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Fourier Transform Infrared/Raman Differentiation and Characterization of *Cis*- and *Trans*-2,5-Dimethoxy-4, β -Dimethyl- β -Nitrostyrenes: Precursors to the Street Drug STP

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ABSTRACT: Fourier transform Raman and infrared spectra of pure *cis*(*Z*)- and *trans*(*E*)-2,5-dimethoxy-4, β -dimethyl- β -nitrostyrene (precursors of the psychotomimetic street drug STP or DOM) were recorded in the solid state. The spectra show characteristic features of the ethylene moiety and of the aryl and nitro substituents which permit ready differentiation and identification of these isomers. A very strong Raman line at 1670 cm⁻¹ from the *cis* isomer for the C=C stretching mode, in comparison with a strong Raman line at 1641 cm⁻¹ for the *trans* isomer, affords primary differentiation of these substances. A second characteristic, of both the Raman and infrared (IR) spectra, is that the frequency of the strong symmetric nitro (NO₂) stretching band is about 40 cm⁻¹ higher in the *cis* (1346 cm⁻¹) than the *trans* isomer (1301 cm⁻¹). All major IR and Raman bands are reported and given vibrational assignments.

KEYWORDS: toxicology, spectroscopic analysis, *cis*(*Z*)- β -methyl- β -nitrostyrene, *trans*(*E*)- β -methyl- β -nitrostyrene, Raman spectrometry, infrared spectrometry

Trans(*E*)-2,5-dimethoxy-4, β -dimethyl- β -nitrostyrene, a readily prepared and abundant geometrical isomer, is the essential precursor of the street drug, (2,5-dimethoxy-4-methylphenyl)isopropylamine, also known as 2,5-dimethoxy-4-methylamphetamine (STP or DOM). Of the large number of alkoxy-substituted α -methylphenethylamines that are known to be psychotomimetic in man (see Ref 1 and references cited therein), DOM and its 4-ethyl homologue (DOET) are among the most potent phenethylamine psychotomimetics known [2]. Indeed, the psychotomimetic effects of these drugs are more reminiscent of those of lysergic acid diethylamide (LSD) than those of the euphorogenic drug mescaline, (3,4,5-trimethoxyphenethylamine), which has a more benign nature [3].

Lešetický et al. [4] have shown nitrostyrenes to predominate in the ground-state *trans*(*E*) configuration of the nitro and phenyl groups. These workers were unable to separate

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pure *cis*(*Z*) isomers, including the ring-unsubstituted parent compound (*Z*)-1-phenyl-2-nitropropene, from their ultraviolet (UV) isomerized reaction products and had to rely on ¹H nuclear magnetic resonance (NMR) spectra for identification of the *Z* and *E* isomers in the mixtures, whose purity and composition were established by gas chromatography. The purpose of this paper is to report the first successful preparation and separation of (*Z*)-2,5-dimethoxy-4,β-dimethyl-β-nitrostyrene from its *E* isomer, together with complete vibrational differentiation and characterization of these two important (*E*,*Z*)-β-methyl-β-nitrostyrenes by Fourier transform infrared (FT-IR) and Fourier transform Raman (FT-Raman) spectroscopy.

Photoisomerization, Separation, and Purification

(*E*)-2,5-Dimethoxy-4,β-dimethyl-β-nitrostyrene (1 g of crystals from toluene-hexane; melting range, 91 to 92°C; Kofler, uncorrected), prepared from the corresponding benzaldehyde, nitroethane, ammonium acetate, and glacial acetic acid [5], was photoisomerized for 48 h in toluene (120 mL) containing benzophenone (10 mg). A Sylvania Photo-ECT (3200 K) photo flood lamp (500 W) assembly, described previously for preparation of (*Z*)-monoethoxy-1-(2-nitro-1-propenyl)benzenes, important precursors to the monoethoxyamphetamines [5], provided the UV source. The ratio of (*Z*) to (*E*) isomerization was monitored by either of two thin-layer chromatography (TLC) methods: (a) reversed-phase TLC using Whatman KC₁₈F plates (5 by 20 cm, 0.25 mm) and methanol, where *R_f* was 0.66 and 0.62 for the *Z* and *E* isomers, respectively; or (b) forward-phase TLC using Analtech silica gel GHLF plates (5 by 20 cm, 0.25 mm) eluted three times with methylene chloride/hexane (1:1), where *R_f* was 0.45 and 0.42 for the *Z* and *E* isomers, respectively.

