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Synthesis, Spectral Studies and Normal Coordinate Analysis of 2,6-Diphenyl-3-Methyl Piperidone

T. CHITHAMBARATHANU,* V. UMAYORUBHAGAN† and V. KRISHNAKUMAR‡
Department of Physics, S.T. Hindu College, Nagercoil-629 002, India

2,6-Diphenyl-3-methyl piperidone has been synthesised and characterised using spectroscopic tools. The FTIR spectrum of this compound has been interpreted by assuming C_s point group symmetry. The normal coordinate analysis has also been carried out by applying Wilson's FG matrix mechanism.

INTRODUCTION

The amino ketones like 2,6-diphenyl piperidones and their substituted compounds have been studied by the researchers in recent years due to their potent analgesic character and pharmacological activities[1]. Further, these crystalline compounds have ring structures and several functional groups. In the present work 2,6-diphenyl-3-methyl piperidone has been synthesised and vibrational analysis has been carried out. The diagonal and interaction force constants for this compound have been obtained in order to address the intermolecular interactions, vibrations and forces between the atoms in the molecules. The potential energy constants reported in the study are very much useful for the better understanding of piperidones and their derivatives.

EXPERIMENTAL

The title compound was synthesised using the method outlined by Selvaraj *et al.*[2] Ammonium acetate (4 g) was taken in a 150 mL conical flask and dissolved in alcohol (20 mL). The solution was slightly warmed. To this solution the mixture of benzaldehyde (11 mL) and 2-butanone (4 mL) was added with consant shaking. The reaction mixture was slowly heated till the colour changed from yellow to orange. The reaction mixture was cooled and diethyl ether (25 mL) was added. The reaction mixture was kept for 3 days. Crystals of 2,6-diphenyl-3-methyl piperidone were obtained (Fig. 1). The crystals obtained were washed with ice- cold alcohol. The products when recrystallised from ethyl alcohol gave pure 2,6-diphenyl-3-methyl piperidone.

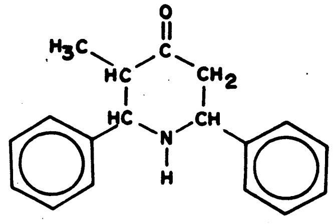

Fig. 1. Molecular structure of 2,6-diphenyl-3-methyl piperidone

The FTIR spectrum of this compound has been recorded on Perkin-Elmer model using

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† Department of Chemistry, S.T. Hindu College, Nagercoil-629 002, India.

‡ Department of Physics, Nehru Memorial College, Puthanampatti-621 007, India.

KBr disc method. The frequencies obtained are correct to within ±1 cm^{-1}.

The experimental molecule is assumed as C_s point group symmetry by treating the methyl and phenyl groups as a single unit. The 42 fundamental modes of vibration are distributed to 29a′ and 13a″ group. The a′ and a″ groups represent the in-plane and out-of-plane vibrations of this compound.

In order to obtain a more complete description of the molecular motions involved in the normal modes of vibration of the compound, a normal coordinate analysis has been carried out.

The normal coordinate analysis was performed using the Wilson's FG Matrix method[3]. The computation of force constants has been carried out using the software developed by Schachtschneader[4] with suitable modifications. The cartesian coordinates (X-matrix) obtained for the optimized structure were input to the G Matrix programme (GMAT). The complete set of internal coordinates were used to form the symmetry coordinates. The output of G Matrix programme consists of the B Matrix as well as the unsymmetrized and symmetrized G Matrix. The initial set of force constants required to solve the secular equation $|FG - E\lambda| = 0$ were taken from the molecules of similar environment[5] and they were subsequently refined using successive approximation technique. The potential energy distribution obtained for this molecule using the final set of force constants are also supporting the assignments proposed in this study.

RESULTS AND DISCUSSION

Force Constants: The valence force constants obtained for 2,6-diphenyl-3-methyl piperidone are presented in Table-1. The values of the force constant between N—H bond, C—N bond, C—C bond and C═O bond are quite reasonable and they produce better frequency fit. The stretching force constant of carbon and carbon bond (f_d) is found to be 3.176 mdyne $Å^{-1}$ which is low when compared to the stretching force constant of C—N bond ($f_s = 5.329$ mdyne $Å^{-1}$) and carbon and oxygen bond ($f_r = 9.153$ mdyne $Å^{-1}$). This is due to the gradual decrease in the electronegativity of the atoms. The values of the force constants f_d and f_r between carbon and hydrogen atoms are found to be 4.975 mdyne $Å^{-1}$ and 4.248 mdyne $Å^{-1}$ respectively. The difference in the values of f_d and f_r indicates that the C—H bond attached with phenyl group has more strain as compared to that of C—H bond attached with CH_3 group. A small variation in the values of the interaction force constants is due to the change in the structural parameters. The interaction force constants are slowly introduced in the force constant refinement process, in order to minimize the difference between the obtained and calculated frequencies. Moreover, in the computation of interaction force constant f_{PQ} (CCC═O) stretch-stretch interaction was added for the conjugated single and double bonds to obtain reasonable frequency fit in the double bond region. In general the values of principle and interaction force constants obtained in this study are fairly in agreement with the values obtained by the earlier workers[5] on some similar type of molecules.

