STRENGTH OF CHELATION IN BENZOINS

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Abstract

The infrared and ultraviolet absorption spectra of substituted benzoins have been studied with a view to find the influence of ring substituents on the strength of chelation in benzoins. The strength of chelation was found to be in the order 4-dimethylamino benzofuroin > 4-dimethylamino benzoin > 4-methoxy benzoin > anisoin > benzoin > furoin.

Introduction

Ultraviolet, infrared and Raman spectroscopy have been used in the detection of the interaction between C=O and OH groups. The formation of -O-H···O=C bond affects considerably the stretching vibrations of both -O-H and C=O linkages.[1-3]

In continuation of the work done in these laboratories on the strength of H bonds formed between substituted phenols and substituted benzaldehydes, acetophenones, methyl and phenyl benzoates[4], the authors were interested in studying the influence of the substituent on the strength of the chelation in benzoin. Evidence for the existence of chelation in benzoin was furnished by infrared spectroscopic studies[5-7]. Substituted benzoins have not attracted the attention of many spectroscopists. Although the uv spectra of a few substituted benzoins were reported[8], the ir spectra of these were not fully studied.

With a view to study the strength of chelation and its dependence on the substituents in phenyl ring attached to >C=O, the uv and ir spectra of the following substituted benzoins have been recorded.

Benzoin (I), 4-methoxy benzoin (II), anisoin (III), 4-dimethylamino benzoin (IV), furoin (V), 4-dimethylamino benzofuroin (VI).

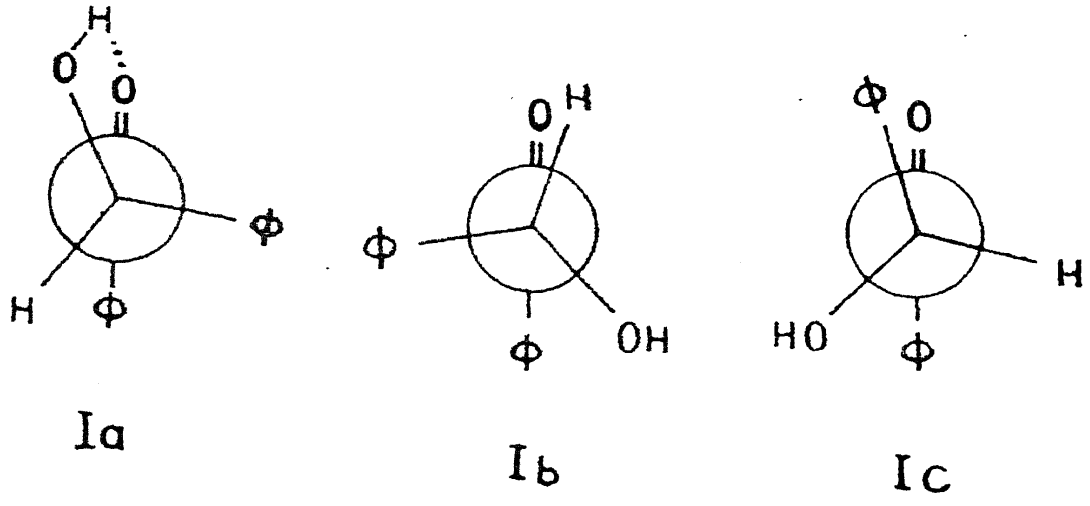
EXPERIMENTAL

The compounds I to VI were prepared by procedures available in the literature.[9-a, b, c] The ir spectra were recorded on Perkin-Elmer 337 grating spectrophotometer in dilute solutions of CCl_4 using 0·5 mm NaCl cells. The uv absorption measurements were made in 95% ethanol using Hilger Watt UVISPEK, and 1 cm fused silica cells. The OH and $\rangle C{=}O$ stretching frequencies together with $\lambda_{max\,(uv)}$ are presented in Table I.

DISCUSSION

Different conformations for benzoin are possible due to free rotation around C—C bond between $\rangle C{=}O$ and —CHOH groups.