Part of the crude isomerization product (~100 mg) was dissolved in the high-performance liquid chromatography (HPLC) solvent [methylene chloride/hexane/isopropanol (5:95:0.05)], and 2 mL of this solution (~50 mg/mL) was injected into a forward-phase silica column Supelcosil PLC-Si (250 by 21.2 mm; particle size, 15 μm) with a flow rate of 28 mL/min. UV detection was performed at 350 nm. The desired *cis* product was collected as the front portion of the first peak eluted from the column. Analytical HPLC showed that this collection consisted of one peak. Evaporation of the solvent produced a yellow solid (25 mg). Recrystallization from hexane produced the pure material (melting point, 72.5 to 73.0°C) (Kofler, uncorrected). Results of ¹H-NMR [80 MHz, deuteriochloroform (CDCl₃) with internal tetramethylsilane (TMS)] were as follows: approximately 6.67 (overlap, ArCH and ArHs); 3.74 and 3.77 (singlets, ArOCH₃); 2.35 (doublet, C(NO₂)CH₃; J, 1.5 Hz); and 2.22 ppm (singlet, ArCH₃). Gas chromatography/mass spectrometry (GC/MS) results were the following: 237(M⁺, base peak), 206, 190, 176, 175, 161, 147, 145, 137, 115, 105, 91, 79, 77, 65, 52, and 42 *m/z*. The composition calculated for C₁₂H₁₅NO₄ was C, 60.75; H, 6.37; and N, 5.90%. The elements found were C, 61.15; H, 6.41; and N, 5.75%. (The microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.)

Equipment and Spectral Procedures

Fourier transform (FT) infrared (IR) spectra were recorded from 4000 to 400 cm⁻¹ with a resolution of 2 cm⁻¹, using a Nicolet 60 SX spectrometer with a deuterated triglyceride sulfate detector. The samples for the IR studies were prepared as fused potassium bromide (KBr) disks (0.3% sample) using spectral-grade KBr.

The samples for FT-Raman spectroscopy were prepared in the form of disks 3 mm in diameter with a KBr backing. The disks were formed in a hand-held minipress. FT-Raman spectra were recorded at the Pervasive Technology (PT) Division of the Thornton

Research Centre, Shell Research Ltd. (Chester, Great Britain). Details of the experimental arrangement have been given in two recent publications [6,7]. The near-IR excitation source is a continuous-wave neodymium/yttrium aluminum garnet (Nd/YAG) laser operating at 1064.1 nm (9397.6 cm^{-1}). The laser beam is focused to a 1-mm spot on the sample, which is placed at one focus of an ellipsoidal mirror. The scattered radiation is collected by this mirror and directed into the Jacquinot stop of a Perkin-Elmer Model 1760 near-IR spectrometer. Laser powers of 100 to 200 mW at the sample were used, and 100 to 200 scans at a nominal resolution of 4 cm^{-1} were performed. The nitrogen-cooled germanium detector covers the spectral range 9400 to 6200 cm^{-1} , which is equivalent to a Raman shift range of 0 to 3200 cm^{-1} . The 0 to 400- cm^{-1} region is obscured by the filter needed to remove the intense Rayleigh scattering and any unscattered laser radiation. The detector response is not linear and is very low in the CH stretching region of the Raman spectrum near 3000 cm^{-1} . The Raman spectra shown in Figs. 1 and 2 were not corrected for detector response and are presented only for qualitative comparison.

