Asian Journal of Chemistry Vol. 9, No. 1 (1997), 30–40

Molecular Mechanics, Laser Raman and Infrared Studies of 1-Hetera-2,6-diphenyl-3-alkyl-4-piperidone

R. SAMBATHU*, P. KOLANDAIVEL and M. JAMBULINGAM†
Department of Physics
Bharathiar University
Coimbatore-641 046, India

Raman and infrared spectra of solid 1-hetera-2,6-diphenyl-3-methyl-4-piperidone and 1-hetera-2, 6-diphenyl-3-ethyl-4-piperidone have been measured. The vibrational assignments have been made for both the molecules. The ethyl substitute in 3-position makes a shift in the vibrational frequencies. A discussion is given on the assignment of both stronger and weaker bonds to fundamental vibrational frequencies. To study about the structure and confirmation of the above molecules, molecular mechanics calculations have been performed. The minimum energy structures of the molecules have been discussed.

INTRODUCTION

The chemical aspects such as preparation, ^1H and ^{13}C NMR and confirmation of different types of aliphatic ketones and cyclohexanones have been extensively studied by various authors[1, 2]. The preparations of different types of 3-alkyl group substituted 1-hetera-2,6-diphenyl-4-piperidone have been reported in the literature[3–6]. Simple six-membered heterocyclic ketones and the corresponding alcohols containing sulphur, oxygen, nitrogen and phosphorus as hetero atoms are observed to exist mostly in the chair confirmation[3]. The 1-heteracyclohexan-4-ones with methyl or ethyl substituent at 3-position used in the present study have been shown from their ^1H and ^{13}C NMR studies to exist in the chair confirmation with the phenyl and alkyl substituents occypying the least strained equatorial positions[7]. The following pictographic representations (Figs. 1 and 2) indicate the structural formulae clearly.

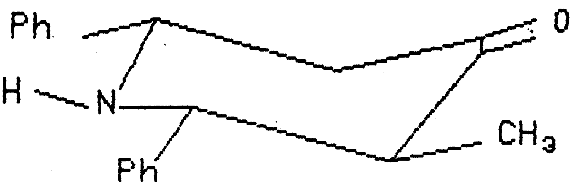

Fig. 1. 1-Hetera-2,6-diphenyl-3-methyl-4-piperidone (MP)

---

†Department of Chemistry, PSG College of Arts and Science, Coimbatore-641 014, India.

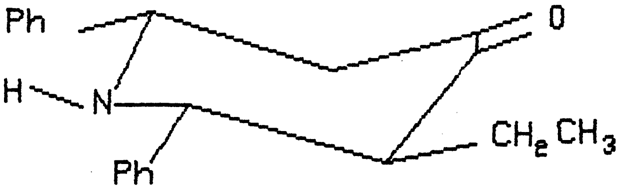

Fig. 2. 1-Hetera-2,6-diphenyl-3-methyl-4-piperidone (EP)

The aim of the present work is to study the vibrational frequencies and the confirmation of the titled compounds. The rotations of methyl and ethyl groups have been performed by using Molecular Mechanics Method, to study the confirmational preference of the molecules.

EXPERIMENTAL

The infrared spectra of 1-hetera-2,6-diphenyl-1-3-alkyl-4-piperidone have been recorded by KBr pellet technique at room temperature in the region 4000–600 cm^{-1} on a Perkin-Elmer 983 grating spectrometer. The Raman spectra of the above compounds are recorded using a Dilor Z24 Raman spectrometer equipped with argon ion laser (excitation line 4880 Å) in the region of 3500–500 cm^{-1} (Figs. 3 and 4).

MM_2 calculations have been performed on appropriate conformers, including half chair, envelop and planer forms by imposing the appropriate symmetry and then minimizing to check if the calculated conformer is a local minimum for the titled compounds. QCMPO10 software package[8] have been used for the above purpose.

RESULTS AND DISCUSSION

The observed spectra are examined assuming C_1 symmetry for the molecules. The frrequencies of infra-red and Raman spectra and the proposed assignments are presented in Table-1. In 1-hetera-2,6-diphenyl-3-alkyl-4-piperidones, four substituent groups (two phenyl and two alkyl) are very widely separated and the interactions between the internal vibrations may be small. The vibrational frequencies assigned to the phenyl part are mainly based on those proposed by the previous workers[9] in the case of mono-substituted benzenes. The characteristic frequencies of the phenyl vibrations are 3110–3018 cm^{-1} (ν_{CH}); 1970–1685 cm^{-1} (combination bands); 1598–1371 cm^{-1} (ν_{CC}); 1214–1000 cm^{-1} (ν_{CH} and ring); 985–730 cm^{-1} (ν_{CH} bending); 700–430 cm^{-1} (ring deformation).