In dilute CCl_4 solution benzoin was found to give single, quite symmetrical vibration band for OH at 3462 cm^{-1} and for $\rangle C{=}O$ at 1681 cm^{-1}. The OH band at 3462 cm^{-1} is lower by 138 cm^{-1} as compared to the monomer band 3600 cm^{-1} of benzyl alcohol (Table I). The lowering in OH frequency suggests the participation of OH in hydrogen bond formation. The insensitivity of OH and $\rangle C{=}O$ bands to changes in concentration indicate the absence of intermolecular hydrogen bonds. So benzoin is stabilised solely as a chelate in CCl_4 solution (Fig. 1 *a*). Similar is the case with other benzoins under study.



Ia Ib Ic

The shifts of OH fundamental frequency is used to establish the reltaive strengths of hydrogen bonds, lower OH frequencies being associated with

stronger hydrogen bonds[10]. As the $\Delta\nu_{OH}$ of benzoin is not so great as in other chelate compounds like salicylaldehyde[11, 12], enols of β-diketones[13–15], chelation in this compound appears to be weak. This is also evident from the very small change in $\rangle C{=}O$ frequency (1681 cm^{-1}) as compared to that in deoxybenzoin[16] (1685 cm^{-1}).

The weak chelation may be due to the absence of conjugation in the chelate ring as found in salicylaldehyde or enols of β-diketones, which is stabilised by resonance. It may also be due to small chelate ring. Chelation in 5 membered ring systems was found to be weaker than in 6 or 7 membered ring systems[17].

The magnitude of $\Delta\nu_{OH}$ in furoin is almost the same as in benzoin. So the strength of chelation in these two compounds may be of the same order. The $\Delta\nu_{OH}$ values in 4-methoxy benzoin (II), 4, 4′-dimethoxy benzoin (Anisoin) (III) and 4-dimethyl amino benzoin (IV) are larger than in the case of benzoin. Likewise in 4-dimethyl amino benzofuroin the $\Delta\nu_{OH}$ is larger than that in furoin (V). The lowering of OH frequency in these compounds is explicable in terms of the donor ability of the carbonyl oxygen atom.

The methoxyl and dimethylamino groups in the 4-position, by their mesomeric interaction, enhance the $\rangle C{=}O$ polarisation and hence the donor ability of the carbonyl oxygen. With the increase in donor ability the carbonyl oxygen attracts the hydrogen of the O–H strongly resulting in a weakening of O–H linkage and lowering of its vibrational frequency.

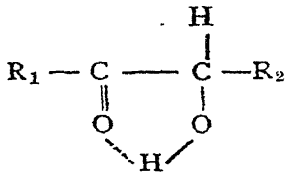
As the strength of hydrogen bond is determined by the magnitude of $\Delta\nu_{OH}$, strength of chelation in benzoins studied, is in the order of 4-dimethylamino benzofuroin > 4-dimethyl amino benzoin > 4-methoxy benzoin =anisoin > benzoin = furoin.

Further, as the donor ability depends upon the extent of $\rangle C{=}O$ polarisation which determines the $\rangle C{=}O$ frequency and λ_{max} of K band in uv absorption spectra, correlations between $\Delta\nu_{OH}$, $\nu_{C=O}$ and λ_{max} are expected. Data in Table I shows good correlations between $\Delta\nu_{OH}$ and $\nu_{C=O}$ in all the benzoins studied. But the correlation of $\Delta\nu_{OH}$, with λ_{max} breaks in the case of furoin and dimethylamino benzofuroin. This

may probably be due to the fact that ν_{OH} and $\nu_{C=O}$ reflect the behaviour of the molecule in the ground state and λ_{max} that of the excited state.

TABLE I

C=O and —OH stretching frequencies (ir) and λ_{max} of K band (uv) in substituted benzoins



	R_1	R_2	ν_{OH} (cm^{-1})	$\Delta\nu_{OH}$ (ν_{OH} — ν_{OH}) benzyl benzoin alcohol	$\nu_{C=O}$ (cm^{-1})	λ_{max} (*nm*)
I	C_6H_5	C_6H_5	3462	138	1681	248
II	4–$OCH_3C_6H_4$	C_6H_5	3455	145	1677	283
III	4–$OCH_3C_6H_4$	4–$OCH_3C_6H_4$	3455	145	1677	283
IV	4–$N(CH_3)_2C_6H_4$	C_6H_5	3435	165	1670	348
V	C_4H_3O (furyl)	C_4H_3O (furyl)	3462	138	1681	277
VI	4–$N(CH_3)_2C_6H_4$	C_4H_3O	3428	184	1659	348

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