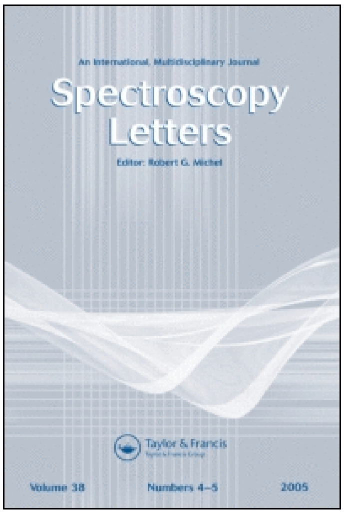

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On the Ground State Frequencies of Some Deriva Tives of 1,3,5,8-Tetra-Azanaphthalene

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ON THE GROUND STATE FREQUENCIES OF SOME DERIVATIVES OF 1,3,5,8-TETRA-AZANAPHTHALENE

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ABSTRACT

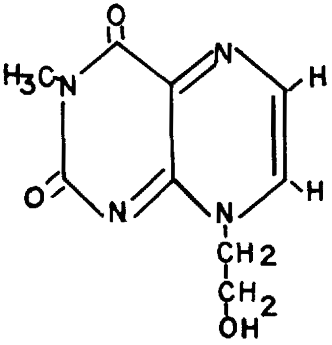
The infrared spectra of three derivatives of 1,3,5,8-Tetra-azanaphthalene viz., 3-Methyl-8-hydroxyethyl-lumazine, 6,7,8-Trimethyllumazine and 2-Dimethylamino-6,7-diphenylpterine have been determined in the region 400 - 4000 cm^{-1} and correlated. Band assignments of these complex molecules are discussed in relation to those of naphthalene, azanaphthalenes and their derivatives. The shifs occuring in symmetric and antisymmetric stretching and symmetric deformation frequencies of C-H in methyl group when attached to the nitrogen have been examined in relation to the structure of the molecules. A strong intermolecular hydrogen bonding in 3-Methyl-8-hydroxy ethyl lumazine and 2-Dimethylamino-6,7-diphenyl pterine has been observed.

INTRODUCTION

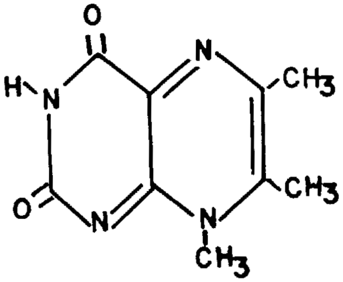
Among the most interesting problems of science to date are determination of the structure and properties of substances of biological importance. Of great significance is the investigation of hydrogen bonding, resonance, isomaric changes, tautomeric equilibria etc. Vibrational spectroscopy provides a sensitive probe formany such biomolecular interactions of interest. The present investigation concerns with the study of infrared spectrum of three biological pigments namely 3-Methyl-8-hydroxyethyllumazine, 6,7,8-Trimethyl lumazine and 2-Dimethylamino-6,7-diphenylpterine (hereafter called compounds A,B and C respectively as shown in Fig. 1) making an assessment of the possibilities of hydrogen bond formation and other effects mentioned above.

EXPERIMENTAL

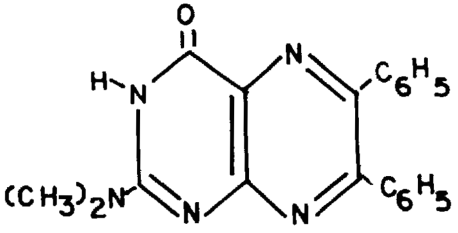
All the compounds were synthesised in pure form by one of us in the Chemical Laboratory, University of Konstauz, West Germany (unpublished work). These compounds were in solid form. The infrared spectra were recorded by dispersing them in KBr dises on double beam grating spectrophotometer model Beckman IR-12 in the region 400 - 4000 cm^{-1}. The accuracy of the frequency measurements was estimated at several specific frequencies to be within ± 0.3 cm^{-1} at 400 cm^{-1}, ± 0.4 cm^{-1} at 740 cm^{-1}, ± 0.6 cm^{-1} at 1330 cm^{-1}, ± 0.7 cm^{-1} at 2220 cm^{-1} and ± 0.8 cm^{-1} at 4000 cm^{-1}. The slit programming was normal.



3-METHYL-8-HYDROXYETHYL LUMAZINE



6,7,8-TRIMETHYL LUMAZINE



2-DIMETHYL AMINO-6,7-DIPHENYLE PTERINE

FIG-1

RESULTS AND DISCUSSION

The frequencies observed are listed in Table 1. All the compounds under present investigation are highly unsymmetrical, therefore all vibrations are allowed in both infrared and Raman spectrum. Further the skeltal motions in azanaphthalenes are practically the same as that of naphthalene, but their intensity and position may differ according to the nature and position of the substituents. A number of band assignments can thus be made on the basis of similarly substituted naphthalenes and azanaphthalenes.