The presence of aromatic ring structure in organic compounds was detected by a series of vibrational bands appearing in the region 1600–1350 cm^{-1} due to C═C skeletal in-plane vibrations[10]. In the present work, the infra-red bands at 1670, 1660, 1600, 1585 and 1550 cm^{-1} are assigned to C═C stretching modes. The corresponding Raman frequencies at 1620, 1610, 1585 and 1571 cm^{-1} are as observed by Chandra[11] and Steele and Lippincot[12].

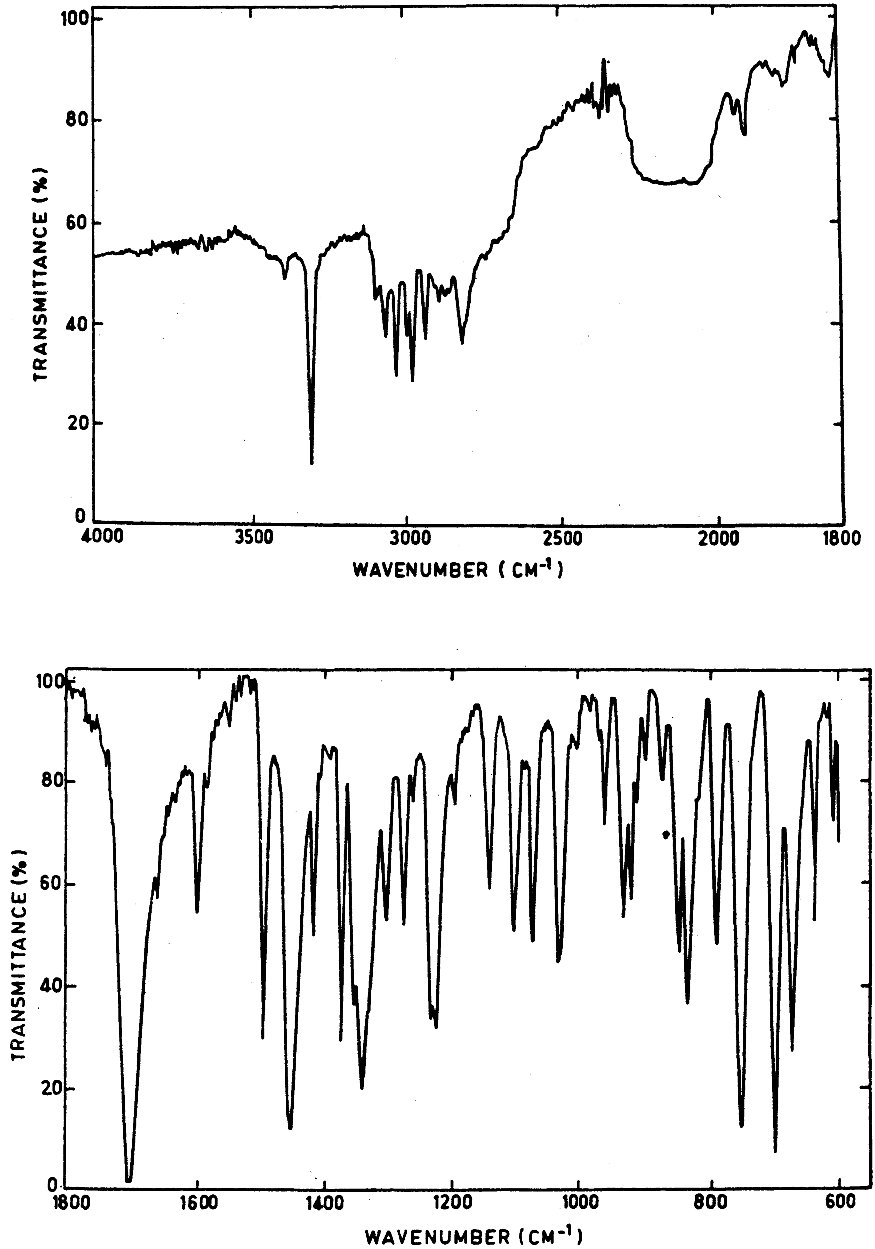

Fig. 3. Infrared spectrum of 1-hetera-2,6-diphenyl-3-methyl-4-piperidone (MP)

