

last long enough to react with a second molecule of the oxidizing agent. If this reaction were to occur, it would preserve the oxidation state of the complexed Co(III).

These experiments also provide evidence for electron transport by the complex organic molecule. This conclusion follows whether it is assumed that the external oxidizing agent attacks the aldehyde end of the ligand or the carboxyl end. If the former, then the odd electron must flow from the aldehyde

end through the molecule to the oxidizing agents; if the latter, two electrons must flow from the aldehyde end, through the molecule to the oxidizing centers. The question of where the attack occurs can perhaps be settled by tracer experiments with the  $H_2O_2$ -Mo(VI) oxidizing mixture but not as readily for the others.

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[CONTRIBUTION FROM THE NIEUWLAND LABORATORIES OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

## Electric Moments of Some *p*-Amino- and *p*-Dimethylamino- $\beta$ -styryl Derivatives<sup>1</sup>

BY ROBERT J. DOLTER AND COLUMBA CURRAN

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Electric moments have been determined for the *p*-amino derivatives of ethyl cinnamate, cinnamionitrile (*trans*) and benzalacetone in benzene and in dioxane, and for *cis*-*p*-aminocinnamionitrile and the *p*-dimethylamino derivatives of ethyl cinnamate, cinnamionitrile (*cis* and *trans*), benzalacetone, cinnamaldehyde and  $\beta$ -nitrostyrene in benzene. The introduction of the vinyl group between the benzene ring and the electron withdrawing groups results in appreciable increases in moments and in an increased solvent effect for the *p*-amino derivatives. Dielectric data indicate *s-cis* and *s-trans* conformations, respectively, for the ketones and aldehyde.

Electric moments, molar refractions and infrared and ultraviolet absorption spectra of *p*-amino and *p*-dimethylamino derivatives of some  $\beta$ -substituted styrenes have been determined to study the effect of increasing length of the conjugated chain on the resonance interaction between electron releasing and electron withdrawing groups and on the increase in  $\pi$ -electron delocalization in hydrogen bonding solvents. The electric moments and some of the refraction data in non-polar solvents are reported in this paper along with the ultraviolet absorption characteristics of *cis* and *trans* isomers.

Otto and Wenzke have reported<sup>2</sup> a moment of 0.37 Debye for styrene, opposite in direction to that of toluene; more recent measurements on styrene have indicated a value between 0.1 and 0.2 Debye. The moments of a series of monosubstituted styrenes determined by Sutton and co-workers<sup>3</sup> have led these authors to conclude that the vinyl group is electron withdrawing with respect to the benzene ring. The lower moment found for *trans*-benzalacetone as compared to the value for *trans*-cinnamaldehyde has been interpreted<sup>4</sup> as indicating an *s-cis* conformation for the ketone and an *s-trans* conformation for the aldehyde. These respective configurations are favored by steric factors.

Previous electric moment studies in this Laboratory<sup>5</sup> on *para*-substituted anilines in benzene and dioxane have indicated an appreciable stabilization of highly polar resonance structures for these compounds in dioxane by hydrogen bonding. The moments of the *p*-aminocinnamyl derivatives have been determined in these two solvents to compare the solvent on the moments of the disubstituted

benzenes and  $\beta$ -styrenes. Two new compounds have been synthesized, *cis*- and *trans*-*p*-aminocinnamionitrile. The compounds other than the nitriles are all *trans*.

### Experimental<sup>6</sup>

*cis*- and *trans*-*p*-Dimethylaminocinnamionitrile were prepared by a modification of the method of Ghosez.<sup>7</sup> Equimolar quantities of *p*-dimethylaminobenzaldehyde and cyanoacetic acid were condensed at 100° in dry pyridine containing 1 ml. of piperidine. The condensate was separated, crystallized from ethanol and decarboxylated by boiling for 36 hr. in pyridine containing a few crystals of  $CuSO_4$ . The solution was poured in water, the resulting precipitate treated with sodium carbonate and the *cis* and *trans* isomers separated by fractional crystallization from aqueous ethanol, m.p. *trans* 168–169°, *cis* 63°. These compounds were new when prepared, but they have since been reported by Coenen and Pestemer.<sup>8</sup>

*Anal.* Calcd. for  $C_{11}H_{12}N_2$ : C, 76.71; H, 7.02. Found: *trans* C, 76.9; H, 7.16; *cis* C, 76.8; H, 6.96.

