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The Nitro Valence Vibrations and Ultraviolet Spectra of *cis*- and *trans*-β-Nitrostyrenes

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The infrared spectra of NO_2 symmetric and asymmetric stretching vibrations and ultraviolet spectra for a series of *cis*- and *trans*-β-nitrostyrene derivatives are examined and correlated with the stereochemical configuration of the structure, the planarity of the conjugated system, and the electronic properties of groups on the carbon bearing the nitro group. From these correlations, the *cis*-, and *trans*-isomers of β-nitrostyrene derivatives have been readily distinguished from each other.

Earlier works on the ultraviolet spectra of β-nitrostyrenes indicated that the trans-compound is characterized by a band of a high intensity in the region of 305—325 mμ.[1,2] In the infrared region, however, only fragmentary work has been carried out on β-nitrostyrenes, though the infrared spectra of conjugated nitroalkenes have often been reported on.[3,4]

In the present investigation the ultraviolet and NO_2 symmetric and asymmetric stretching vibrations of several *cis*- and *trans*-β-nitrostyrene derivatives have been examined with a view to obtaining structural correlations. In particular, we

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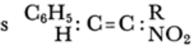
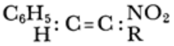
[1] E. A. Braude, E. R. H. Jones and G. G. Rose, *J. Chem. Soc.*, **1947**, 1104.

[2] J. P. Freeman and T. E. Stevens, *J. Org. Chem.*, **23**, 136 (1958).

[3] H. Shechter and J. W. Shepherd, *J. Am. Chem. Soc.*, **76**, 3617 (1954).

[4] J. F. Brown, Jr., *ibid.*, **77**, 6341 (1955).

TABLE 1. NO_2 GROUP STRETCHING VIBRATIONS OF β-NITROSTYRENE DERIVATIVES AND RELATED NITRO-COMPOUNDS

Compds. No.	Substituent R	Asym. Band cm⁻¹	Asym. Band ε_{as}	Sym. Band cm⁻¹	Sym. Band ε_s
a) *trans*-β-Nitrostyrenes	 $\begin{matrix}C_6H_5\\H\end{matrix}:C=C:\begin{matrix}R\\NO_2\end{matrix}$				
1 5,6)	$CO\cdot C_6H_5$	1525	430	1318	490
2 5)	$CO\cdot OC_2H_5$	1530	400	1330	420
3 7)	Br	1543	320	1314	670
4 8)	H	1523	440	1346	1140
5 9)	C_6H_5	1520	430	1325	620
6 10)	CH_3	1520	440	1326	830
b) *cis*-β-Nitrostyrenes	 $\begin{matrix}C_6H_5\\H\end{matrix}:C=C:\begin{matrix}NO_2\\R\end{matrix}$				
7 5)	$CO\cdot C_6H_5$	1538	440	1377	130
8 5,11)	$CO\cdot OC_2H_5$	1538	700	1370	170
9 5,12)	C_6H_5	1530	1080	1376	120
c) Primary aliphatic nitro-compds.	$R\cdot CH_2\cdot NO_2$				
10	$CO\cdot C_6H_5$	1566	1010	1336 1326	170 210
11	$CO\cdot OC_2H_5$	1568	1020	1335	250
12	H	1562	610	1376	190
13	C_6H_5	1564	610	1373	190
14	CH_3	1554	560	1366	130
d) Related aromatic nitro-compds.					
15	*p*-Nitrodiphenyl	1518	480	1347	1290
16	*o*-Nitrodiphenyl	1530	780	1356	300
17	9-Nitrophenanthrene	1519	420	1352	330

detected explicit differences in the NO_2 stretching vibration bands exhibited by each member of a cis-trans pair in these compounds. This work has been carried out in connection with a study of the stereochemical configuration of styrene derivatives obtained from the Knoevenagel reaction with aromatic aldehydes and primary nitroalkanes. The NO_2 stretching vibration bands of some primary nitroalkanes and aromatic nitro compounds have been also examined for the sake of comparison.

Experimental

Compounds. β-Nitrostyrene derivatives were prepared either according to the methods given in the references cited, or by methods which will be described in a separated publication; their physical constants are presented in Table 2. The other compounds were commercial products or were prepared by standard procedures.