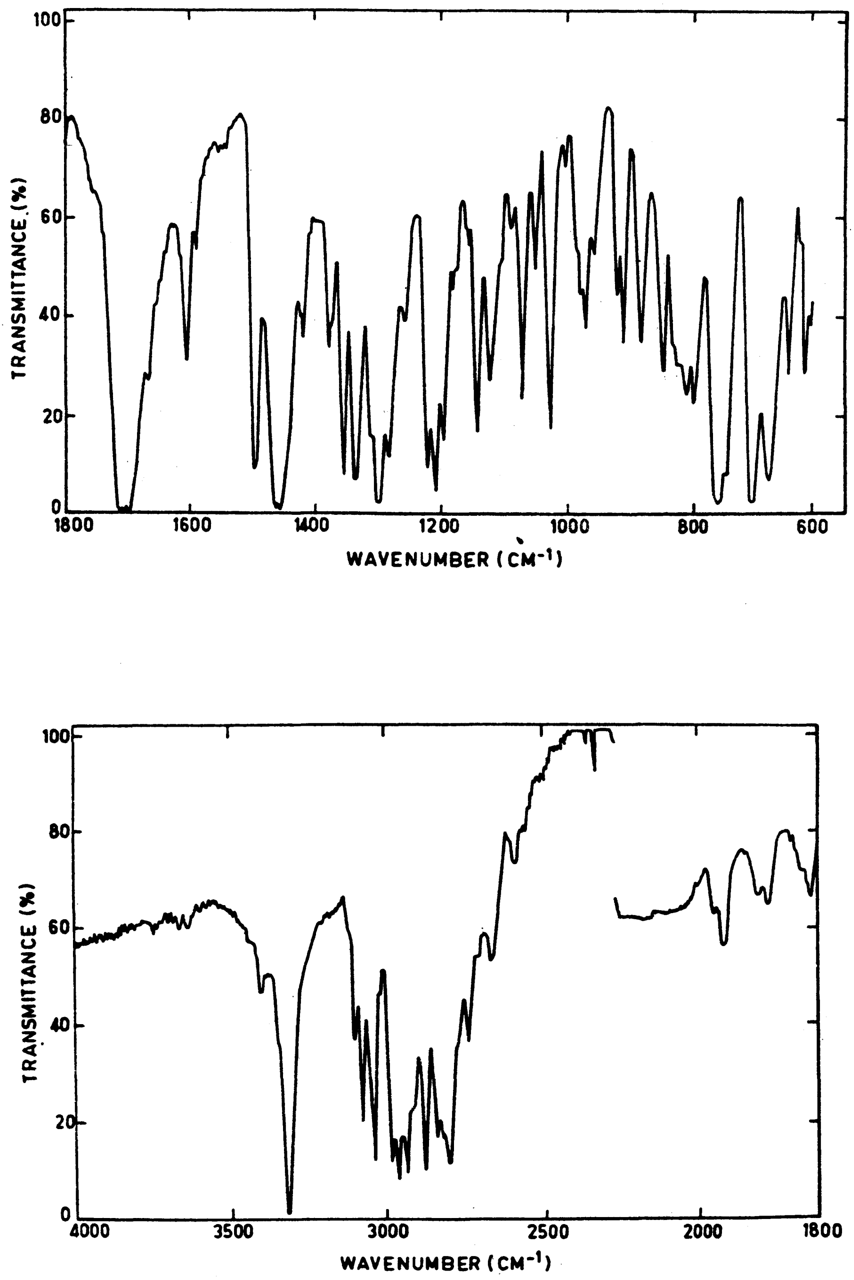

Fig. 3. Infrared spectrum of 1-hetera-2,6-diphenyl-3-ethyl-4-piperidone (EP)

