

1956

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### Recommended Citation

Dolter, Robert J.; Winch, Bradley; Kissane, James; Junk, Gregor; Howie, Milham; and McFadden, Philip (1956) "A Comparison of the Geometrical and Electronic Structures of Some Styrenes," *Proceedings of the Iowa Academy of Science*, 63(1), 391-397.

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## Authors

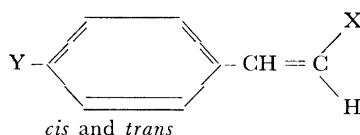
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## A Comparison of the Geometrical and Electronic Structures of Some Styrenes

By REV. ROBERT J. DOLTER, BRADLEY WINCH, JAMES KISSANE,  
GREGOR JUNK, MILHAM HOWIE AND PHILIP MCFADDEN

### INTRODUCTION

For several years investigators in this laboratory have been interested in preparation and isolation of the pure *cis*- and *trans*-isomers of the beta substituted styrenes and their phenyl substituted derivatives and in the identification and elucidation of their geometrical and electronic structures. The following general structural formula is typical of the compounds discussed in this paper.



X and Y represent common organic functional groups. The difference between the dipole moments of geometrical isomers such as these is usually large enough that one can easily assign the proper structure from a comparison of the observed values with those predicted by vector addition of bond and group moments. Also it has been found experimentally that the *trans*-isomer has a greater molar refraction than the *cis*.

In addition to being useful for assigning the proper geometrical structures to isomeric styrenes, these two properties shed much light on the electron displacements or shifts operative in such highly conjugated molecules.<sup>1a</sup> Due to the electron donating or withdrawing powers of most organic functional groups these molecules are conjugated from end to end and are normally characterized by a high degree of resonance stabilization resulting from the formation of polycentric pi-bonds. The molecular dipole moment is directly related to all the permanent polarizations within a molecule, both the local inductive displacements along the dicentric sigma- and pi-bonds and the long range mesomeric effects along the polycentric pi-bonds, but it is especially sensitive to the latter type. As a result, the presence and extent of this mesomeric effect is readily revealed in the significant differences which occur between the observed and predicted moments of conjugated molecules.<sup>1b, 1c</sup>

On the other hand, the molar refraction, when it is determined at finite wave lengths such as the sodium D line, is to a good first approximation directly proportional to the electronic polarizability of a molecule,  $\alpha_E$ ,<sup>1c, 1d</sup>

$$R_D = \frac{4}{3} \pi N \alpha_e$$

where  $N$  is Avagadro's number. The molar refraction is thus a measure of this valuable molecular property. The electronic polarizability involves the valence electrons of the atoms almost exclusively and the bonding electrons primarily<sup>14</sup> and has been conveniently divided by Ingold<sup>15</sup> into the inductomeric effect, which is associated with the electrons occupying moncentric atomic orbitals and dicentric molecular orbitals, and the electromeric effect, which is associated with the electrons in the polycentric pi-orbitals. The inductomeric effect has been found to be practically constant for a great many atoms and groups, as evidenced by the good agreement between the experimental molar refractions of non-conjugated molecules and those calculated from atomic and group refractions. However, appreciable differences are usually obtained between the observed and calculated refractions of highly conjugated systems in which the formation of polycentric pi-bonds is possible, and these exaltations, the values of which depend somewhat on the choice of the additive constants, are commonly taken as a measure of the electromeric polarizability<sup>14, 15</sup>, that is, the electron mobility of the polycentric pi-bonds.

The predicted values of molar refraction used in obtaining the exaltations recorded in Table II were computed by adding the refractions of the substituent groups to that of styrene less the proper number of hydrogens. As a result, the exaltations are not a measure of the total electromeric effect but only that due to interaction of the substituents with the styrene nucleus and with each other.

## EXPERIMENTAL

### *Preparation and Purification of Compounds*

*cis- and trans-Cinnamionitriles.* Benzaldehyde and cyanoacetic acid were condensed to form benzalcyanoacetic acid according to the procedure in ORGANIC SYNTHESSES.<sup>2</sup> The latter compound was decarboxylated to a mixture of *cis-* and *trans-*cinnamionitriles by refluxing for 6 hrs. in pyridine.<sup>16</sup> This mixture was separated into the pure *cis-* and *trans-*isomers by a series of 13 fractional distillations through a modified Vigreux column at a pressure of 12 mm. followed by fractional crystallization. The physical properties (*cis-* m.p.  $-5.5^\circ$ ,  $n_D^{20} = 1.5844$ , and *trans-* m.p.  $23.5^\circ$ ,  $n_D^{20} = 1.6031$ ) were in close agreement with the values reported by Kistiakowsky and Smith.<sup>17</sup>