Results

The maximum (*Z*) to (*E*) isomer ratio occurs after approximately four days (that is, the approximate lifetime of a photo lamp) of photoisomerization exposure. The course of isomerization was most easily and reliably followed by reversed-phase TLC and visual detection because gas-liquid chromatography (GLC) monitoring resulted in partial con-

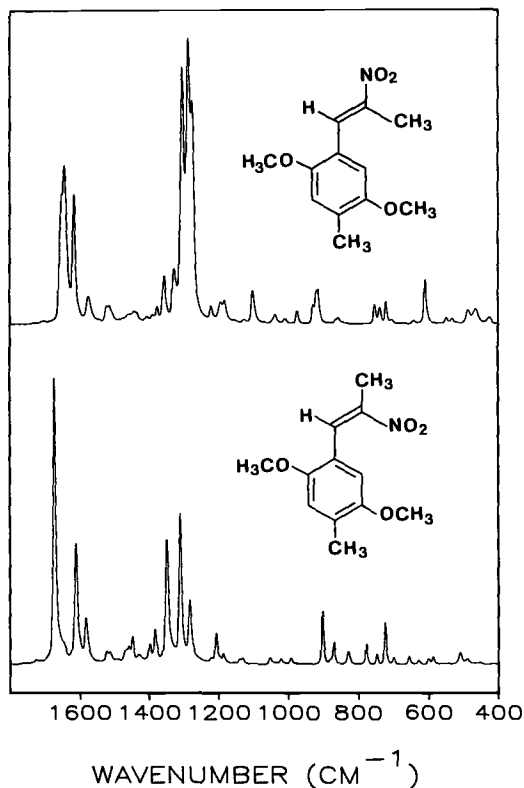


FIG. 1—FT-Raman spectra of *cis*(*Z*)- (bottom) and *trans*(*E*)-2,5-dimethoxy-4, β -dimethyl- β -nitrostyrene (top).

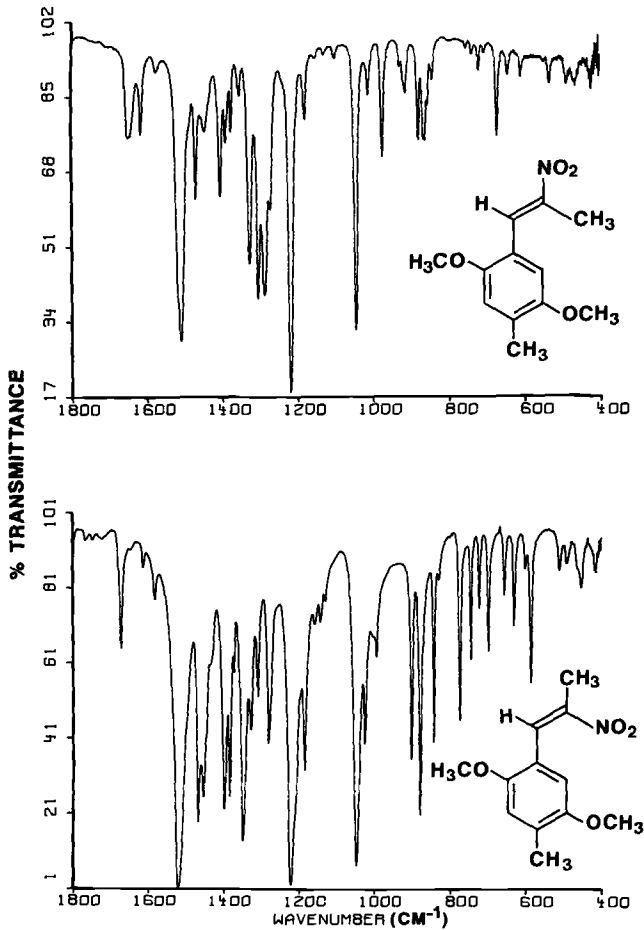


FIG. 2—FT-IR spectra of *cis(Z)*- (bottom) and *trans(E)*-2,5-dimethoxy-4,β-dimethyl-β-nitrostyrene (top).

version of the (*Z*) isomer to the (*E*) form on the injector. Although it can be used, forward-phase TLC, in general, was found to be less reliable for separation of these isomers and for prediction of their order of elution. The formation, separation, and purification of (*Z*)-2,5-dimethoxy-4,β-dimethyl-β-nitrostyrene is the first recorded instance of preparation of a *solid cis*-β-methyl-β-nitrostyrene derivative.