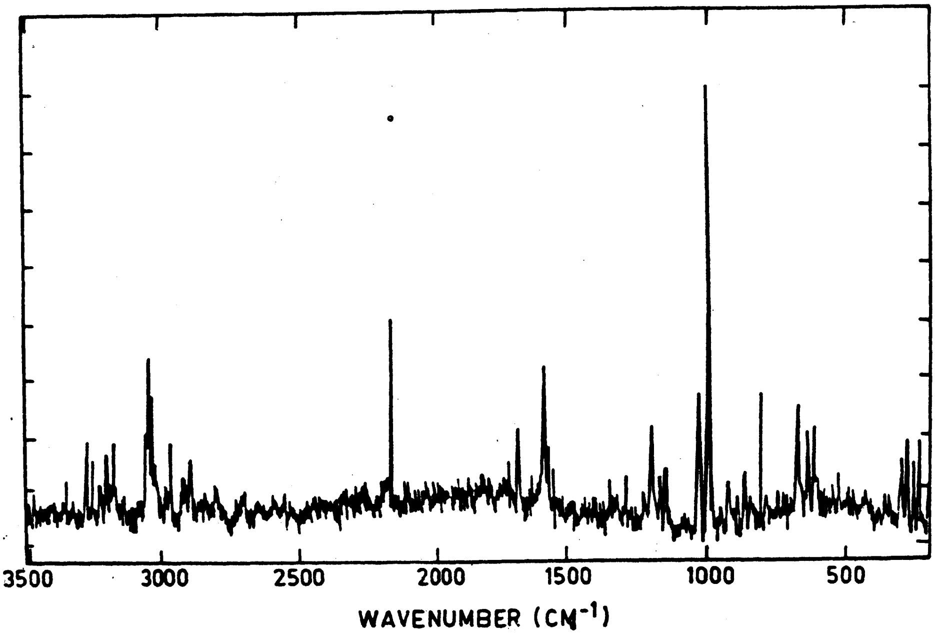

Fig. 4. Raman spectrum of 1-hetera-2,6-diphenyl-3-methyl-4-piperidone (MP)

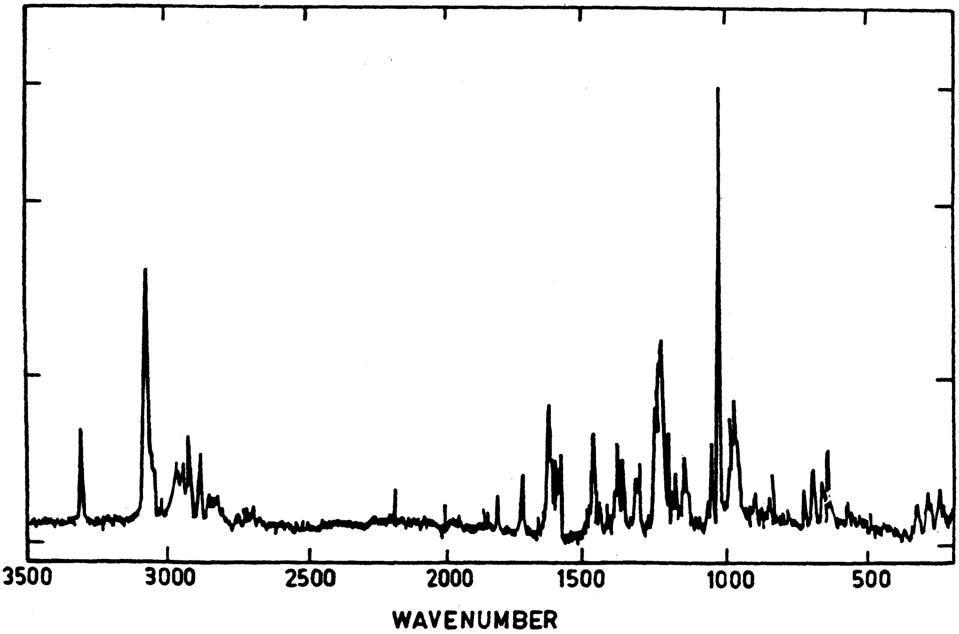

Fig. 4. Raman spectrum of 1-hetera-2,6-diphenyl-3-ethyl-4-piperidone (EP)

TABLE-1
ASSIGNMENTS OF THE VIBRATIONAL FREQUENCIES OF 1-HETERA-2,6-DIPHENYL-3-ALKYL-4-PIPERIDONE.