*cis- and trans-p-Nitrocinnamionitriles.* p-Nitrobenzalcyanoacetic acid was prepared by condensing equimolar amounts of p-nitrobenzaldehyde and cyanoacetic acid in pyridine in the presence of a trace of piperidine as a catalyst. After separation and purification, this product was decarboxylated as above to a mixture of *cis-* and

*trans*-p-nitrocinnamionitriles.<sup>16</sup> The mixture was separated into its components by a series of fractional crystallizations from aqueous ethanol and finally from petroleum ether. The *trans* melted at 202.6°, in good agreement with the value reported by Brady and Thomas.<sup>15</sup> The *cis* melted at 106.5°-107° and was previously characterized by Dolter.<sup>19</sup>

*trans*-p-Nitro-beta-bromostyrene was made by the method of Dann, Howard and Davies.<sup>3</sup> 36 g. of *alpha*-beta-dibromo-beta-(p-nitrophenyl) propionic acid was refluxed for 6 hrs. with a 30% sodium acetate soln. Steam distillation yielded 9 g. of a *cis* and *trans* mixture of p-nitro-beta-bromostyrene. Only 1.9g. of pure *trans*-isomer was isolated from this mixture. M.p. 158.5-160°.

*trans*-p-Bromo-beta-nitrostyrene was made by the method of Campbell, Anderson and Gilmore.<sup>4</sup> Equimolar amounts of nitromethane and p-bromobenzaldehyde were condensed in a minimum amount of absolute methanol containing a trace of piperidine and n-butylamine. This product was purified by recrystallizing several times from absolute ethanol and once from benzene. M.p. 149.7-150°.

*trans*-p-Dimethylamino-beta-nitrostyrene was prepared by the method of Drain and Wilson.<sup>5</sup> p-Dimethylaminobenzaldehyde and nitromethane were condensed in methanol in the presence of one ml. of aqueous methylamine. The product was purified by recrystallizing several times from absolute ethanol. M.p. 183°.

p-Dimethylamino-beta-methyl-beta-nitrostyrene was also prepared by the method of Drain and Wilson.<sup>5</sup> Nitroethane was condensed with p-dimethylaminobenzaldehyde. The purified product melted at 123.5-124.4°.

*Cinnamalacetone* (*trans*-*trans*-3,5-Hexadiene-2-one-6-phenyl) was prepared by the procedure of Plati, Strain and Warren.<sup>6</sup> The product was purified by recrystallizing several times from absolute ethanol. M.p. 68°.

*Cinnamalacetaldehyde* (*trans*-*trans*-2,4-Pentadienal-5-phenyl) was prepared by the method of Vorlander and Daehn.<sup>7</sup> 100g. of cinnamaldehyde and excess acetaldehyde yielded only 2 g. of final product. The compound was purified from reactants and by-products by a series of fractional distillations at reduced pressure. The measurements were made immediately on the freshly distilled material. B.p. 159-163° at 23.5 mm.

*Benzene*. Practical benzene was fractionated through a Hemple column containing glass beads. The constant boiling middle fraction was then shaken successively with concd. sulfuric acid, dil. sodium hydroxide and water; after standing several days over anhydrous calcium chloride the benzene was again fractionated through a self-lagging column filled with Rachig rings. B.p. 79° (uncor.),  $n_D^{25} = 1.4985$ ,  $d_4^{25} = 0.87323$ .

*Measurements and Calculations.* All measurements were made at 25°. Densities were determined in a precisely calibrated 6 ml. pycnometer. Indices of refraction for the sodium D line were measured with an Abbé refractometer. Dielectric constants were determined in a commercial 25  $\mu\mu\text{f.}$  cell<sup>8</sup> by means of the heterodyne zero beat method with capacity removed from the circuit. The weighings were of such magnitude that the weight fraction was never subjected to an experimental error of more than one part per thousand.

