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VIBRATIONAL SPECTRA AND STRUCTURES OF THE cis AND trans ISOMERS OF LINEAR BENZINDIGO

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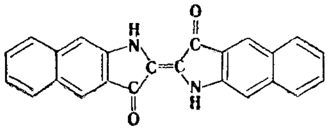
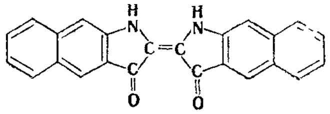
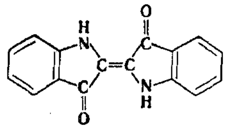
The resonance Raman and IR spectra of the cis and trans isomers of linear benzindigo were investigated, and the frequencies of the vibrations of the multiple bonds were assigned. The large splitting of the frequencies of the symmetrical (ν_s) and asymmetrical (ν_{as}) vibrations of the carbonyl groups of the trans isomer of benzindigo and indigo is associated with the electronic interaction of these groups in the process of vibration.

Recently in the synthesis of 2,3,2',3'-benzindigo the cis isomer (II) was isolated along with the trans isomer (I) [1]. This is evidently the first instance of the isolation of a stable isomer with a cisoid orientation of the carbonyl groups relative to the central double bond of the unsubstituted indigoid chromophore. Thus far, trans-cis photoisomerization of some alkyl and acetyl derivatives of indigo in dilute solutions has been observed; however, when irradiation was discontinued, the small amount of the cis form that was produced was rapidly converted to the more stable trans form.


I


II


III

In the present research we investigated the resonance Raman (RR) and IR spectra of isomers of linear benzindigo and assigned the frequencies of the vibrations of the multiple bonds. For comparison we examined the vibrational spectra of indigo (III), which exists exclusively in the trans form [3].

The nearer absorption band in the electronic spectrum of trans-benzindigo (I) is shifted 72 nm to the long-wave side as compared with the corresponding band of indigo with retention of the contour and approximately the same intensity (Table 1). Thus the added condensed benzene rings make a relatively small contribution to the lower $\pi \to \pi^*$ transition and a more substantial contribution to the next transition. In the case of cis isomer II

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TABLE 1. Parameters of the Electronic Spectra of Benzindigo and Indigo Isomers (solutions in dioxane)

Indigo III		trans-Benzindigo I		cis-Benzindigo II	
λ_{max}, nm	ε_{max}	λ_{max}, nm	ε_{max}	λ_{max}, nm	ε_{max}
600	15 000	672	11 000	540	9 000
550 sh	8 000	610 sh	5 000		
347 sh				335 sh	
332 sh	10 000	343	26 000	325	34 000
				318 sh	
287	24 000	280	17 500		

the lower $\pi\to\pi^*$ transition has a higher energy; this is in agreement with the value observed in experiments on the trans-cis photoisomerization of indigo derivatives [2], as well as with the predictions of quantum-mechanical calculations [4-6].

The vibrational spectra of isomers I and II should differ substantially. As in the case of III, for the centrosymmetric I molecule one can expect rather strict observance of alternative prohibition, whereas in the case of cis isomer II the frequencies of most of the IR spectrum should coincide with the frequencies of the Raman lines. Data from the IR and Raman spectra of I-III above 1200 cm^{-1} are presented in Table 2; only the Raman lines and their possible analogs in the IR spectra are presented at 500-1200 cm^{-1}. The lines of an argon laser that fall in the region of least absorption were selected in each case for the Raman excitation.*

It follows from the data in Table 2 that in the case of trans-benzindigo (I) only one Raman line in the region of the frequencies of the vibrations of the multiple bonds coincides with the band of the IR spectrum. There are only four coincidences in the vibrational spectra of I. In the case of indigo III the frequencies of five bands of the IR spectrum coincide with the frequencies of the Raman lines. Some of these coincidences are undoubtedly chance events. In contrast to I and III, all of the Raman lines of isomer II have analogs in the IR spectrum. These data constitute evidence for the absence of a center of symmetry and make it possible to assign a structure with a cisoid orientation of the carbonyl groups to the II molecule.