1-Hetera-2,6-diphenyl-3-methyl-4-piperidone		1-Hetera-2,6-diphenyl-3-ethyl-4-piperidone		Assignments
Infrared	Raman	Infrared	Raman	
3750 vw	—	3750 vw	—	N—H stretching
3660 vw	—	3660 vw	—	N—H stretching
3620 vw	—	3620 vw	—	N—H stretching
—	3480 w	—	—	N—H stretching
3400 vw	—	3400 vw	—	(2 × 1705) overtone band
—	3360 w	—	—	N—H stretching
3310 vs	—	3320 vs	3310 w	N—H stretching
—	3281 w	—	—	N—H stretching
—	3206 w	—	—	N—H stretching
—	3160 w	—	—	N—H stretching
3070 s	—	3070 s	3064 w	C—H stretching
3035 s	3032 s	3040 s	—	C—H stretching
2980 s	—	2980 w	—	Asymmetric CH_3 stretching
—	2963 w	—	—	Asymmetric CH_3 stretching
2935 s	—	2930 w	2920 w	Asymmetric CH_2 stretching
2895 vw	2890 w	2880 s	2876 w	Symmetric CH_3 stretching
—	—	2840 vw	2840 w	Symmetric CH_2 stretching
2820 s	—	2800 s	2815 w	N—CH_3 stretching
2360 w	—	2360 vw	—	1660 + 700
2330 w	2330 w	2335 vw	2305 w	1495 + 835; 1540 + 790 1350 + 980; 1070 + 1260 1225 + 1105
1975 vw	—	1975 vw	—	1300 + 670; 1000 + 970
1960 w	—	1960 w	—	* 1110 + 850
1920 vw	—	—	—	1070 + 850; 1000 + 920
1905 vw	—	—	—	1070 + 835
1890 w	—	1895 vw	—	1140 + 750; 960 + 930
1865 vw	—	—	—	1225 + 640; 1195 + 670
1840 w	—	—	—	1140 + 700
1815 w	1820 w	1810 w	1803 w	965 + 850
1705 vw	1710 w	1710 vs	1710 w	C═O stretching
1660 vw	—	1670 vw	—	C═C stretching
1600 s	1620 w	1605 s	1610 w	C═C stretching
1585 vw	1585 w	1585 vw	1571 w	C═C stretching
1550 vw	—	1555 vw	—	C═C stretching
1495 vs	1500 vw	1495 vs	—	Asymmetric CH_3 deformation
1450 vs	—	1455 vs	—	CH_2 scissors deformation

1-Hetera-2,6-diphenyl-3-methyl-4-piperidone		1-Hetera-2,6-diphenyl-3-ethyl-4-piperidone		Assignments
Infrared	Raman	Infrared	Raman	
1415 s	—	1420 w	—	CH_2 deformation
1375 vs	1390 vw	1380 s	1368 w	Symmetric CH_3 deformation
1350 vw	—	1355 vs	—	Symmetric CH_3 deformation
1340 vs	—	1340 vs	—	CH_2 wagging
1300 s	1300 w	1300 vs	1280 w	CH_2 wagging
1275 s	—	1275 vw	—	In-phase CH_2 twisting
1260 vs	—	1255 vw	—	In-phase CH_2 twisting
1225 s	—	1225 w	—	CH_2 twisting
1195 w	—	1195 w	—	C—H in-plane bending
1140 s	—	1140 vs	—	CH_3 rocking
1110 s	1120 w	1120 s	1120 w	CH_3 rocking
1070 s	1070 w	1070 s	1068 w	C—H in-plane bending
—	—	1050 s	1050 w	C—H in-plane bending
1030 vs	1026 w	1025 vs	1020 vs	Ring breathing
960 s	968 vw	970 s	972 w	N—H out-of-plane bending
930 s	—	—	—	C—H out-of-plane bending
920 s	--	915 s	—	C—H out-of-plane bending
875 w	861 w	885 s	875 w	C—C—C in-plane bending
850 s	—	850 s	—	C—C—C in-plane bending
835 vs	—	—	—	C—C—C in-plane bending
790 s	—	800 s	—	C—C—C in-plane bending
—	—	760 s	—	Aromatic C—H Wagging
750 vs	750 vw	745 vs	755 w	Aromatic C—H Wagging
700 vs	—	700 vs	—	C—N bending
670 vs	—	670 s	—	N—H out-of plane bending
640 s	—	640 s	—	C—H out-of-plane bending
610 s	615 w	610 s	615 w	C—H out-of-plane deformation
—	575 vs	—	563 vw	C—C linkage
—	527 vw	—	—	C—C linkage
—	485 vw	—	472 vw	C—C linkage
—	415 vw	—	430 vw	C—C linkage
—	375 vw	—	—	** C—C linkage
—	360 vw	—	353 vw	C—C linkage
—	300 vw	—	318 vw	C—C linkage
—	276 w	—	289 vw	C—C linkage
—	228 w	—	242 vw	C—C linkage
—	195 vw	—	—	C—C linkage

*Combination bands **Bending and torsional motions of C—C linkages.
vw–very weak; w–weak; s–strong; vs–very strong

The strong bands at 1030 cm^{-1} in IR and 1026 cm^{-1} in Raman *in 1-hetera-2,6-*diphenyl-3-methyl-4-piperidone (MP) and at 1025 cm^{-1} in IR and 1020 cm^{-1} in Raman in 1-hetera-2,6-diphenyl-3-ethyl-4-piperidone (EP) have been assigned to ring breadthing mode. This is in agreement with the literature values[13].