FT-Raman spectra of solid *cis(Z)*- and *trans(E)*-2,5-dimethoxy-4,β-dimethyl-β-nitrostyrene are compared in Fig. 1. A similar set of FT-IR spectra is presented in Fig. 2 for the same spectral range (1800 to 400 cm⁻¹) and in Fig. 3 for the C-H stretching region (3200 to 2600 cm⁻¹). FT-Raman and IR spectra of *cis(Z)*- and *trans(E)*-2,5-dimethoxy-4,β-dimethyl-β-nitrostyrene are compared in Figs. 4 and 5, respectively. The wave numbers (cm⁻¹) for these spectra are listed in Table 1.

Discussion

Very little has been reported on the vibrational spectra of β-nitrostyrene and its β-alkyl or ring substituted derivatives. Currie et al. [8] reported an IR frequency of 1658

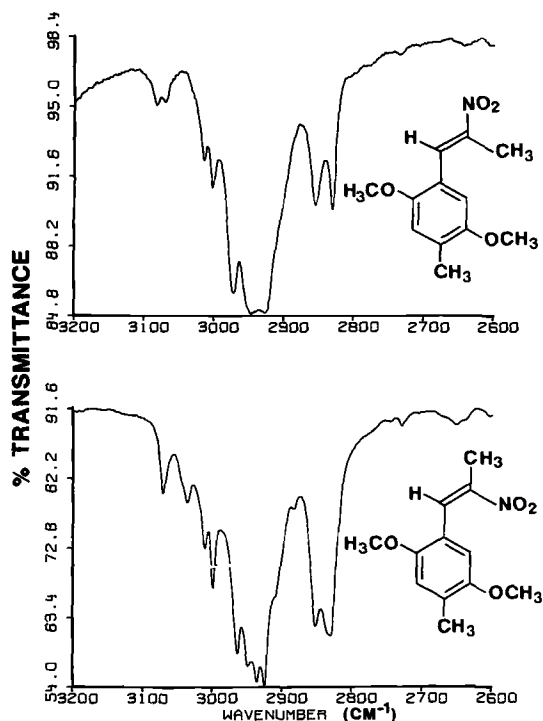


FIG. 3—FT-IR spectra of the C-H stretching region for *cis*(Z)- (bottom) and *trans*(E)-2,5-dimethoxy-4,β-dimethyl-β-nitrostyrene (top).

cm^{-1} for the $\nu_{\text{C}=\text{C}}$ mode of β-methyl-β-nitrostyrene. This is 24 cm^{-1} higher than the frequency of this mode (1634 cm^{-1}) in the parent compound, *trans*-β-nitrostyrene [8]. The higher frequency was attributed to reduced conjugation due to increased steric hindrance by the β-methyl group. The observed frequencies in the present case of ring-substituted *cis*- and *trans*-β-methyl-β-nitrostyrenes are also higher than that of the parent compound. Each of these reported substances probably existed primarily as *trans*-isomers, and the state (solid, film, or solution) of each substance examined was not indicated. Paperno et al. [9] reported some (unassigned) IR frequencies for *para*-methoxy-β-nitrostyrene of unspecified *cis/trans* composition. Zatssepina et al. [10] reported 2935 cm^{-1} for C-H stretching in β-nitrostyrene of unspecified state and isomeric composition.