TABLE-1
VALENCE FORCE CONSTANTS OF 2,6-DIPHENYL-3-METHYL PIPERIDONE
(in the units of mdyne $Å^{-1}$, mdyne rad^{-1} and mdyne $Å^{-1}$ rad^{-2})

Types of constants	Parameters	Coordinates	Value
Diagonal Constants:			
Stretching	f_D	N—H	5.941
	f_d	C—H	4.975
	f_Q	C=O	9.153
	f_p	C—C	3.176
	f_s	C—N	5.329
	f_r	C—H	4.248
Bending	f_α	CCC	0.983
	f_β	CNC	0.591
	f_r	NCH	0.437
	f_p	CCH	0.315
	f_σ	CCO	0.663
Stretch-stretch	f_{pp}	CC CC	0.173
	f_{ss}	CN CN	0.214
	f_{Ds}	NH CN	0.201
	f_{sd}	CN CH	0.193
	f_{PQ}	CC C=O	0.376
Interaction constants:			
Stretch-bend	$f_{d\alpha}$	CH CCC	0.195
	$f_{p\alpha}$	CC CCC	0.201
	$f_{s\beta}$	CN CNC	0.326
	$f_{\alpha\beta}$	CH CNC	0.127
	$f_{Q\alpha}$	CO CCC	0.155
Bend-bend	$f_{\alpha\alpha}$	CCC CCC	0.029
	$f_{\alpha\beta}$	CCC CNC	0.031
	$f_{\alpha r}$	CCC NCH	0.036
	$f_{\beta r}$	CNC CCH	0.059

Vibrational Assignments: The vibrational analyses of piperidone and its derivatives have been carried out by several researchers. Most of these assignments are purely tentative and based on functional group frequency approach. In the present investigation complete vibrational assignments of 2,6-diphenyl-3-methyl piperidone are made based on the results of the normal coordinate analysis and potential energy distribution values which are given in Table-2.

TABLE-2
VIBRATIONAL ASSIGNMENTS OF 2,6-DIPHENYL-3-METHYL PIPERIDONE

Species	Observed frequency (cm^{-1}) FTIR	Calculated frequency (cm^{-1})	Assignments (% PED)
a′	3326 w	3332	N—H stretching (99)
a′	3311 s	3316	N—H stretching (100)
a′	3095 w	3098	C—H stretching (99)
a′	3063 w	3069	C—H stretching (98)
a′	3029 n	3036	C—H stretching (99)
–	2963 m	1510 + 1456	C—H asymmetric stretching in CH_3
–	2908 m	1590 + 1310	C—H symmetric stretching in CH_3
–	2873 m	1510 + 1353	C—H stretching in CH_2
–	1952 w	1140 + 818	–
–	1905 w	1275 + 634	–
–	1815 vw	1005 + 818	–
a′	1707 vs	1701	C═O stretching (100)
a′	1650 m	1642	C═O stretching (99)
–	1624 m	956 + 660	–
a′	1608 w	1614	C—N stretching (96)
a′	1590 w	1582	C—N stretching (97)
a′	1540 w	1531	C—C stretching (98)
a′	1510 w	1502	C—C stretching (96)
a′	1493 ms	1488	C—C stretching (97)
a′	1456 ms	1455	C—C stretching (100)
–	1441 ms	1026 + 421	CH_3 deformation
–	1417 m	795 + 720	CH_2 scissoring
a′	1376 ms	1364	C—N stretching (94)
a′	1353 m	1340	C—N stretching (92)
a′	1326 m	1318	C—N stretching (97)
a′	1310 m	1302	C—C stretching (100)
a′	1294 m	1287	N—H in-plane-bending (88)
a′	1275 m	1268	N—H in-plane-bending (86)
a′	1216 m	1202	C—H in-plane-bending (88)
a′	1140 m	1131	C—H in-plane-bending (84)
a′	1094 m	1088	C—H in-plane-bending (82)
a′	1069 m	1054	C—H in-plane-bending (86)
a′	1026 m	1021	C—C—C trigonal bending (89)
a′	1005 m	992	C—C—C trigonal bending (84)
a′	957 vw	947	C—C stretching (breathing) (82)
a″	924 m	912	N—H out-of-plane bending (78)