TABLE 2. ULTRAVIOLET SPECTRA OF β-NITROSTYRENES ($C_6H_5\cdot CH : C(R)\cdot NO_2$)

Compds. No.	Substituent R	Mp, °C	λ_{max} mμ	ε
a) *trans*-Nitrostyrenes				
1	$CO\cdot C_6H_5$	91.5—92.5	257 313	16900 13800
2	$CO\cdot OC_2H_5$	(n_D^{20} 1.5780)	223 308	8400 14800
3	Br	67	229 324	8500 13800
4	H	57	227 309	8100 17200
5	C_6H_5	74	228 314	12800 13400
6	CH_3	64	224 304	9100 12300
b) *cis*-Nitrostyrenes				
7	$CO\cdot C_6H_5$	103—104	297	19200
8	$CO\cdot OC_2H_5$	72.5—73	280	17800
9	C_6H_5	128	282	23300

Infrared Spectra. The measurements were made in chloroform on a Nihon-Bunko model DS-402G grating infrared spectrophotometer with the following settings:

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5) S. Watarai, K. Yamamura and T. Kinugasa, to be published.

6) A. Dornow, A. Müller and S. Lüpfer, *Ann.*, **594**, 191 (1956).

7) W. E. Parkam and J. L. Bleasdale, *J. Am. Chem., Soc.*, **73**, 4664 (1951).

8) D. E. Worall, "Organic Syntheses," Coll. Vol. I, p. 413 (1948).

9) D. N. Robertson, *J. Org. Chem.*, **25**, 47 (1960).

10) H. B. Hass, A. G. Susie and R. L. Heider, *ibid.*, **15**, 8 (1950).

11) A. Dornow and H. Menzel, *Ann.*, **588**, 40 (1954).

12) F. Heim, *Ber. deutsch. chem. Ges.*, **44**, 2016 (1911).

mechanical speed 84/84 gears; electrical speed 4; suppression 0 (*i.e.*, speed 20 min for the 1100—2000 cm^{-1} region); gain 8; resolution 5. The frequency values obtained are considered to be accurate to ± 2 cm^{-1}.

The apparent molar extinction coefficients were calculated from ε_{as}, or $\varepsilon_s=(1/cl)\cdot\log_{10}I_0/I$, where c=molar concentration, l=path length in cm, I_0/I= peak optical density. Rock-salt cells with path lengths of 0.1 mm and 0.05 mm were employed for the 0.1 M solutions.

The data are presented in Table 1.

Ultraviolet Spectra. The spectra were measured on a Hitachi model EPS-3 recording spectrophotometer, or on a Hitachi Perkin-Elmer model 139 UV-Vis. spectrophotometer, in 99.5% alcohol at dilutions of about $3—5\times10^{-5}$ mol, using 1 cm silica cells. The data are presented in Table 2 and Fig. 1.

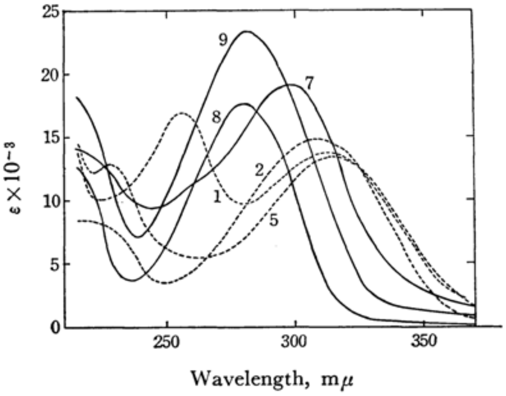

Fig. 1. Ultraviolet spectra of *cis*- and *trans*-β-nitrostyrenes ($C_6H_5\cdot CH{=}C(R)\cdot NO_2$): R=benzoyl, 1, 7; carbethoxy, 2, 8; phenyl, 5, 9.

----: $\begin{matrix}C_6H_5\\H\end{matrix}\!:C{=}C:\!\begin{matrix}R\\NO_2\end{matrix}$

——: $\begin{matrix}C_6H_5\\H\end{matrix}\!:C{=}C:\!\begin{matrix}NO_2\\R\end{matrix}$

Results and Discussion

Infrared Spectra. It was shown for the characteristic nitro asymmetric and symmetric stretching bands of conjugated nitroalkenes that the conjugation of the nitro group by attachment to an ethylenic double bond leads to a fall in both frequencies, and that the symmetric stretching band is nearly as strong as the asymmetric.[3,4]

In the case of β-nitrostyrenes, steric hindrance or extended conjugation of nitro groups through the attachment of the phenyl group must be considered to occur, according to whether cis- or trans-isomer are present respectively.