The Raman spectra (Fig. 1) have two strong bands near 1600 cm^{-1} and a second group of strong bands near 1300 cm^{-1} . The relative intensities and frequencies of these bands provide a basis for differentiation of these isomers based on their Raman spectra. The spectra are also rich in bands between 1700 and 400 cm^{-1} such that the pattern of bands would make unequivocal identification of either isomer straightforward by comparison with reference spectra. The IR spectra, on the other hand, while showing some similar features (see Figs. 2 and 3), are surprisingly rich in contrasting detail for such closely related substances, that no difficulty would be experienced in identifying and differentiating either isomer by comparison with IR reference spectra. The IR spectra are dominated by three very strong absorptions near 1520 , 1220 , and 1045 cm^{-1} . The assignments given in Table 1 of these and other features are based on the usual group frequency arguments of Socrates [11] and Dollish et al. [12].

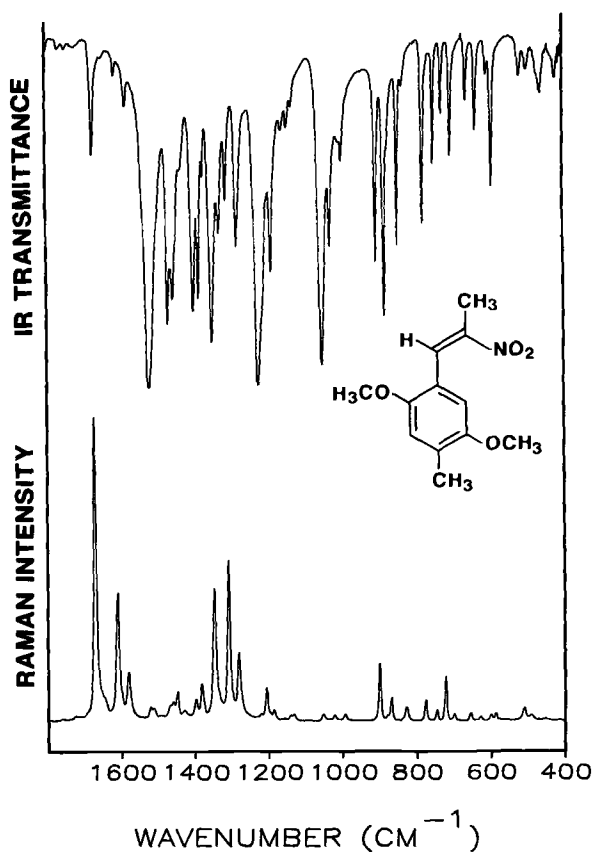


FIG. 4—FT-Raman spectrum (bottom) and IR spectrum (top) of *cis(Z)*-2,5-dimethoxy-4, β -dimethyl- β -nitrostyrene.

Vibrational Modes of the (E,Z) β -Methyl- β -Nitrostyrene Structures

The dominating features of the Raman spectrum for the *cis(Z)* compound are the extremely strong band at 1670 cm^{-1} and strong bands at 1609 , 1346 , and 1307 cm^{-1} (Fig. 1). In contrast, the *trans(E)* compound displays three extremely strong bands at 1301 , 1283 , and 1272 cm^{-1} and two strong bands at 1641 and 1614 cm^{-1} . The very strong band at 1670 cm^{-1} in the spectrum of the *cis* isomer is attributed to ethylenic C=C stretching, which appears at a lower frequency (1641 cm^{-1}) for the *trans* isomer.

Both isomers show similarly strong bands for aromatic C=C stretching near 1610 cm^{-1} . The *trans* isomer shows a very strong Raman band at 1301 cm^{-1} for symmetric NO₂ stretching, which appears less strongly at 1346 cm^{-1} for the *cis* isomer. The corresponding antisymmetric NO₂ stretching vibration gives rise to a weak Raman line near 1515 cm^{-1} for each isomer. The corresponding IR bands are very strong (Fig. 2). A very strong band at 1283 cm^{-1} in the Raman spectrum of the *trans* isomer is attributed to one of the antisymmetric C-O-C stretching modes of the methoxy groups attached to the aromatic ring. A corresponding weaker band is seen at 1307 cm^{-1} for the *cis* isomer. The spectrum of the *trans* isomer has a strong band at 1272 cm^{-1} assigned to C=C stretching of the aromatic ring. A band of medium intensity at 1280 cm^{-1} is attributed to the same vibrational mode in the *cis* isomer.