Species	Observed frequency (cm^{-1}) FTIR	Calculated frequency (cm^{-1})	Assignments (% PED)
a″	818 m	824	N—H out-of-plane bending (74)
a″	795 m	802	C—H out-of-plane bending (76)
a″	784 m	778	C—H out-of-plane bending (72)
a″	766 s	760	C—H out-of-plane bending (78)
a″	750 s	759	C—C—C out-of-plane bending (66)
–	740 w	1140 – 402	CH_2 rocking
a″	720 w	699	C—C—C out-of-plane bending (64)
a′	600 s	652	C—N—C in-plane bending (82)
a′	634 w	626	C=O in-plane bending (86)
a′	614 w	604	C=O in-plane bending (88)
a″	586 w	574	C—C—N out-of-plane bending (69)
a″	510 w	501	C—N—C out-of-plane bending (66)
a″	463 w	454	C—N—C out-of-plane bending (62)
a″	438 w	420	C—C—O out-of-plane bending (59)
a″	421 w	411	C=O out-of-plane bending (61)
a″	402 w	389	C=O out-of-plane bending (68)

N—H Vibrations: Bands observed at 3326 and 3311 cm^{-1} are assigned to (N—H) stretching vibrations. A small shift of frequency from the characteristic value of (N—H) group is due to the carbonyl group associated with the (N—H) group in the compound. Normally the intensity of the (N—H) band is strong in this region for piperidones. But in the recorded spectra, it is observed that the peak at 3326 cm^{-1} is less intense and the peak at 3311 cm^{-1} is strong intense. The reduction in intensity is due to the nature and position of the substituents. In the present compound, the methyl group attached in the third position of the piperidone is responsible for the reduction of intensity of the band at 3326 cm^{-1}. This interpretation has also been confirmed by the literature[5]. The in-plane and out-of-plane bending vibrations of the N—H group were identified at 1510 and 818 cm^{-1} respectively.

C—H Vibrations: According to Bellamy the presence of multiple bands in the region 3100–3000 cm^{-1} is due to C—H stretching vibrations. The compound chosen for the present investigation belongs to cyclohexanone group and therefore the bands due to (C—H) group normally appear to the right of 3100 cm^{-1}. The aromatic phenyl group attached with the second and sixth positions of the cyclohexanone is also confirmed by these bands. In the present study the IR bands observed at 3095 cm^{-1}, 3063 cm^{-1} and 3029 cm^{-1} have been assigned to (C—H) stretching vibrations. The medium IR bands observed at 2963 cm^{-1} and 2908 cm^{-1} are assigned to (C—H) asymmetric and symmetric stretching vibrations respectively in methyl group. The assignments proposed for this group are also supported by the literature[6]. The (C—H) in-plane and out-of-plane bending vibrations are given in Table-2.

C=O Vibrations: A great deal of structural information of a molecule can be derived from the exact position of the carbonyl stretching absorption peaks. The interaction of the carbonyl group with a hydrogen donor group does not produce such a drastic change in the frequency of (C=O) stretch as done by the interaction of N—H stretch. The carbonyl group at the fourth position of cyclohexane ring may interact with the other groups of the molecule and give rise to a complex pattern of spectrum. In general, the characteristic (C=O) stretching vibrations of cyclic ketones are found over a relatively wide range depending on the ring size. The ring size of the cyclic ketone can also be established in this way. In the vibrational analysis of 2,6-diphenyl-4-piperidone, Ramasamy *et al.*[5] identified the carbonyl stretching vibrations at 1694 cm^{-1}. In the present investigation the (C=O) stretching vibrations of 2,6-diphenyl-3-methyl piperidone have been identified at 1707 cm^{-1}. If a compound contains a carbonyl group, the absorption caused by (C=O) stretching is generally among the strongest present. Accordingly the present compound has shown a very strong absorption peak at 1707 cm^{-1}. A frequency shift of 13 cm^{-1} between 2,6-diphenyl-4-piperidone and the present compound is due to the ring strain. The frequency increases with ring strain[7]. Hence it may be confirmed that the title compound undergoes more strain.

Carbon-Carbon Vibrations: The IR bands observed between 1650–1540 cm^{-1} are due to C=C stretching vibrations. These assignments are made in accordance with the assignments proposed by Varsanyi[8].

Group Vibrations: The assignments of scissoring, rocking and twisting modes of CH_3 and CH_2 groups are given in Table-2 and these assignments are in good agreement with the literature values.

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