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BENZINDOLES

XII.* SPECTRA AND THREE-DIMENSIONAL STRUCTURES OF [6,7]- AND [4,5]BENZOSKATOLIDENEACETONES

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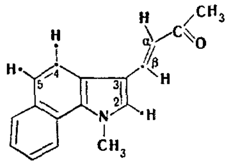
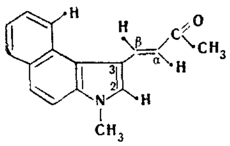
It was found by means of their IR, UV, and PMR spectra that [6,7]benzoskatolideneacetones have a side chain in the trans-s-cis form, whereas the [4, 5] isomers have a side chain in the cis-s-cis form. It was concluded from the integral intensities of the bands of the vibrations of the double bond ($A_{C=C}$) and the parameters of the UV spectra that the investigated molecules have a planar structure. The $A_{C=C}$ integral intensities in the IR spectra exceed the previously observed values and, in the case of [6,7]benzoskatolideneacetones, reach ~6 · 10^4 mole^{-1}/liter · cm^{-2}.

In a previous paper [1] we described the synthesis of [6,7]- and [4,5]benzoskatolideneacetones, leaving open the question of their conformations.



I



II

In the most preferable, from the point of view of electronic interactions, planar (or close-to-planar) structures I and II, first of all, transoid or cisoid orientation of the exocyclic $C_\alpha - C_\beta$ bond relative to the $C_2 - C_3$ bond and, second, an s-trans or s-cis orientation of the carbonyl group relative to the $C_\alpha - C_\beta$ bond are possible. Thus the side chains of the I and II molecules may, in principle, have four forms: trans-trans (1), trans-cis (2), cis-trans (3), and cis-cis (4). An examination of the molecular models shows that only the 3 and 4 conformations are real in the case of [4,5]benzoskatolideneacetones (II), and forms 1 and 2 are excluded because of strong nonvalence repulsions of the α-H and 8-H protons of the $C_\alpha - C_8$ bonds. The 3 and 4 forms are also sterically more favorable for [6,7]benzoskatolideneacetones, but one cannot exclude forms 1 and 2, in which there is only a relatively small nonvalence interaction of α-H and 4-H. Insofar as the mutual orientation of the exocyclic $C_\alpha - C_\beta$ bond and the carbonyl group is concerned, their orienta-

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*See [1] for communication XI.

D. I. Mendeleev Moscow Chemical and Technological Institute. Institute of Biophysics, Ministry of Public Health of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1347-1352, October, 1975. Original article submitted November 19, 1974.

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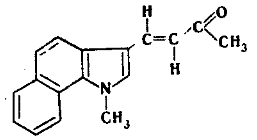
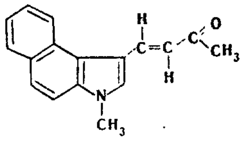
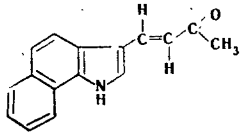
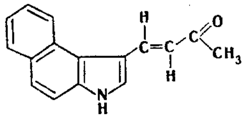
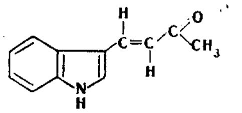
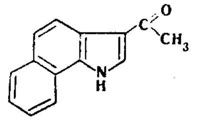
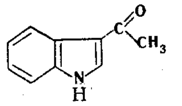
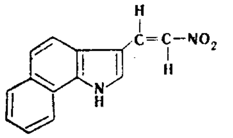
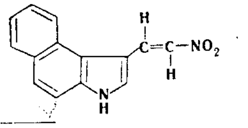
TABLE 1. Parameters of the IR and UV Spectra of [6,7]- and [4,5]-Benzindole Derivatives

	Compound	IR spectrum				UV spectrum	
		$\nu_{C=C'}$ cm^{-1}	$A_{C=C'}$ 10^{-4} mole^{-1}/liter·cm^{-2}	$\nu_{C=O'}$ cm^{-1}	$A_{C=O}$ 10^{-4} mole^{-1}/liter·cm^{-2}	λ_{max}, nm	ε_{max}
1	2	3	4	5	6	7	8
I		1600, 1622	4,6	1666, 1690	1,8	218 267 357	30000 30000 23200
II		1597, 1615	2,8	1662, 1685	2,1	225 305 325 375	38000 17700 16700 9000
III		1601, 1623	6,1	1668, 1691	2,4	216 267 327 355	29000 28000 18000 23600
IV		1601, 1618	2,0	1667. 1685	1,8	222 297 315 362	38000 15200 14600 9600
V		1599 1624	3,9	1666, 1685	2,0	222 275 353	25800 11700 27200
VI		—	—	1669	2,3		
VII		—	—	1661	2,0		
VIII		1627	2,5	1505, 1530sh* 1328, 1340 sh†	1,6 4,1	260 393	26400 21200
IX		1622	1,3	1507, 1515* 1300, 1330†	1,6 5,5	227 245 303 328 412	32400 27600 12400 12000 14000