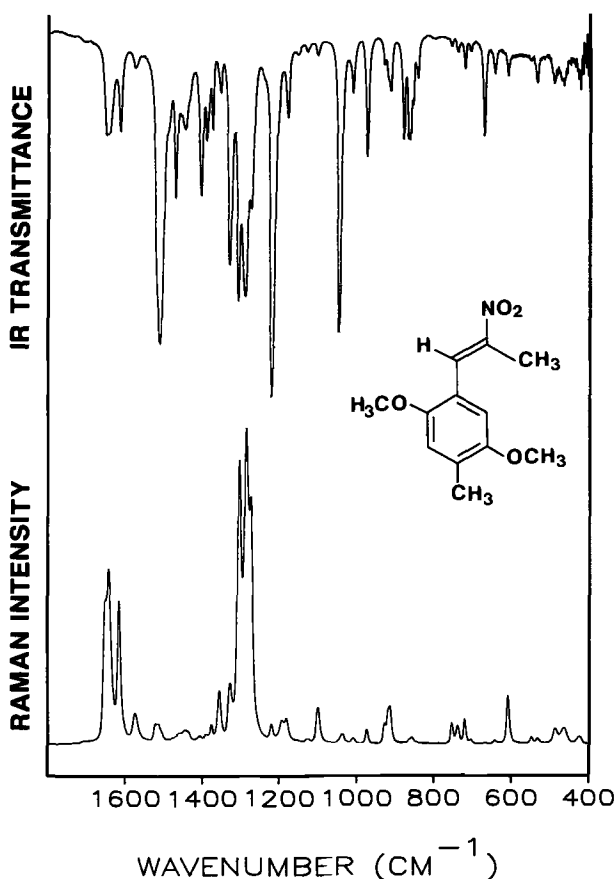


FIG. 5—FT-Raman spectrum (bottom) and IR spectrum (top) of *trans(E)*-2,5-dimethoxy-4,β-dimethyl-β-nitrostyrene.

The IR spectra of the (*E*) and (*Z*) isomers are compared in (Fig. 2). Each spectrum has three very strong absorptions near 1520, 1220, and 1045 cm^{-1} due to antisymmetric NO_2 stretching, antisymmetric C-O-C stretching, and symmetrical C-O-C stretching, respectively. Many other strong-to-medium bands serve to characterize and differentiate the IR spectra of these two isomers, and their assignments are summarized in Table 1. Even the weak-to-medium-intensity bands of the CH stretching region (Fig. 3) permit these two isomers to be readily differentiated. Raman and IR spectra of each isomer are compared as montages in Figs. 4 and 5 to show the complementary nature of these two spectroscopic techniques and the value of their combined use in making vibrational assignments.

In the region of the IR spectrum between 3100 and 2800 cm^{-1} (Fig. 3), CH stretching modes of four different groups can be identified [11]. The single ethylenic CH stretch is attributed to weak bands near 3070 cm^{-1} in each isomer, while the two aromatic CH stretching modes occur near 3015 and 3000 cm^{-1} . Symmetric and antisymmetric CH_3 stretching modes give rise to absorption between 3000 and 2900 cm^{-1} , while the doublets centered near 2840 cm^{-1} are due to CH_3 stretching of the ether O- CH_3 groups.

TABLE 1—Observed wave numbers (cm^{-1}) of bands in the FT-Raman and IR spectra of *cis*(Z)- and *trans*(E)-2,5-dimethoxy-4, β -dimethyl- β -nitrostyrene.^a