By comparing the parameters of the IR and Raman spectra one can assign the bands of the vibrations of the multiple bonds of I-III. In the centrosymmetric molecules of trans isomers I and III the frequencies of the symmetrical and asymmetrical vibrations of the carbonyl groups will prove to be degenerate in the absence of a kinematic and electronic interaction; the symmetrical C=O vibration should show up in the Raman spectrum, while the asymmetrical vibration should give an intense band of the same frequency in the IR spectrum. However, this sort of degeneracy is absent in this case. The highest-frequency Raman band at ∿1700 cm^{-1} should be assigned to the symmetrical vibration of the carbonyl groups (ν_s) in I and III, while the intense band in the IR spectrum at ∿1630 cm^{-1} should be assigned to the asymmetrical vibration (ν_{as}). The splitting of the frequencies ($\Delta = \nu_s - \nu_{as}$) is thus ∿70 cm^{-1}. Since the C=O groups in the I and III molecules are separated by three bonds, the corresponding coefficients in the matrix of the kinematic interactions are close to zero [7]. Consequently, the reason for the large difference in the ν_s and ν_{as} frequencies in the indigo and trans-benzindigo molecules is the electronic interaction of the carbonyl groups in the process of vibration. Let us note that this sort of splitting also occurs for thioindigo. A comparison of the recently obtained RR spectrum of thioindigo [8] with the IR spectrum [9] makes it possible to conclude that the introduction of a sulfur atom lowers the Δ value to 30 cm^{-1}.

The vibration of the centrosymmetric double bond in I and II is inactive in the IR spectrum and should give a line of high intensity in the Raman spectrum; we assign the doublet at ∿1580 cm^{-1}, the intensity of which exceeds the intensity of the band at 1700 cm^{-1} under preresonance conditions, to this vibration. The Raman line of medium intensity at ∿1630 cm^{-1} evidently belongs to the vibrations of the multiple bond of the five-membered ring,

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*We will examine the resonance Raman spectra of benzindigo isomers and the UV spectra in various aggregate states in greater detail in our next communication.

TABLE 2. Fragments of the Raman and IR Spectra of Benzindigo and Indigo Isomers*

Indigo III				trans-Benzindigo I		cis-Benzindigo II			
Raman	IR			Raman	IR	Raman	IR		
KBr	KBr	dioxane	$C_{16}O_2N_2D_2$	KBr	KBr	KBr	KBr	$CHCl_3$	$C_{24}O_2N_2D_2$
	3260		2440		3360		3397	3462	2520
1704 i	—			1708 i	—	1713 i	1709 i	1715	1711
1692 i									
				—	1654 i				
1630 m	1626 i	1627 i	1618	1630 m	1630 vi	1635 m	1632 m	1636	1631
—	1613 i	1611							
	1600 sh	1600sh				1603 m	1600 i	1602	1602
1587 i	1583 m	1583	1584	1585 i	—				
1574				1575		1560 vw	1560 vi	1562	1558
						1515 w			
					1505 w	1500 w			
—	1482 i	1482	1457						
1463 m	1461 i	1461		—	1460 m				
				1450 m	—				
				—	1438 w	1430 i	1430 m		
—	1410 m			1415 m	1415 m	1417 sh	1417 m		
—	1391 m			1406					
				—	1380 m	1380	1375 m		
				1370 i		1370			
1363 vi	—			—	1362 w				
					1337 m	—	1332 m		
1312 w	—					1320 m	1320 m		
—	1298 m								
				1270 w	1270 w				
					1260 w				
1250 i	—			1250 m	—				
1227 w	—								
	1220 vw			1216	—				
				—	1200 i				
				—	1172 i	1160 vw	—		
1149 m	—			1155 m	1155 m	1140 m	1140 m		
				—	1120 i				
						—	1110		
						1090 w	1087 m		
						1074 m	1070 m		
942 m	—								
765 w	760 vw			762 m	762 vw				
						642 w	639 m		
600 m	—					548 w	550 m		

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*Abbreviations: i is intense, sh is shoulder, m is medium, and vw is very weak.

and its coincidence with the band of the IR spectrum is a chance occurrence. It is apparent from Table 2 that the frequencies and the distribution of the intensities at 1450–1700 cm^{-1} for benzindigo (I) and indigo (III) are virtually identical in both the IR and Raman spectra.

