weak; w, weak; m, medium; ms, medium strong; s, strong.

C—C Vibrations

It is well established¹³ that benzene derivatives show C=C stretching modes between 1600 and 1450 cm⁻¹. In the present investigation the C=C stretching bands are identified at 1640 and 1564 cm⁻¹ respectively. The band appeared at 1037 cm⁻¹ has been assigned to C—C—C trigonal bending. The out-of-plane bending vibrations of carbon group have been identified at 743 cm⁻¹.

C=O Vibrations

The carbonyl group appearing in the fourth position of the compound may interact with other groups of the molecule. The interaction of the carbonyl group with hydrogen-donor group does not produce such drastic and characteristic changes in the frequency of C=O stretch as it does by the interaction of C—H stretch group. If a compound contains a carbonyl group, the absorption caused by C=O stretching is generally appear as very strong band. The complex pattern of C=O stretching bands observed in the spectrum of 1-methyl-2,6-dimethyl piperidone can be ascribed to the presence of the combination bands which borrow intensity through the fermi-resonance mechanism from C=O stretching fundamentals. A great deal of structural interaction can be derived from the exact position of carbonyl stretching absorption peak¹⁴. According to Danuta Michalska⁵, in the spectra of pyrimidine bases the carbonyl stretching mode occurs in the region 1730–1700 cm⁻¹. Similarly in the case of uracil and its derivatives, the carbonyl stretching vibration appears between 1700 and 1675 cm⁻¹. Consideration of these factors leads us to assign the weak and medium IR bands appearing at 1810 and 1732 cm⁻¹ to C=O stretching vibrations. Based on the results of the normal coordinate analysis and PED calculations the bands appeared at 601, 570, 515, 435, 421 and 405 cm⁻¹ have been assigned to C—C—N, C—N—C, N—C—H, C—C—H, C—H—C and C—C—O out-of-plane bending vibrations. The PED calculations have been made using the relation

$$\text{PED} = \frac{F_{ii} L_{ia}^2}{\lambda_a}$$

where PED is the combination of the *i*th symmetry coordinate to the potential energy of the vibration whose frequency is ν_a , F_{ii} the potential constant, L_{ia} the L matrix element and $\lambda = 4\pi^2 c^2 \nu_a^2$.

The PED calculations based on the final set of force constants also support the vibrational analysis made in this study.

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