<i>Cis</i> (Z)		<i>Trans</i> (E)		Assignment ^b
Raman	IR	Raman	IR	
			3082 vw	combination
	3071 w		3070 vw	$\equiv\text{CH}$ str
	3035 w			combination
	3010 w		3014 w	arom CH str
	2999 w		3002 w	arom CH str
	2964 m		2971 m	asym CH_3 str
	2949 m		2946 m	asym CH_3 str
2924 vw	2925 m	2924 vw	2926 m	sym CH_3 str
	2852		2854 w	asym CH_3 str (OCH_3)
2836 vw	2830 m	2844 vw	2831 w	sym CH_3 str (OCH_3)
1670 vvs	1672 m	1641 s	1645 w	$\text{C}=\text{C}$ str
1609 s		1614 s	1616 w	arom $\text{C}=\text{C}$ str
1580 w	1582 vw	1573 w	1575 vw	arom $\text{C}=\text{C}$ str
1520 vw	1519 vs	1513 w	1510 s	asym NO_2 str
	1467 s		1470 m	asym (O) CH_3 def
1447 w	1453 s	1442 w	1448 w	asym CH_3 def
	1398 s		1405 m	arom $\text{C}=\text{C}$ str
1380 w	1383 s	1375 m	1376 w	sym CH_3 def
1346 s	1348 s	1301 vs	1305 s	sym NO_2 str
	1327 m	1324 m	1328 s	arom $\text{C}=\text{C}$ str
1307 s	1309 w			arom $\text{C}=\text{C}$ str
1280 m	1280 m	1283 vvs	1288 s	asym C-O-C str
		1272 vs	1274 m	CH_3 rock
	1221 vs	1219 vw	1220 vs	asym C-O-C str
1205 w	1207 ssh			CH_3 rock
1185 sh	1185 ms	1181 w	1180 w	β CH
		1099 m	1100 w	(O) CH_3 rock
1051 vw	1047 vs	1036 vw	1046 s	sym C-O-C str
1020 vw	1025 m		1010 w	β CH
991 vw	993 w	973 vw	973 m	(O) CH_3 rock
899 m	902 ms	912 m	913 w	$\equiv\text{CH}$ out-of-plane def
	879 s		879 m	C-C str
868 w	871 msh	855 vw	866 m	C-N str
827 w	843 ms		842 w	C-C str
776 w	775 m	751 w	754 vw	γ CH
745 vw	746 w	737 w	736 vw	C-C str
722 m	723 w	718 w	720 w	γ CH
698 vw	699 m			arom ring def
654 vw	656 w	669 vvw	671 m	alkene skeletal vibration
628 vw	630 w	641 vvw	642 w	NO_2 def
585 vw	586 m	607 m	608 w	arom ring def
	531 w	532 vw	534 w	C-O-C def
510 vw	511 w			alkene skeletal def
490 vw	492 w	487 w	489 w	NO_2 rock
452 vvw	455 w	465 w	465 w	arom ring def

^aRelative intensities are denoted by v = very, s = strong, m = medium, w = weak, sh = shoulder.

^bstr = stretch, γ = out-of-plane deformation, β = in-plane deformation, def = deformation, arom = aromatic, sym = symmetric, asym = antisymmetric.

Differentiation of the Cis and Trans Isomers

A general characteristic which differentiates the *cis*- from the *trans*-isomer is the Raman line attributed to the C=C stretching mode. This line is observed at a higher frequency in the spectrum of the *cis* isomer and is usually stronger in the spectrum of the *cis* than of the *trans* isomer. A similar frequency and intensity pattern is observed for other parts of *cis*- and *trans*-β-nitrostyrenes (unpublished information). A second characteristic is the IR and Raman frequencies of the very strong symmetric NO₂ stretching band, which are about 40 cm⁻¹ higher in the *cis* than in the *trans* isomer. The explanation for both observations may lie in the more nonplanar nature of the *cis* isomer because of steric hindrance between the NO₂ group and the substituted aromatic ring. In the *trans* structure, the molecule is expected to approach planarity, allowing increased conjugation between the ethylenic double bond and the aromatic ring. It is well documented [10] that conjugation lowers the frequency of the C=C stretching mode. Conjugation also extends to the electron withdrawing NO₂ group in the planar *trans* isomer, with a resulting lowering of the frequency of the NO₂ stretching vibration (see Table 1). Lowering of the symmetric NO₂ stretching frequency in the *trans*-isomer is also facilitated by the electron releasing groups (that is, methyl and methoxy) at the *para* and *ortho* positions, respectively, of the aromatic ring. Another feature that differentiates the *trans*- from *cis*-isomer is a weak band near 1100 cm⁻¹, which only appears in the Raman spectra of the *trans*-isomer. This band may be due to one of the two in-plane aromatic CH bending modes expected in this region [10].