The following alternative is possible in the assignment of the vibrations of cis isomer II: It may be assumed that the splitting of the frequencies of the vibrations of the carbonyl group is small in the case of an unsymmetrical structure and that ν_s = 1713 cm^{-1} and ν_{as} = 1709 cm^{-1} (Table 2). On the other hand, a high-intensity band at 1560 cm^{-1}, which is extremely weak in the Raman spectrum and may be associated with ν_{as} of the CO group, is present in the IR spectrum of II. In this case, however, it will be necessary to assume that $\Delta = \nu_s - \nu_{as}$ = 140 cm^{-1}, which is too large and is hardly the real value for this molecule. The line at 1603 cm^{-1}, the intensity of which in the Raman spectrum depends markedly on the approach to resonance conditions (see our next communication), can be assigned to the vibrations of the central double bond in II.

Bands related to vibrations in which the CNH angles participate significantly may also lie in the examined interval. To ascertain the extent of such participation we obtained the spectra of deuterated samples of indigo and benzindigo II.* The position and intensity of bands with frequencies above 1520 cm^{-1} remain virtually unchanged in the IR spectrum of deuterated cis isomer II (Table 2). The changes in the frequencies of the vibrations of the double bonds are also insignificant in the spectrum of 75% deuterated indigo. Thus the angular coordinates make a small contribution to the form of the vibrations found at 1500-1700 cm^{-1}.

In conclusion, let us note that the concept of the existence of strong intramolecular hydrogen bonds that stabilize the trans configuration of the indigoid chromophore is widely held in the literature [9, 10]. The fact of the isolation of a stable cis isomer of benzindigo shows that if $C{=}O\cdots HN$ intramolecular bonds do exist, they do not make a decisive contribution to the energy balance of cis-trans isomerization. The relatively weak intermolecular hydrogen bonds in I (ν_{NH} = 3360 cm^{-1} for the crystalline state) indicate that the low solubility of indigo and benzindigo (I is even less soluble than III) is evidently associated with specific stacking interactions of the aromatic rings.

EXPERIMENTAL

The Raman spectra of KBr pellets of the compounds were obtained with a Spex-Ramalog-6 spectrometer with excitation by the 458, 488, and 514 nm lines of an argon laser. The accuracy in the measurement of the frequencies was ±2 cm^{-1}. The IR spectra were recorded with a Perkin-Elmer 180 spectrometer; 0.1- and 1-mm thick KBr cuvettes were used in the measurements of solutions. The frequencies were measured with an accuracy of ±1 cm^{-1}. The lines of the IR and Raman spectra were regarded as coincident if the difference in their frequencies did not exceed 4 cm^{-1}. The UV spectra were obtained with a Shimadzu MPS-50 spectrophotometer in 1- and 2-cm thick cuvettes; the dioxane was purified by the standard method.

Deuteration of Indigo and Benzindigo. d_2-2,2',3,3'-Benzindigo (the cis isomer) was obtained by refluxing 20 mg (0.056 mmole) of the undeuterated substance with 2 ml of CD_3OD for 2 h. After evaporation of the solvent *in vacuo*, the residue was dried in a vacuum desiccator to give 15 mg (75%) of a product with mp 268-270°C. d_2-Indigo was obtained by refluxing 15 mg (0.05 mmole) of indigo for 2 h in 1.5 ml of CD_3OD and 1 ml of dry pyridine. The mixture was maintained at 20°C for 12 h, after which the solvent was evaporated *in vacuo*, and the residue was dried in a desiccator to give 10 mg (66.2%) of deuterated product with mp ∿400°C.

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*We were unable to perdeuterate trans isomer I in appreciable amounts despite wide variation in the deuteration conditions; this is evidently explained by the extremely low solubility of I.