Both asymmetric and symmetric stretching bands of *trans*-β-nitrostyrenes, as shown in Table 1(a), appear at lower frequencies than those of the corresponding bands of the primary aliphatic nitro-compounds Table 1(c); the relative intensities of both nitro stretching bands show, on the whole, a higher apparent molar-extinction coefficient of the symmetric band (ε_s value) than that of the asymmetric band (ε_{as} value), in contrast to the case of the primary aliphatic nitro-compounds. Since a number of factors caused by substituents on the carbon atom bearing the nitro group influence the NO_2 stretching bands of the *trans*-β-nitrostyrenes, it may be supposed that the structural correlation with these bands is complicated. However, some interesting relation seems to exist between the structural features and the data on the ε_s values. The intensity of the ε_s value relative to the ε_{as} value has been, in general, still higher than those of the corresponding bands of the conjugated nitroalkenes; this reveals the increased conjugation effect through the attachment of the phenyl group. The highest ε_s value has been observed in the β-nitrostyrene itself (No. 4). Such a pronouncedly high value may be correlated with the planarity of the extended conjugation system in this molecule.

In the case of substituted *trans*-β-nitrostyrenes in which the ethylenic β-carbon atom holds simultaneously the nitro group and the other substituents, the following factors may be expected to influence the NO_2 stretching bands: a) a pair composed of the phenyl group and the other substituents in the *cis*- position interfere sterically with each other, and the resultant steric hindrance to the planarity of the benzal group may be expected to reduce the conjugation effect of the phenyl group. b) The conjugation of the nitro group should also be altered with the nature of the β-substituent. Table 1(a) indicates that this expectation is justified; the ε_s values for these derivatives are lower than that of β-nitrostyrene and vary with the nature of the other substituents. For compounds in which the electron-attracting group is attached to the carbon bearing the nitro group, such as α-nitro-*cis*-chalcone*2 (No. 1) or ethyl-α-nitro-*cis*-cinnamate*2 (No. 2), the ε_s values have been reduced and shown to be nearly equal to the corresponding ε_{as} values. Similar reductions in ε_s values have also been shown in *p*-substituted nitrobenzenes carrying electron-attracting groups.[4,13]

Asymmetric bands of the *trans*-nitro systems, on the other hand, have been only slightly affected by other substituents; their ε_{as} values vary around 400.

In the case of the *cis*-β-nitrostyrene structure, on the other hand, the steric hindrance of the nitro group must be considered. It is clear from a study of molecular models that the nitro group and the phenyl group cannot occupy the coplannar configuration with the plane of ethylenic linkage simultaneously. When the nitro group is nearly

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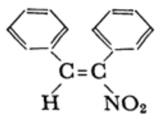
*2 β-Benzoyl-, and β-carbethoxy-*trans*-β-nitrostyrenes correspond to *cis*-chalcone and ethyl-*cis*-cinnamate respectively.

13) A. R. Katritzky and P. Simmons, *Rec. trav. chim.*, **79**, 361 (1960).

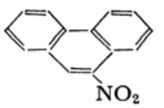
coplanar and only the phenyl group is twisted out of plane, the spectral consequences should resemble that of the corresponding the *trans*-isomers. It is well known, on the other hand, that a pronounced decrease in ε_s value, accompanied by a shift to a higher frequency of the symmetric band, was also encountered for highly sterically-hindered *o*-, or *o, o'*-disubstituted nitrobenzenes.[13,14]

Table 1(b) shows that the *cis*-nitrostyrene systems reveal distinct differences from the *trans*-β-nitro systems in their NO_2 stretching vibration bands. A striking reduction in ε_s value, with an accompaning rise in frequency around 1375 cm^{-1}, and, reversely, an increase in ε_{as} value, have been observed, unlike as in the *trans*-nitro system. Hence the order of their relative intensities of both NO_2 stretching bands is reversed in *cis*- and *trans*-isomers. These variations in frequencies and in the intensities of the bands in cis-trans pairs resemble those of corresponding bands shown between *o*- and *p*-nitrodiphenyls (Table 1(d), Nos. 15 and 16). It is clear, therefore, that, in the *cis*-nitrostyrene system, the conjugation of the nitro group with the ethylenic linkage is sterically hindered by the adjacent phenyl group.

Furthermore, it is interesting to compare the data on α-nitro-*cis*-stilbene (No. 5) with those on 9-nitrophenanthrene (No. 17) with respect to the steric situation of NO_2 groups. Distinct differences between their ε_s values, as shown in Table 1(d) have been observed. These differences may be correlated with the different steric circumstances around each nitro group. In 9-nitrophenanthrene there is a steric interaction between the nitro group and the hydrogen atom at the peri position of another ring (the peri effect) because of the planarity of the phenanthrene nucleus, whilst in α-nitro-*cis*-stilbene such a steric effect is diminished by the distortion of phenyl groups from the plane of the conjugated system.



