

THE LOW-TEMPERATURE INFRARED SPECTRUM OF THE *s-trans* FORM OF BENZALACETONE

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The infrared spectrum of the *s-trans* form of benzalacetone was measured at the liquid nitrogen temperature. Absorption bands in the region between 1700–400 cm^{-1} were interpreted.

The structure of α,β -unsaturated ketones has been studied by vibrational spectroscopy^{1,5}. Molecules of these compounds exist in two nonequivalent forms with *s-cis* (I) or *s-trans* (II) coplanar double bonds. In liquid state or in solution, many α,β -unsaturated ketones exist as equilibrium mixtures of both conformers the population of which depending primarily on internal structural effects, changes slightly with temperature.



I



II

Benzalacetone (4-phenyl-3-buten-2-one) exists in liquid state as a mixture of *s-cis* and *s-trans* forms (their ratio was estimated to be 3 : 7 under normal conditions^{5,6}). Owing to this fact, the infrared spectrum of liquid or dissolved benzalacetone is rather complex. The spectrum of a sample at -170°C becomes simpler (Fig. 1); the more stable *s-trans* form predominates in the polycrystalline solid under these conditions. When heated again to room temperature, the original equilibrium mixture results. The infrared spectrum of liquid benzalacetone has not yet been analyzed. On the other hand, an interpretation of the low-temperature spectrum of its isolated *s-trans* form becomes possible (Table I). This also makes an understanding of the liquid spectrum easier. The analysis is in part supported by results of the analysis of the spectra of $\text{C}_6\text{H}_5\text{CH}=\text{CDCOCD}_3$, prepared in the 80% isotopic purity from benzaldehyde and hexadeuterioacetone. The bands not found in the low-temperature spectrum of benzalacetone but present in its room-temperature spectrum were assigned to the vibrations of the less stable *s-cis* form, though this need not be always

valid. However, the bands at 1690 and 1608 cm^{-1} in the room-temperature spectrum can be with certainty attributed to the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ vibrations of the *s-cis* form.

TABLE I

Assignment of Frequencies [cm^{-1}] in IR Spectra of Benzalacetone

No ^a	Assignment	Temperature		
		room		liquid-N
		<i>s-cis</i>	<i>s-trans</i>	<i>s-trans</i>
	C=O stretch.	1 690 m ^b	1 667 vs	1 657 vs
	C=C stretch.	1 608 vs	1 624 sh	1 635 vs
8a	ring stretch.		1 594 sh	1 595 m
8b	ring stretch.	1 574 m		1 576 w
19a	ring stretch.	1 494 m	—	—
19b	ring stretch.		1 450 s	1 450 s
	antisym. bend. CH ₃			1 438 m ^c
	antisym. bend. CH ₃	1 421 w-br		1 419 m ^c
	in-plane bend. HC=CH	1 377 sh		1 387 w ^c
	sym. bend. CH ₃	1 358 s-br		1 362 vs ^c
14	ring stretch.	1 328 w	1 336 i	1 336 w
3	β phenyl CH bend.	1 294 w		1 300 m
	chain mixed mode	1 257 vs-br		1 270, 1 264 m ^d
20a	X-sensitive	1 203 s		1 209 m
		1 178 s-br		—
9a/9b	β phenyl CH bend.	1 150 i		1 157, 1 154 w ^d
15	β phenyl CH bend.	1 072 w		1 076 s
18a	β phenyl CH bend.	1 026 sh		1 029 m
	rocking CH ₃	1 005 sh?		1 007 m ^c
1/12	ring breathing	985 sh?		995 m
	out-of-plane bend. HC=CH	974 vs-br		979, 972 vs ^d
17a/17b	γ phenyl CH bend.	—		929 m
10a	γ phenyl CH bend.	—		848, 843 w ^d
12/1	X-sensitive	—		823 m
11	γ phenyl CH bend.	747 vs		757 vs
4	α CCC	699 vs		699 vs
6b	Γ CC	—		619 w or 609 m
		—		583 m
6a	X-sensitive	545 m	558 m	558 m
16b	X-sensitive	—		478 s or 469 s

^a The description of phenyl vibrations see ref.⁶; ^b relative intensity: vs very strong, s strong, m medium, w weak; sh shoulder, br broad band; ^c sensitive to deuteration; ^d splitting due to effects in crystal unit.

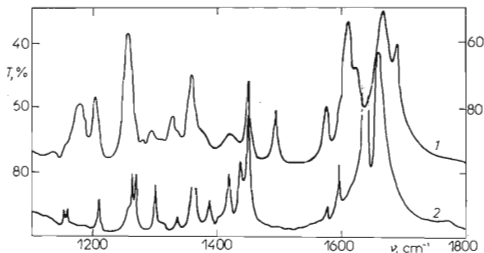


FIG. 1

IR Spectrum of Benzalacetone

1 Room temperature; 2 liquid nitrogen temperature.

EXPERIMENTAL

Infrared spectra were recorded with a Perkin-Elmer 621 spectrometer. The low-temperature spectra were obtained with a commercial VLT-1 cell (RIIC-Beckman, London) with AgCl windows. The same cell was also used for measurements of the room-temperature spectra. The temperature in the cell was checked by a thermocouple. The accuracy of wavenumbers given is about $\pm 2 \text{ cm}^{-1}$.

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