C—H Vibrations

The 2,6-dichloropyridine (three hydrogen atoms are left around the ring) gives rise to two C—H stretchings, five C—H out-of-plane deformations and two (C—H) in-plane bendings. The hetero-aromatic structure shows the presence of C—H stretching vibrations in the region 3100–3000 cm^{-1} which is the characteristic region for the ready identification of this structure. In this region the bands are not affected appreciably by the nature of substituents.

In benzene derivative, studies show that the C—H stretching frequencies arise from the modes a_{1g} (3070 cm^{-1}), e_{2g} (3035 cm^{-1}) and e_{1u} (3040 cm^{-1}) and two degenerate modes e_{2g} (1195 cm^{-1}) and e_{1u} (1070 cm^{-1}) and two non-degenerate modes b_{2u} (1068 cm^{-1}) and a_{2g} (1050 cm^{-1}) vibrations involving C—H in-plane bending[14]. Thus, the frequencies at 1275, 1260, 1225, 1195, 1140, 1110 and 1070 cm^{-1} (IR) have been assigned to C—H in-plane bending modes. These assignments agree well with the values given in the literature[10, 15, 16]. Evidence is presented to show that the stronger IR absorption bands from 2000 to 1650 cm^{-1} in benzene derivatives normally arise from summation tones of the out-of-plane C—H bending vibrations[17]. The C—H out of plane deformation modes arise from b_{2g} (985 cm^{-1}), e_{2u} (970 cm^{-1}), e_{1g} (850 cm^{-1}) and a_{2u} (671 cm^{-1}) modes of benzene and they are expected to occur in the region 600–1000 cm^{-1}.[18, 19]

The vibrational bands at 2980 cm^{-1} in IR and 2963 cm^{-1} in Raman correspond to the asymmetric CH_3 stretching and the bands at 2935 cm^{-1} and 2930 cm^{-1} (IR) in MP and EP and at 2920 cm^{-1} (Raman) in EP correspond to asymmetric CH_2 stretching vibrations[20, 21]. The symmetric CH_3 and CH_2 vibrations absorb at 2880 cm^{-1} and 2830 cm^{-1} respectively. This agrees well with the values of Fox[20] and Wiberley[22]. Presently, bands at 2895 cm^{-1} in IR and 2890 cm^{-1} in Raman in MP, and 2880 cm^{-1} in IR and 2876 cm^{-1} in Raman in EP have been assigned to symmetric CH_3 stretching modes. The bands at 2840 cm^{-1} in IR and Raman in EP are due to symmetric CH_2 stretching in ethyl substituent in 3-position of the piperidone ring. This band is not present in 3-methyl-4-piperidone. Methyl group on nitrogen[23, 24] absorbs near 2800 cm^{-1}. The strong bands at 2820 cm^{-1} and 2800 cm^{-1} in IR and its counterpart 2815 cm^{-1} in Raman are assigned to N—CH_3 stretching vibrations.

The asymmetric CH_3 deformmation absorbs near 1465 cm^{-1} and the symmetric deformation near 1375 cm^{-1}.[25] The IR band at 1495 cm^{-1} in both compounds and the Raman band at 1500 cm^{-1} have been assigned to asymmetric CH_3 deformations. The bands at 1375 cm^{-1} and 1350 cm^{-1} in MP and 1380 cm^{-1} and 1355 cm^{-1} in EP (IR) and 1390 cm^{-1} in MP and 1368 cm^{-1} in EP (Raman) are assigned to symmetric CH_3 deformations. The bands at 1450 cm^{-1} in MP and 1455 cm^{-1} in EP in IR are due to asymmetric CH_2 deformation and at 1415 cm^{-1} in MP and 1420 cm^{-1} in EP in IR are due to symmetric deformations[26, 27]. In the normal hydrocarbons, a CH_2 wagging vibration absorbs near 1310 cm^{-1}.[28] Presently, the CH_2 wagging vibrations lie at 1340 cm^{-1} and 1300 cm^{-1} in IR and 1300 cm^{-1} in MP and 1280 cm^{-1} in EP in Raman in both the compounds.

Piperidone ring

Bands in the region from 3700–3100 cm^{-1} are usually due to various OH and NH stretching vibrations[29]. Hence, the weak bands at 3750, 3660, 3620 and 3310 cm^{-1} in IR and at 3480, 3360, 3310, 3281, 3206 and 3160 cm^{-1} in Raman are due to N—H stretching vibrations. These bands may be due to the presence of some unmethylated 4-piperidone as impurity. A very strong line in the region 1705 cm^{-1} in MP and 1710 cm^{-1} in EP in IR and its counterpart in the region 1710 cm^{-1} in Raman in both testing compounds are corresponding to C═O stretching vibrations[30]. The vibrational bands near 1660, 1600, 1585 nad 1550 cm^{-1} in IR and near 1620 and 1585 cm^{-1} in Raman are assigned to C═C stretching vibrations as reported by Kamaraj[31].