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*Asymmetrical (ν_{as}) NO_2 vibration.

†Symmetrical (ν_s) NO_2 vibration.

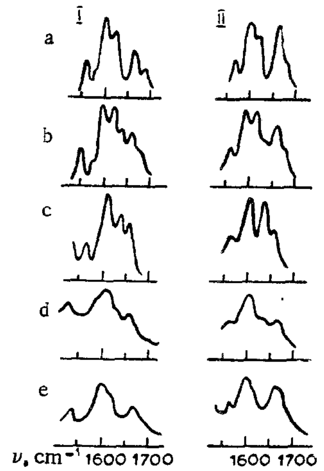

Fig. 1

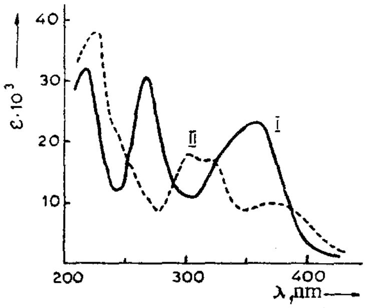

Fig. 2

Fig. 1. Region of double-bond stretching vibrations in the IR spectra of [6,7]benzoskatolideneacetone (I) and [4,5]benzoskatolideneacetone (II): a) solution in tetrahydrofuran; b) solution in chloroform; c) crystal at 35°; d) crystal at 145°; e) melt at 180°.

Fig. 2. UV absorption spectra of [6,7]benzoskatolideneacetone (I) and [4,5]benzoskatolideneacetone (II) in ethanol.

tion is not directly determined by the cyclic system in either I or II. From the point of view of the nonvalence interactions, the situation here is the same as in alkyl vinyl ketones [2]. Two doublets at ~1600, 1620, and at ~1660, 1690 cm^{-1} are observed in the IR spectra of solutions of I and II (Fig. 1a) in the region of double bond vibrations. The high-frequency doublet should be assigned to the vibrations with primary participation of $C=O$, whereas the low-frequency doublet should be ascribed to stretching vibrations of the $C=C$ bond. This is specifically indicated by the decrease in the intensity of the bands at 1660 and 1690 cm^{-1} and the appearance of a shoulder on the long-wave side (1645 cm^{-1}) in the spectra of chloroform solutions of both compounds (Fig. 1b); the observed redistribution of the intensities is explained by the formation of a hydrogen bond between the carbonyl group and the proton of chloroform (the solvent).

Three bands at ~1615, 1640, and 1670 cm^{-1} appear in the spectra of crystals of I and II instead of the expected two bands (Fig. 1c). The specific form of these spectra is due to intermolecular interactions in the crystals (or, more accurately, to the nonequivalent orientation of the $C=O$ bonds in the crystal lattice). In fact, no substantial changes are observed in the spectra when suspensions of I and II in mineral oil are heated to 120°. Redistribution of the intensity of the bands at 1600-1700 cm^{-1} occurs as the melting point is approached (Fig. 1d), and the spectrum of the melt (Fig. 1e) qualitatively reproduces all of the features of the spectrum of the solution.