The specific polarization at infinite dilution for the solute was calculated from the relationship of LeFevre and Vine.<sup>9</sup>

$${}_{\infty} p_2 = p_1 (1 - \beta/d_1) + 3 \alpha/d_1 (\epsilon_1 + 2)^2$$

Here  ${}_{\infty} p_2$  is the specific polarization of the solute at infinite dilution,  $p_1 = \epsilon_1 - 1/d_1 (\epsilon_1 + 2)$ ,  $\epsilon_1$  is the extrapolated dielectric constant of the solvent,  $d_1$  is the extrapolated density of the solvent,  $\beta$  is the slope of the linear plot of density vs. solute weight fraction and  $\alpha$  is the slope of the linear plot of dielectric constant vs. solute weight fraction. The specific refraction at infinite dilution for the solute was calculated from a relation proposed by Palit.<sup>10</sup>

$${}_{\infty} r_2 = r_1 (1 - \beta/d_1) + 6n_1\gamma/d_1 (n_1^2 + 2)^2$$

Here  ${}_{\infty} r_2$  is the specific refraction of the solute at infinite dilution,  $r_1 = n_1^2 - 1/d_1 (n_1^2 + 2)$ ,  $n_1$  is the refractive index of the solvent and  $\gamma$  is the slope of the linear plot of index of refraction vs. solute weight fraction. The dipole moments were calculated from the relation,

$$\mu = 0.221 ({}_{\infty} P_2 - R_D)^{1/2}$$

where  ${}_{\infty} P_2$  is the total molar polarization of the solute at infinite dilution and  $R_D$  is the molar refraction for the sodium D line.  $R_D$  is assumed to equal the distortion polarization. The constants for these equations are shown in Tables I and II. The slopes and intercepts were obtained either by the method of least squares or, in a few cases, from a graphical plot. Table II contains the total molar polarizations of the solute, the molar refractions, the dipole moments,  $\mu$ , and the interaction exaltations,  $\Delta R$ .

#### DISCUSSION

Both the larger exaltation of refraction and the larger dipole moment of *trans*-cinnamionitrile are evidence for a greater degree of polycentric pi-bonding in this isomer than in the *cis*-cinnamionitrile. This is to be expected since steric hindrance between the phenyl and the cyano groups will prevent the atoms from achieving the same degree of coplanarity in the *cis*. However, a part of this difference in dipole moment is no doubt due to a shorter charge separation in the *cis*-isomer resulting from its curved chain as compared to the extended chain of the *trans*. The much smaller dipole

**Table I**  
Slope-Intercept Data for Dilute Solutions of Styrenes in Benzene at 25°

<i>Compound</i>	$\epsilon_1$	$\alpha$	$d_1$	$\beta$	$n_1$	$\gamma$
<i>cis</i> -Cinnamionitrile	2.2743	10.72	0.87348	0.143	1.4980	0.081
<i>trans</i> -Cinnamionitrile	2.2742	14.51	.87346	.140	1.4976	0.096
<i>cis</i> - <i>p</i> -Nitrocinnamionitrile	2.2683	15.21	.87323	.290	1.4985	.091
<i>trans</i> - <i>p</i> -Nitrocinnamionitrile	2.2705	0.867	.8700	.275	1.4960	.132
<i>trans</i> - <i>p</i> -Nitro- $\beta$ -bromo-styrene	2.2715	4.58	.8733	.409	1.4983	.115
<i>trans</i> - <i>p</i> -Bromo- $\beta$ -nitro-styrene	2.2716	4.89	.8726	.406	1.4977	.125
<i>trans</i> - <i>p</i> -Dimethylamino- $\beta$ -nitrostyrene	2.2730	33.1	.87326	.165	1.4977	.243
<i>p</i> -Dimethylamino- $\beta$ -methyl- $\beta$ -nitrostyrene	2.2730	26.3	.87029	.206	1.4986	.233
<i>trans-trans</i> -Cinnamalacetone	2.2690	8.36	.87275	.143	1.4976	.156
<i>trans-trans</i> -Cinnamalacetaldehyde	2.2697	10.21	.87288	.156		

**Table II**  
Molar Polarizations, Molar Refractions, Dipole moments and Interaction Exaltations

<i>Compounds</i>	$\infty P_2$	$R_D$	$\mu$	$\Delta R$
<i>cis</i> -Cinnamionitrile	298.0	41.5	3.54	0.8
<i>trans</i> -Cinnamionitrile	389.5	43.5	4.12	2.8
<i>cis</i> - <i>p</i> -Nitrocinnamionitrile	539.0	48.1	4.90	0.8
<i>trans</i> - <i>p</i> -Nitrocinnamionitrile	69.9	53.2	0.90	5.9
<i>trans</i> - <i>p</i> -Nitro- $\beta$ -bromostyrene	238.2	55.6	2.98	5.5
<i>trans</i> - <i>p</i> -Bromo- $\beta$ -nitrostyrene	251.6	57.3	3.08	7.2
<i>trans</i> - <i>p</i> -Dimethylamino- $\beta$ -nitrostyrene	1254	79.0	7.58	24.0
<i>p</i> -Dimethylamino- $\beta$ -methyl- $\beta$ -nitrostyrene	1077	80.4	6.98	20.9
<i>trans-trans</i> -Cinnamalacetone	320.8	64.6	3.54	11.5
<i>trans-trans</i> -Cinnamalacetaldehyde	348.9	(60*)	3.80	