The vibrational bands at 1260 and 1225 cm^{-1} in IR in both compounds have been assigned to CH_2 twisting. The frequencies in the region 2360–1915 cm^{-1} are corresponding to the overtones and combination bands for the characteristics of monosubstituted benzene compounds as reported by Whiffen[17], Young *et al.*[32] and Bellamy[33].

Additional (nonfundamental) absorption bands may occur because of the presence of overtones (with greatly reduced intensity), combination bands (the sum of two or more different wavelengths) and difference bands (the difference of two or more different wavelengths).

The bands at 875, 850, 835 and 790 cm^{-1} absorptions in IR and 861 cm^{-1} band in MP in Raman and 885, 850 and 800 cm^{-1} absorptions in IR and 875 cm^{-1} band in EP in Raman have been assigned to C—C—C in-plane bending modes. The above assignment agrees well with the existing literature values[34, 35]. In both compounds, the absorption bands near 750 cm^{-1} in IR and Raman are due to aromatic (C—H) wagging as observed by Kamaraj[31]. A strong band at 670 cm^{-1} in IR corresponds to N—H out-of-plane bending and this may be due to the unmethylated piperidone impurity. The IR bands at 640 and 610 cm^{-1} in MP and EP are assigned to C—H out-of-plane bending. The various weak bands observed below 600 cm^{-1} in Raman in both compounds are probably associated with bending and torsional motions of C—C bond linkages as Duncan *et al.*[36] observed.

The structural parameters for the minimum energy confirmation of the 1-hetera-2,6-diphenyl-3-alkyl-4-piperidone are computed. The computed bond lengths and bond angles are having reasonable agreements with the experimentally observed values (available with authors). The final steric energy, van der Waals energy and dipole moments of the molecules are presented in Table-2. It is obtained in general when the steric energies increased; changes are noted in the variations of dipole moments and bendings and increase in the case of van der Waals energies. Also, it is observed that bond angles increase with the increase of steric energies whereas the stretch-band energies remain unchanged for both the molecules.

TABLE-2
MINIMUM ENERGY CONFIRMATION

1-Hetera-2,6-diphenyl-3-methyl-4-piperidone	
Final steric energy is	9.4601 Kcals
Compression	1.1098
Bending	2.5803
Stretch-bend	0.1259
Van der Waals 1,4-energy	17.5333
Torsional	–8.0646
Dipole moment	3.091 D
1-Hetera-2,6-diphenyl-3-ethyl-4-piperidone	
Final steric energy is	8.4058 Kcals
Compression	1.1222
Bending	1.7740
Stretch-bend	0.1316
Van der Waals 1,4-energy	18.3831
Torsional	–7.4032
Dipole moment	3.099 D

In the present investigation, the methyl group (CH_3) of 1-hetera-2,6-diphenyl-3-methyl-4-piperidone which is having interaction with carbon atom ($C—CH_3$) has been rotated from 0 to 360°. For each angle, the steric energy value has been calculated. Similarly, for the molecule, 1-hetera-2,6-diphenyl-3-ethyl-4-piperidone, the ethyl group (CH_2CH_3) which is having interaction with carbon atom ($C—CH_2CH_3$) has been rotated from 0 to 360° and the final steric energy values have been obtained. The detailed study of this will be published elsewhere.

The dipole moments of polyfunctional polar molecules are difficult to predict in molecular mechanics programmes due to the presence of induced dipole and dipole-dipole interactions[37, 38]. In the present work, the determined dipole moments largely depend on the electrostatic interactions. However, attempts have been made to reproduce accurate dipole moments, simultaneously with energies and geometries. It has been observed that if the steric energy changes, the van der Waals energy and the dipole moments are also changed. The theoretically predicted values ae having reasonable agreements with the available experimental values.

ACKNOWLEDGEMENT

Authors are thankful to Aruljothi Computer Centre, Coimbatore for providing facilities for the computational works and neat typing.

REFERNECES

1. S.F. Tayyani, Th. Zeegens-Huyskers and J.L. Wood, *Spectrochim. Acta*, **35A**, 1265 (1979).
2. Waleed A. Lik, Al-Rashid and Mohsin F. El-Bermani *Spectrochim. Acta*, **47A**, 35 (1991).
3. K. Ramalingam, K.D. Berlin, N. Satyamurthy and R. Sivakumar, *J. Org. Chem.*, **44**, 471 (1979).