The frequencies and integral intensities of the bands of the $C=C$ and $C=O$ vibrations ($A_{C=C}$ and $A_{C=O}$) of solutions in tetrahydrofuran (THF) of ketones I and II, as well as benzoskatolideneacetones III and IV and skatolideneacetone V, are presented in Table 1. For comparison, the $A_{C=O}$ values of benzindolyl ketones VI and indolyl ketone VII are also given. It is seen from the data in Table 1 that the intensity of the bands of the carbonyl group directly attached to the indole ring is substantially lower than the usual value for α,β-unsaturated ketones [3, 4] and amounts to $\sim 2 \cdot 10^4$ $mole^{-1}/liter \cdot cm^{-2}$. This value remains practically unchanged over the entire series of investigated compounds, regardless of the structure of the cyclic system. At the same time, the intensity of the vibration with primary participation of the double bond differs sharply as a function of the type of fusion of the benzindole ring: $A_{C=C} \approx A_{C=O}$ for [4,5]benzoskatolideneacetones II and IV (for which only a cis conformation of the exocyclic double bond relative to the ring is possible). On the other hand, the $A_{C=C}$ values for [6,7]benzoskatolideneacetones I and III and skatolideneacetone V exceed the $A_{C=O}$ value by a factor greater than two. Such high integral intensities of the band of the $C=C$ vibrations in the IR spectra, which reach $\sim 6 \cdot 10^4$ $mole^{-1}/liter \cdot cm^{-2}$ in the case of ketone III, are noted here for the first time, insofar as we know. Substantial differences are also observed in the UV spectra: The long-wave absorption band in the spectra of the [6,7] isomers is almost twice as intense as the corresponding band of the [4,5] isomers (Table 1 and Fig. 2). Consequently, conditions for

TABLE 2. Chemical Shifts and Spin–Spin Coupling Constants in the PMR Spectra

[6,7]Benzindole derivatives

Compound	NH	N-CH$_3$	CO—CH$_3$	2-H	$J_{1,2}$, Hz	α-H	β-H	$J_{\alpha,\beta}$, Hz	5-H	4-H	$J_{4,5}$, Hz	Solvent
I	—	4,27	2,27	7,91		6,68	7,81	17,5	7,62	8,00	8,5	$(CD_3)_2SO$
	—	4,11	2,27	7,20		6,64	7,67	16,0	7,51	7,81	9,0	$CDCl_3$
	—	3,05	2,03	6,38		6,71	7,71	16,0	7,38	7,72	8,7	C_6D_6
III	12,57	—	2,29	7,94	1,5	6,75	7,85	16,0	7,57	7,97	8,5	$(CD_3)_2SO$
V	11,69	—	2,23	7,85	1,0	6,63	7,76	16,0				$(CD_3)_2SO$
VIII	*	—	—	8,25		8,06	8,41	13,5	7,63	8,00	9,0	$(CD_3)_2SO$
X	12,56	—	2,29	2-CH$_3$ 2,60		6,70	7,80	16,0	7,53	7,93	9,0	$(CD_3)_2SO$

[4,5]Benzindole derivatives

	NH	N-CH$_3$	CO—CH$_3$	2-H	$J_{1,2}$, Hz	α-H	β-H	$J_{\alpha,\beta}$, Hz	6-H	7-H	$J_{6,7}$, Hz	8-H	
II	—	3,89	2,34	8,01		6,62	8,31	16,0		7,65†		8,37	$(CD_3)_2SO$
IV	12,05	—	2,33	8,00	~1	6,68	8,32	15,5		7,56†		8,37	$(CD_3)_2SO$
IX	12,41	—	—	8,31	~1	8,11	8,85	13,0	7,60	7,64	9,0	8,35	$(CD_3)_2SO$

* Not observed because of the low concentration.

†The AB quartet degenerates to a singlet.

electronic interaction of the side chain with the cyclic system are more favorable in [6,7]benzoskatolideneacetones I and III and skatolideneacetone V, and this may occur in the case of a transoid configuration of the exocyclic double bond.

This conclusion is confirmed by an examination of model compounds with a side chain containing a double bond conjugated with a nitro group (Table 1, VIII and IX). In this case, the band of C = C vibrations also has an anomalously high intensity and, in the case of 3-nitrovinyl[6,7]benzindole, exceeds the intensity of the band of asymmetrical vibrations of the nitro group (ν_{as}). This circumstance and the substantial differences in the character of the long-wave absorption band in the UV spectra of VIII and IX (Table 1) constitute evidence for a trans orientation of the $C_\alpha-C_\beta$ bond in the [6,7] isomer and a cis orientation in the [4,5] isomer. The position of the C = C band and the magnitude of the $A_{C=C}$ intensities of the nitrovinyl derivatives confirm the correctness of the assignment of the vibrations in the spectra of the carbonyl-containing compounds.