Ring Vibrations

Out of the four bands usually found in the range 1620 - 1560 cm^{-1} and five bands in the range 1500 - 1350 cm^{-1} as ring stretching vibration in naphthalene, azanaphthalenes and most of their derivatives[1,2,3,4,5,6], only two bands in the first range and one band in the second range have been observed in all the three compounds. Their counterpart bands in naphthalene[1] are belonging to the species B_{1g} and A_g respectively. However the two bands in compound B at 1510 cm^{-1} and 1390 cm^{-1} may be due to skeletal stretching mode and can be correlated with the species B_{3u} and A_g of naphthalene. The other ring vibrations are shown in table 1 and their probable mode of vibrations are indicated therein. The larger shift in ring modes observed does indeed indicate considerable coupling with the CO group.

Group frequencies

Carbonyl group:

The compounds A and B belong to the class of compounds containing the group CO-NH-CO in cyclic materials generally designated as cyclic discyclimides. The diacyclimides have been extensively studied by Randall et al[7] and the carbonyl frequencies well characterised. The carbonyl frequencies observed by Randall et al were in the range 1720 - 1780 cm^{-1} for the 4 position carbonyl and in the range 1655 - 1712 cm^{-1} for the 2 position carbonyl group. In the present investigation the two carbonyl frequencies in compounds A and B were identified with one lying between 1720 - 1760 cm^{-1} attributed to 4 position and the other between 1690 - 1695 cm^{-1} correlated with 2 position carbonyl group (Table 1). From Table 1 it is apparent that the 4 position carbonyl frequency in compound A is less by 40 cm^{-1} than the corresponding 4 position carbonyl frequency in compound B. This lowering of the frequency may be due to the presence of CH_3 group at 3 position in compound A. Our results agree fairly well with those obtained by Culbertson et al[6] for alkylated quinazalones substituted at 2 or 3 position or both.

In compound C the 4 position stretching frequency of carbonyl group has, however, been obtained at 1670 cm^{-1}. Although a slight shifting may occur in carbonyl stretching frequency due to vibrational coupling with NH deformation

TABLE 1

VIBRATIONAL ASSIGNMENTS OF THE FUNDAMENTAL FREQUENCIES OF THREE DERIVATIVES OF 1,3,5,8-TETRA-AZANAPHTHALENE

Frequencies in waves numbers			corresponding frequencies in naphthalene cm^{-1}	Species D_{6h}	Modes of vibration
3-Methyl-8-hydroxy ethyl Lumazine	6,7,8-Trimethyl Lumazine	2-Dimethyl amino-6,7-diphenyl Pterine			
	420(vs)				
435(vs)	430(vs)	430(vs)	400	A_u	op skeletal distortion
460(vs)	450(vs)	450(vs)	475	B_{1u}	op skeletal bending
470(s)					
520(vs)	495(vs)	500(vs)	512	A_g	ip skeletal distortion
		540(s)			
560(vs)	530(vs)	555(vs)			
580(vs)	565(vs)	580(vs)	581	B_{3u}	ip skeletal distortion
630(s)					
670(vs)	620(vs)	670(vs)	620	B_{2u}	ip skeletal distortion
	720(ms)	710(ms)			CH out of plane bending
		740(mw)			CH out of plane bending
770(s)	775(s)	765(s)	762	A_g	ip skeletal distortion

810(s)		795(s)			op CH bending
		810(s)			2x420, 2x430
870(s)	845(s)	875(s)	876	B_{3u}	Skeletal breathing
	900(s)	905(s)			495+430, 500+430
950(w)		950(w)			2x460, 2x450
985(s)	1000(s)	1010(s)			
1050(s)	1035(s)	1030(s)	1024	A_g	Skeletal breathing
1060(s)	1080(s)	1080(s)			
1120(w)					
1170(ms)		1160			CH planar deformation
1215(s)	1200(s)				
1240(vs)	1230(vs)	1230(vs)			N-CH_3 stretching
1290(s)	1265(s)	1270(s)			
		1300(ms)			C-N stretching
1340(ms)					
1355(ms)	1350(ms)	1360(vs)			CH_3 symmetric deformation
	1390(ms)		1379	A_g	CC stretching

Continued.