4. B. Harikrishnan and E.V. Sundaram, *Indian J. Chem.*, **16A**, 322 (1978).
5. P.S. Radhakrishnamurthy and Ramakrishna Panda, *Indian J. Chem.*, **8**, 949 (1970).
6. Arthur I. Vogel, A Text-book of Practical Organic Chemistry including Qualitative Organic Analysis, ELBS and Longmans-Green Co. Ltd., 3rd Ed. (1968).
7. P. Nanjappan, K. Ramalingam, M.D. Herd, P. Arujanan and K.D. Berlin, *J. Org. Chem.*, **45**, 4622 (1980).
8. N.L. Allinger and Y.H. Yuh, Quantum Chemistry Program Exchange, University of Georgia, Athens (1980).
9. V.B. Singh and I.S. Singh, *Indian J. Pure and Appl. Phys.*, **6**, 81 (1968).
10. S. Mohan and N. Sundaraganesan, *Spectrochim. Acta.*, **47A**, 1111 (1991).
11. K. Chandra, *Indian J. Pure and Appl. Phys.*, **4**, 213 (1966).
12. D. Steele and E.R. Lippincott, *J. Mol. Spectroscopy*, **6**, 238 (1961).
13. B.B. Lal. M.P. Srivastava and I.S. Singh, *Indian J. Pure and Appl. Phys.*, **11** 615 (1973).
14. A.R. Katritsky, *Quart. Rev.*, **13**, 353 (1959).
15. E.F. Moorey, *Spectrochim. Acta*, **20**, 1343 (1964).
16. G. Joshi and N.L. Singh, *Spectrochim. Acta*, **23A**, 1341 (1967).
17. D.H. Whiffen *Spectrochim. Acta*, **7**, 253 (1955).
18. H.W. Thomson and R.B. Temple, *J. Chem. Soc.*, 1432 (1948).
19. G. Varsanyi, *Acta Chim., Hung.*, **50**, 225 (1966).
20. J.J. Fox and A.E. Martin, *Proc. Roy. Soc. (London)*, **A167**, 257 (1938).
21. G.A. Noville and H.F. Shurvell, *J. Raman Spectroscopy*, **21**, 9 (1990).
22. S.E. Wiberley, S.C. Bunce and W.H. Baver, *Anal. Chem.*, **32**, 217 (1960).
23. R.D. Hill and G.D. Meakings, *J. Chem. Soc.*, 760 (1958).
24. W.B. Wright, Jr., *J. Org, Chem.*, **24**, 1362 (1959).
25. H.L. Mcmurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).
26. Gerd Schrumpt and Thomas Alshuth, *Spectrochim. Acta*, **43A**, 939 (1987).
27. A.O. Diallo and D.N. Waters, *Spectrochim. Acta*, **44A**, 1109 (1988).
28. H.B. Henbest, G.D. Meakins, B. Nicholls and K.J. Taylor, *J. Chem. Soc.*, 1459 (1957).
29. Norman B. Colthup, Lawrance H. Daly and Stephen E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press. New York, p. 319 (1975).
30. C.N.R. Rao, G.K. Goldmann and C. Hurie, *J. Phy. Chem.*, **63**, 1311 (1959).
31. V. Kamaraj, Ph.D. Thesis, University of Madras (1987).
32. C.W. Young, R.B. Duvall and N. Wright, *Analyt. Chem.*, **23**, 709 (1951).
33. L.J. Bellamy, The Infra-red Spectra of Complex Molecules, Methuen, London (1954).
34. R. Golse and L.V. Thol, *Comp. Rend. Acad. Sci. Paris*, **230**, 210 (1950).
35. D.F. Eggers and W.E. Lingen, *Anal. Chem.*, **28**, 1328 (1956).
36. A.B.F. Duncan, W. Gordy, R. Norman Jones, F.A. Matsen, C. Sandorty and W. West, Chemical Applications of Spectroscopy, Interscience Publishers New York, 1st Ed., p. 351 (1967).
37. U. Burkert and N.L. Allinger, Molecular Mechanics, American Chemical Society, Washington, D.C. (1982).
38. A.Y. Meyer, N.L. Allinger and Y. Yuh, *Isr. J. Chem.*, **20**, 57 (1980).

(*Received*: 30 April 1996 *Accepted*: 16 August 1996) AJC-1149