Advantage of Near-IR Excitation

The FT-Raman technique has proved to be a simple and rapid method for obtaining fluorescence-free Raman spectra of these two β-nitrostyrenes. These compounds are colored dark orange and fluoresce under visible excitation. This makes conventional Raman spectroscopy difficult. Excitation of Raman spectra in the near-IR region virtually eliminates problems of sample damage and fluorescence.

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References

- [1] Shulgin, A. T., *Handbook of Psychopharmacology*. Vol. 11, *Stimulants*, Plenum Publications, New York, 1978, p. 243.
- [2] Shulgin, A. T., *Handbook of Experimental Pharmacology*. Vol. 55, *Alcohol and Psychomimetics: Psychotropic Effects of Centrally Acting Drugs*, Part III, Springer-Verlag, Berlin, 1981, p. 3.
- [3] Ragan, F. A., Hite, S. A., Samuels, M. S., and Garey, R. E. "4-Bromo-2,5-Dimethoxyphenethylamine: Identification of a New Street Drug," *Journal of Analytical Toxicology*, Vol. 9, March/April 1985, pp. 91-93.
- [4] Lešetický, L., Flieger, M., and Drahorádová, E., "Thermodynamics of E-Z-Isomerization of β-Alkyl-β-Nitrostyrenes," *Collection of Czechoslovakian Chemical Communications*, Vol. 41, 1976, pp. 2744-2748.

- [5] By, A. W., Lodge, B. A., Sy, W.-W., Zamecnik, J., and Duhaime, R., "Chemicals and Physical Properties of (Z)- and (E)-Monoethoxy-1-(2-Nitro-1-Propenyl)Benzenes: Important Precursors to the Monoethoxyamphetamines," *Canadian Society of Forensic Science Journal*, Vol. 23, Nos. 2 and 3, 1990, pp. 91-107.
- [6] Bergin, F. J. and Shurvell, H. F., "Applications of Fourier Transform Raman Spectroscopy in an Industrial Laboratory," *Applied Spectroscopy*, Vol. 43, No. 3, 1989, pp. 516-522.
- [7] Shurvell, H. F. and Bergin, F. J., "Raman Spectra of L(+)-Glutamic Acid and Related Compounds," *Journal of Raman Spectroscopy*, Vol. 20, 1989, pp. 163-168.
- [8] Currie, D. J., Lough, C. E., McClusky, F. K., and Holmes, H. L., "Effect of Functional Group Conformation on the Infrared Spectra of Some Gem Difunctional Phenylethylene Derivatives," *Canadian Journal of Chemistry*, Vol. 47, 1969, pp. 3147-3152.
- [9] Paperno, T. Ya., Perekalin, V. V., and Sopova, A. S., "The Infrared and Ultraviolet Spectra of Some Substituted Nitroalkenes," *Journal of Applied Spectroscopy (U.S.S.R.)*, Vol. 19, No. 4, 1973, pp. 1299-1302.
- [10] Zatssepina, N. N., Tupitsyn, I. F., and Kolodina, N. S., "IR-Spectral Study of Electronic Interactions in Substituted Propenes and Similar Compounds," *Journal of General Chemistry of the USSR*, Vol. 49, No. 10, 1979, pp. 2075-2081.
- [11] Socrates, G., *Infrared Characteristic Group Frequencies*, Wiley and Sons, New York, 1980.
- [12] Dollish, F. R., Fateley, W. G., and Bentley, F. F., *Characteristic Raman Frequencies of Organic Molecules*, Wiley, New York, 1974.

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