\*Estimated

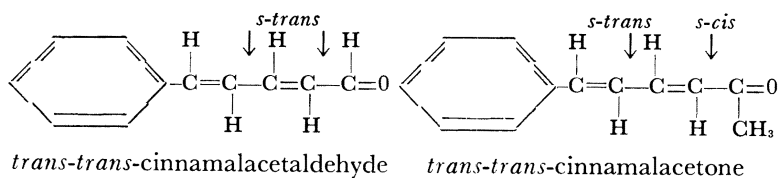
moment of *trans*-*p*-nitrocinnamionitrile, 0.9 D. as compared to 4.90 D. for its *cis* counterpart, is to be expected, since the strongly polar nitro and cyano groups oppose each other in the *trans* while they reinforce each other in the *cis*. The moment of 0.9 for the *trans* is about 0.8 larger than the predicted value and is directed toward the more strongly electron withdrawing nitro group. This increment along with the greater exaltation of the *trans*, 5.9 ml. as compared to 0.8 ml., is evidence for an appreciable mesomeric and electro-meric interaction between the nitro and the cyano groups with the cyano, which normally is electron withdrawing, acting as the electron donor.

The compounds, *trans*-*p*-bromo- $\beta$ -nitrostyrene and *trans*-*p*-nitro- $\beta$ -bromostyrene, were chosen in order to study the pi-

electron displacements in the styrene nucleus. The slightly larger dipole moment and molar refraction of the former is evidence that an electronic shift from the ring toward the vinyl group is preferred and corroborates the conclusion of Otto and Wenske<sup>11</sup> that the small dipole moment of styrene itself is directed toward the vinyl group. However the dipole moments and the molar refractions of both isomers considered here are appreciably larger than the predicted values, which indicates a significant amount of polycentric bond formation in each compound.

The configuration of *p*-dimethylamino- $\beta$ -methyl- $\beta$ -nitrostyrene is not known, but it is postulated that the nitro and phenyl groups are *trans* to each other. This compound was chosen, together with *trans*-*p*-dimethylamino- $\beta$ -nitrostyrene, in order to determine the steric effect of the  $\beta$ -methyl group upon the mesomeric and electromeric interaction between the strongly electron releasing dimethylamino and the strongly electron withdrawing nitro groups. Although some steric inhibition of resonance is present in the  $\beta$ -methyl compound, as is shown by the smaller dipole moment and the smaller exaltation of refraction, a very great amount of interaction still remains in this derivative.

The last two compounds listed in Table II, cinnamalacetone and cinnamalacetaldehyde, were selected in order to study a secondary type of geometrical isomerism prevalent in molecules containing a conjugated chain of double bonds. In a simple diene system, such as that found in butadiene or acrolein, polycentric  $\pi$ -bonding will cause the four participating atoms to lock in either of two extreme coplanar structures, a curved arrangement called the *s-cis* and an extended arrangement called the *s-trans*. In the absence of steric effects the *s-trans* has been found to be slightly more stable.<sup>15</sup> Thus Sutton<sup>12</sup> and coworkers have concluded that cinnamaldehyde, which has a dipole moment of 3.63 in agreement with that calculated for an *s-trans* structure, exists predominantly in an *s-trans* configuration, while benzalacetone, with an unexpectedly small moment of only 3.31, has an *s-cis* configuration because of the steric effect of the methyl group. Four extreme coplanar configurations are possible for the triene systems present in *trans-trans*-cinnamalacetone and *trans-trans*-cinnamalacetaldehyde. On the bases of the experimental dipole moments obtained in this research, 3.80 for the aldehyde and 3.54 for the ketone, it seems safe to conclude that cinnamalacetaldehyde has an *s-trans-s-trans* configuration and that cinnamalacetone has an *s-trans-s-cis*.





## ACKNOWLEDGEMENT

The authors wish to thank the Rt. Rev. Dr. George N. Schulte for his help during the course of the research, Richard Hess for his invaluable assistance in obtaining and computing the dielectric data and John A. Dupont for preparing the pure *cis*- and *trans*-cinnamionitriles.

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