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NOTES

Synthesis, Infrared Spectra and Normal Coordinate Analysis of 3-Bromo-7,8 Benzochromanone

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The infrared and Fourier far infrared spectra of synthesized compound 3-bromo-7,8 benzochromanone has been recorded in the range 600–4000 cm^{-1} and 100–600 cm^{-1}. The observed frequencies have been assigned to various modes of vibrations on the basis normal coordinate calculations.

The benzopyran nucleus is a widely prevalent ring system being present in a variety of naturally-occuring compounds like chromanones, xanthones, flavones etc. Several naturally occuring 4-chromanones isolated from plants have evinced considerable interest in terms of their biological importance and potentials as drugs. These compounds are potential synthons for the construction of many important oxygen heterocycles. The pharmacological activity of many derivatives of 4-chromanones have been extensively investigated[1–4]. Recently Ravikumar *et al*[5] have investigated the crystal structure of the title compound. However the vibrational analysis of 3-bromo-7,8 benzochromanone using Infrared data has not been reported so far. In the present paper the normal coordinate treatment was carried out in order to support the assignments of the fundamentals.

The title compound was synthesised by the method of kasturi *et al*[6]. "The infrared spectra of 3-bromo-7,8 benzochromanone has been recorded in Perkin Elmer IR 781 double beam grating spectrophotometer in the region 600–4000 cm^{-1}. The Fourier far infrared spectra have also been recorded for the above compound using Polytech FIR 30 in the region 100–600 cm^{-1}. The normal coordinate calculations were performed using the program given by Schachtschneider[7]. The valence force field was used for both in-plane and out-of-plane vibrations. The initial force constants were taken from benzene derivatives. The calculated frequencies were close to the observed values, lending confidence to the assignments mode.

The observed frequencies of 3-bromo-7,8 benzochromanone along with their relative intensities and probable assignments are presented in Table 1. The observed spectra are explained on the basis of C_s point group symmetry which leads to two types of vibrations distributed as Γ vib=28 A′ +11 A″. All vibrations are active in infrared.

In general the bands around 1400 cm^{-1} to 1650 cm^{-1} in benzene derivatives are assigned to skeleton stretching C–C bonds. The actual positions are determined not so much by the nature of the substituents

but by the form of substitution around the ring. The five bands observed at 1477, 1529, 1580, 1608 and 1628 cm^{-1} in 3-bromo-7,8 benzochromanone have been assigned to C=C aromatic stretching vibrations. The medium bands at 1000 cm^{-1} and 975 cm^{-1} are assigned to ring breathing mode which is unaffected by substitution in 3-bromo-7,8 benzochromanone. The in-plane carbon bending vibrations are assigned to 669 and 559 cm^{-1} in 3-bromo-7,8 benzochromanone from the knowledge of carbon bending vibrations in benzene. The carbon out-of-plane bending vibrations are derived from the non degenerate b_{2g} (703 cm^{-1}) and degenerate e_{2u} (404 cm^{-1}) modes of benzene. The former is found to be constant in substituted benzenes[8] and in the present case it is observed at 707 cm^{-1} in 3-bromo-7,8 benzochromanone. Further e_{2u} component of benzene gives rise to two non-totally symmetric components and the bands observed at 498 and 470 cm^{-1} in 3-bromo-7,8 benzochromanone are assigned to this vibrations. The bands at 1235 and 1039 cm^{-1} in 3-bromo-7,8 benzochromanone are assigned to $=C-\hat{O}-C$ bending vibrations. The C-C-C trigonal bending non-degenerate b_{1u} vibration of benzene gives rise to 1018 cm^{-1} in 3-bromo-7,8 benzochromanone.

In general the aromatic structure shows the presence of C–H stretching vibrations in the 3000–3100 cm^{-1} which permits a ready identification of the structure. In this region the bands are not appreciably affected, by the nature of the substitutents. The frequencies at 3070 and 3000 cm^{-1} in 3-bromo-7,8 benzochromanone have been assigned to C–H stretching modes. The C–H in-plane-bending and C–H out of plane bending vibrations are given in Table 1. They are in good agreement with Singh *et al*[9]. The band at 1205 cm^{-1} is assigned to C–O stretching vibration while >C=O conjugated bond stretching frequency is assigned to 1662 cm^{-1} in 3-bromo-7,8 benzochromanone. This observation is in agreement with Ravikumar *et al*[10].

TABLE 1

OBSERVED AND CALCULATED FREQUENCIES AND DISTRIBUTION OF POTENTIAL ENERGY FOR 3-BROMO-7, 8 BENZOCHROMANONE

Species	Observed IR	Calculated	Description (PED%)
A″	221 m	232	τ(C–H)(71)
	240 w		(905–669)
	299 w		(765–470)
	340 w		(1580–1235)
A′	365 w	370	δ(CC)(70)
A′	398 s	398	ν(C–Br)(98)
A″	470 m	485	π(CCC)(82)
A″	498 m	499	π(CCC)(69)
A′	559 m	568	β(CCC)(85)
A′	580 s	586	β(C=O)(81)

TABLE 1 (contd.)

Species	Observed IR	Calculated	Description (PED%)
A′	669 m	671	β(CCC)(84)
A″	707 w	717	π(CCC)(74)
A″	742 m	746	π(C–H)(78)
A″	765 s	769	π(C–H)(81)
A″	775 s	788	π(C–H)(85)
A″	798 m	798	π(C–H)(90)
A′	833 s	841	ν(CC)(100)
A″	905 m	916	π(C–H)(89)
A″	951 m	955	π(C–H)(69)
A″	962 w	968	π(C–H)(72)
A′	975 w	982	Ring breathing mode ν(CC)(95)
A′	1000 m	1012	Ring breathing mode ν(CC)(97)
A′	1018 m	1026	C–C–C trigonal bending (82)
A′	1039 m	1045	=C–$\hat{O}$–C bending(87)
A′	1092 s	1098	β(C–H)(90)
A′	1123 s	1135	β(C–H)(92)
A′	1143 s	1148	δ(CCC)(76)
A′	1157 m	1158	β(C–H)(81)
A′	1205 s	1216	ν(C–O)(99)
A′	1235 s	1242	β(=C–$\hat{O}$–C)(94)
	1262 m		(765+498)
A′	1288 w	1299	β(C–H)(92)
A′	1363 m	1369	δ(CCC)(84)
A′	1390 s	1396	ν(CC)(100)
	1418 m		(1018+398)
	1449 s		(742+707)
A′	1477 m	1481	ν(C=C)(100)
A′	1529 s	1535	ν(C=C)(99)
A′	1580 s	585	ν(C=C)(98)
A′	1608 s	1618	ν(C=C)(99)
A′	1628 s	1634	ν(C=C)(99)
A′	1662 s	1674	>C=O conjugate (91)
A′	1707 m	1717	ν(C=O)(98)
	1762 vw		(1000+765)
	1875 w		(1205+669)
	1917 w		(962+951)
	1950 m		(2×975)
	2345 w		(1580+765)
	2378 vw		(1477+905)
A′	3000 m	3008	ν(C–H)(99)
A′	3070 m	3076	ν(C–H)(99)

The C–Br stretching frequency is usually obtained below the region 400 cm^{-1}. In accordance to the above conclusion the very strong band at

398 cm^{-1} in 3-bromo-7,8 benzochromanone is assigned to C–Br stretching mode.

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