Table 1 continued

1365(w)) 1380(w)) 1395(w)) 1430(w))					Arising due to interaction of OH and CH_3 groups.
1450(s)) 1460(s))	1410(s)) 1450(ms))	1430(s)) 1440(s))			CH_3 Antisymmetric deformation.
1510(sh)		1500(ms)			2x770, 2x765
1540(s)	1500(s)	1540(s)	1576	A_g	CC stretching
	1510(s)		1508	B_{3u}	CC stretching
	1525(s)				2x775
1610(ms)	1605(ms)	1590(ms)	1586	B_{1g}	CC stretching
1635(vs)	1620(vs)	1610(vs)	1625	B_{1g}	CC stretching
	1630(vs)				NH deformation
		1625(s)			2x810
1695(s)	1690(s)				C_2=0 stretching vibration
1720(ms)	1760(ms)	1670(s)			C_4=0 stretching vibration
	2760(ms)				2x1540
2880(ms)	2820(ms)	2915(ms)			CH_3 symmetric stretching vibration attached to nitrogen.
	2850(ms)				CH_3 symmetric stretching vibration attached to carbon.
	2960(ms)				CH_3 antisymmetric stretching vibration attahced to carbon.

2960 (ms)	2980 (ms)	2980 (ms)	CH_3 antisymmetric stretching vibration attached to carbon.
3050 (ms)		3080 (ms)	CH stretching vibration
	3020 (mw)		1510 + 1500
	3080 (mw)		2 x 1510
3300 (mw)			
3360 (ms)			1695 + 1635
3390 (ms)			OH stretching vibration
	3400 (s)	3130 (s)	NH stretching vibration

s = strong, ms = medium strong, w = weak, mw = medium weak, vs = very strong.

mode[8], this large shifting may be explained assuming strong intermolecular hydrogen[9,10] bonding which is being evidenced by very low value of NH stretching (3130 cm^{-1}) frequency.

Methyl group:

The overall frequency ranges of methyl group in variously substituted tolunes, methylnaphthalenes and anthracenes, methylated polycyclic aromatics and heterocyclies[11] are ν_a^2 (2984 - 2967 cm^{-1}), ν_a^1 (2956 - 2938 cm^{-1}), ν_s(2931 - 2919 cm^{-1}), $2\delta a$(2873 - 2859 cm^{-1}), and $2\delta s$ (2830 - 2740 cm^{-1}).

Henbest et al[12] however observed that when methyl group is attached to oxygen instead of carbon, the symmetric CH_3 stretching vibration is lowered by about 50 cm^{-1} and antisymmetric CH_3 stretching vibration is raised up by about the same amount. Dalton et al[13], Hill and Meakins[14] and Braunholtz et al[15] reached at similar conclusion when CH_3 group is attached to the nitrogen atom and associated the band in the 2800 cm^{-1} region with that of CH_3 symmetric stretching mode but with one important reservation. They pointed out that the medium to strong band does not normally occur in this region as symmetric mode of $-N-CH_3$ or $-N-(CH_3)_2$ groups for molecules in which nitrogen lone pair of electron is no longer present as such i.e. when it is fully involved in bond formation.

A medium strong band is present at 2820 cm^{-1} in compound B in which CH_3 group is attached to the nitrogen atom present in the ring at 8 position, whereas no such band was observed in compound A where CH_3 group is attached to ring nitrogen at 3 position and in compound C in which two methyl groups are attached to the same nitrogen of amino group attached to the ring at 2 position (see Fig. 1). In view of the above facts it may therefore be concluded that in compounds A and C the nitrogen lone pair electrons are somehow involved in bond formation. A medium strong band at 2740 cm^{-1} may be taken as overtone of symmetric methyl deformation ($2 \times \delta_s$ = 2660 cm^{-1}). In compounds A and C any band around it is undetectable. The intensification of the band in compound B may be due to the fact that it has picked up the appreciable intensity from its ee closest CH fundamental (2820 cm^{-1}) through Fermi resonance[11]. The two strong bands at 2850 cm^{-1} and 2960 cm^{-1} in compound B may be correlated to symmetric and antisymmetric modes of CH_3 attached to the carbon atom of the ring.

Although a corresponding shift of symmetric deformation mode of methyl nitrogen compounds has been less studied, we have noted the similar trend of shift (1355 cm^{-1} in A, 1330 cm^{-1} in B and 1360 cm^{-1} in C) as discussed above. No splitting of CH_3 symmetric deformation mode in compound C has been observed indicating thereby that the angle between two methyl groups attached to the same nitrogen atom is very small. Further a pair of frequencies in all the three compounds noted in the range 1410 - 1460 cm^{-1} may however be correlated with asymmetric deformation mode of the CH_3 group[16]. However overall slight shifting in the frequencies may be due to the presence of corbonyl as a polar group in the ring[11].

Hydroxyl group :

In most of the alcohols the OH for monomers, dimers and polymers occurs at 3642, 3434 and 3346 cm^{-1} respectively[17,18]. A broad band near 3400 cm^{-1} in compound

A is an indication of the hydrogen bonding of the type OH ... OH. The band at 1120 cm^{-1} may be due to OH planar deformation mode. The weaker frequencies in the region 1365 - 1430 cm^{-1} in compound A are probably arising due to interaction of OH bonding with the adjacent methyl group.[19]

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