α-Nitro-*cis*-stilbene (No. 5)
(β-Phenyl-*trans*-β-nitrostyrene)



9-Nitrophenanthrene
(No. 17)

A similar influence of the peri effect of the hydrogen atom on the relative intensities of NO_2 stretching bands has also been observed in other poly-nucleus-aromatic nitro-compounds, such as α-nitronaphthalene, 5-nitroquinoline, 4-nitro-isoquinoline, and 9-nitroanthracene,[15] in our laboratory.

Other characteristic bands of these β-nitrostyrenes will be discussed in a separate publication.

Ultraviolet Spectra. The spectra have been measured in an alcohol solution; their characteristics are summarized in Table 2. In accordance with the previous results,[1,2] all *trans*-nitrostyrenes examined show characteristic bands of a high intensity in the region of 304—324 mμ. *trans*-β-Nitrostyrene (No. 4) has been shown to have the highest absorptivity in this region of all *trans*-β-nitrostyrenes studied; this is consistent with the infrared data which indicate that this nitro group is more fully conjugated than that of the other substituted nitrostyrene derivatives. *cis*-α-Nitrochalcone (No. 1) exhibited an additional intense absorption at 257 mμ characteristic of an isolated benzoyl group.

The *cis*-nitrostyrene systems examined, on the other hand, exhibited no absorption maxima around 310 mμ, and showed very strong absorptions in the shorter-wavelength region of 280—295 mμ; therefore, *cis*-, and *trans*-isomers of β-nitrostyrene derivatives have been readily distinguished from each other, Fig. 1, shows. No separated peak of isolated benzoyl-group absorption in the 240—250 mμ region has been observed in α-nitro-*trans*-chalcone (No. 7), unlike the cases of α-bromo-,[16] and α-phenyl-*trans*-chalcones.[17]

It should be noted that the absorption maximum of ethyl α-nitro-*trans*-cinnamate (No. 8) is shifted slightly to a longer wavelength than that of the *trans*-ethyl cinnamate (275 mμ[18]), while the absorption maxima of α-nitro-*trans*-chalcone (No. 7) and stilbene (No. 9) are shifted to wavelengths shorter than those of the corresponding bands of the parent compounds, *trans*-chalcone (307.5 mμ[17]) and *trans*-stilbene (295 mμ[19]). This difference seems to be ascribable to the different degrees of contributions of effective conjugations of *trans*-substituted-styrene systems and *cis*-nitrostyrene systems in these crossed conjugation systems.

Configurations of Knoevenagel Reaction Products. Ethyl α-nitrocinnamate (mp 72.5—73°C) and α-nitrochalcone (mp 91.5—92.5°C) have been known to be products from the condensation reactions of benzaldehyde and ethyl nitroacetate[11] or ω-nitroacetophenone[6] respectively, but their stereochemical configurations have not hitherto been assigned. From the above data of the infrared and ultraviolet spectra, however, these nitrostyrene derivatives and their new stereoisomers, obtained by appropriate isomerizations,

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[14] T. Kinugasa and S. Watarai, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 472, 476 (1962).

[15] a) K. Nakamura and R. Nakashima, *ibid.*, **83**, 226 (1962); b) S. Watarai and T. Kinugasa, unpublished work.

[16] R. E. Lutz, D. F. Hinkley and R. H. Jordan, *J. Am. Chem., Soc.*, **73**, 4647 (1951).

[17] W. B. Black and R. E. Lutz, *ibid.*, **75**, 5997 (1953).

[18] Y. Urushibara and M. Hirota, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **82**, 358 (1961).

[19] E. A. Braude, *J. Chem. Soc.*, **1949**, 1902.

can be identified as α-nitro-*trans*- and-*cis*-ethyl cinnamates (n_D^{20} 1.5780), and α-nitro-*cis*- and *trans*-chalcones (mp 103—104°C), respectively.

It is noteworthy that ethyl α-nitro-*trans*-cinnamate, which has a *cis*-β-nitrostyrene structure, has been produced predominantly from the Knoevenagel reaction, whereas, in general, *trans*-β-nitrostyrene derivatives have been obtained from this reaction when nitromethane, nitroethane, phenylnitromethane, and ω-nitroacetophenone are condensed with benzaldehydes. The details of these reactions and of the isomerizations of each compound will be published in the future.

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