The conformational differences in the [6,7]- and [4,5]benzoskatolideneacetone molecules should lead to changes in the chemical shifts of the PMR signals of the 2-H, α-H, and β-H protons, as well as the protons of the $COCH_3$ methyl group. The observed difference in the chemical shifts of the corresponding protons (Table 2) is small, but in all cases coincides in sign with the proposed value. The 2-H proton in the [4,5] derivatives that have a side chain in the cis form draws near to the exocyclic double bond. Correspondingly, the signal of the 2-H proton in the spectrum of ketone II is shifted to weak field by 0.1 ppm as compared with the spectra of I and III. The considerable changes in the chemical shift of the β-H proton on passing from the [6,7] to the [4,5] isomers are due to the closeness in the latter case of β-H to the [4,5]-fused ring.

An approximate calculation of the effect of the π current on the chemical shift of the α-H protons shows that in the case of a trans conformation of the side chain the α-H signal should be found at weaker field by 0.1-0.2 ppm as compared with the cis conformation. The observed differences for I and II, and III and IV are 0.06-0.07 ppm.

In order to obtain definitive proof of the spatial orientation of the side chain of the I and III molecules, we synthesized the model compound 2-methyl[6,7]benzoskatolideneacetone (Table 2, X),* for which a cisoid orientation of the exocyclic $C_\alpha-C_\beta$ double bond is known to be excluded because of the steric interactions of the α-H and C_α atoms with the methyl group in the 2 position. As seen from Table 2, the chemical shifts of the α-H, β-H, 4-H, and 5-H protons in X are close to the values in III. If the III molecule did have a side chain with a cis conformation, the 4-H and β-H chemical shift should have been found at weaker field as compared with X.

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*Compound X was obtained as a mixture with the starting aldehyde by condensation of 2-methyl-3-formyl-[6,7]benzindole with acetone on aluminum oxide [1].

Insofar as the s-trans or s-cis forms of the carbonyl group are concerned, it is known that the frequency of the C = C vibrations is lower for the cis isomers of alkyl vinyl ketones, whereas the intensity is higher than the intensity observed for the trans isomers [2, 5, 6]. The doublet splitting of the C = C and C = O bands in the spectra of I and II, the high $A_{C=C}$ value, and the symbatic character of the change in the intensity of both bands on passing from one solvent to another indicate that an equilibrium between the s-cis and s-trans forms with predominance of the s-cis form exists in solutions (and in melts at high temperatures). As seen from Fig. 1 (spectra d and e), the low-frequency component at ~1600 cm^{-1} is intensified in the spectrum of fused [4,5]benzoskatolideneacetone (for which only forms 3 and 4 are possible because of steric hindrance) as the temperature rises, and at high temperatures (180°) its intensity exceeds the intensity of the components at ~1620 cm^{-1}. Similar changes occur in the spectrum of fused [6,7]-benzoskatolideneacetone (Fig. 1, spectra d and e). It is known [7] that for α,β-unsaturated ketones the change in the chemical shifts in the PMR spectra on passing from solutions in $CHCl_3$ or CCl_4 to solutions in benzene is positive for the protons situated behind the plane passing through the carbonyl carbon atom perpendicular to the C = O bond; the protons situated in front of this plane give a negative $\Delta = \delta_{CHCl_3} - \delta_{C_6H_6}$ value. If the compounds under consideration have a carbonyl group with an s-cis form, a high-field shift of the CH_3CO protons and a low-field shift of the β-H proton should be observed on passing to an aromatic solvent. In the case of an s-trans conformation, one may expect only high-field shifts. The experiment carried out for [6,7]benzoskatolideneacetone (Table 2) indicates the s-cis form of the carbonyl group.

EXPERIMENTAL

The IR spectra were obtained with a UR-10 spectrometer. Cuvettes of constant thickness were used in the measurement of the intensities; four to five solutions of varying concentration were prepared for each compound. The spectral slit width was 2.3 cm^{-1}. The intensity was determined by measurement of the areas [8]; the accuracy in the measurements of the A values did not exceed ±20% in the case of overlapped bands. During the temperature measurements the cuvette was placed in a brass cylinder with a spiral wound around it; the temperature was recorded by means of a thermocouple in direct contact with the sample and was maintained constant at ±1°.

The PMR spectra were recorded with a Varian HA-100D spectrometer with hexamethyldisiloxane as the internal standard. The accuracy in the measurements of the chemical shifts was ±0.01 ppm, whereas the accuracy in the measurement of the spin–spin coupling constants was ±0.1 Hz.

The UV spectra of ethanol solutions of the compounds were obtained with a Schimadzu MPS-50L spectrophotometer.

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