*cis*- and *trans*-Aminocinnamionitrile were prepared by condensing *p*-nitrobenzaldehyde and cyanoacetic acid as above. The condensate forms within an hour at room temperature. Decarboxylation was complete in 5 hr. The *cis* and *trans* isomers of the nitro derivative were separated by fractional crystallization from 95% ethanol, m.p. 202° and 107°. These were reduced in boiling ammoniacal ferrous sulfate solution. The *trans* amino isomer was purified by recrystallization from aqueous ethanol, m.p. 109–110°, and the *cis* from water, m.p. 94°.

*Anal.* Calcd. for  $C_9H_8N_2$ : C, 74.97; H, 5.59. Found: *trans* C, 75.2; H, 5.80; *cis* C, 75.3; H, 5.59.

Ethyl *p*-aminocinnamate was prepared by condensing *p*-nitrobenzaldehyde with malonic acid, decarboxylating, esterifying with HCl and reducing in boiling ammoniacal ferrous sulfate solution. The product was crystallized from ethanol, m.p. 73.5°.

*p*-Aminobenzalacetone was prepared by three procedures. (a) *p*-Nitrobenzaldehyde and acetone were condensed in alcoholic KOH, dehydrated with acetic anhydride and reduced as above. (b) Benzalacetone was nitrated and the *p*-isomer was reduced. (c) Polymeric *p*-aminobenzalde-

(1) Presented at the 121st Meeting of the American Chemical Society, Milwaukee, Wis., April, 1952.

(2) M. M. Otto and H. H. Wenzke, *THIS JOURNAL*, **57**, 294 (1935).

(3) K. B. Everard, L. Kumar and L. E. Sutton, *J. Chem. Soc.*, 2815 (1951).

(4) J. B. Bently, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *ibid.*, 2957 (1949).

(5) C. Curran and G. K. Estok, *THIS JOURNAL*, **72**, 4575 (1950).

(6) A more detailed description of the preparation of these compounds is given in the Ph.D. thesis of Rev. Robert J. Dolter, University of Notre Dame.

(7) J. Ghosez, *Bull. soc. Chim. Belg.*, **41**, 477 (1932).

(8) M. Coenen and M. Pestemer, *Z. Elektrochem.*, **57**, 785 (1953).

TABLE I  
 MOLAR REFRACTIONS AND ELECTRIC MOMENTS IN BENZENE AND DIOXANE SOLUTION AT 25°

Compound	Solvent	100w <sub>2</sub>	$\Delta D/wf_2$	$\Delta n/wf_2$	$\Delta d/wf_2$	$P_2$	$MR_D$	$\mu$
Ethyl <i>p</i> -aminocinnamate	B	1.1-5.0	8.19	0.134 <sup>a</sup>	0.205	345	64.1	3.70
	D	0.8-7.1	12.2	.235	.096	432	65.8	4.23
Ethyl <i>p</i> -dimethylaminocinnamate	B	.8-6.2	9.09	.136	.167	436	76.9	4.18
<i>cis-p</i> -Aminocinnamionitrile	B	.41-0.46	19.0	...	.207	554	51	4.95
<i>trans-p</i> -Aminocinnamionitrile	B	.3-1.8	30.5 <sup>a</sup>	.187	.219	864	51.8	6.30
	D	.3-4.3	42.6	.304	.110	1051	54.3	6.98
<i>cis-p</i> -Dimethylaminocinnamionitrile	B	.84-0.85	20.9	...	.164	725	64	5.68
<i>trans-p</i> -Dimethylaminocinnamionitrile	B	.8-2.2	31.7	.178	.171	1074	64.3	7.03
<i>p</i> -Aminobenzalacetone	B	.3-2.2	17.0 <sup>a</sup>	.180	.211	558	57.8	4.94
	D	.4-5.0	24.9	.298	.097	702	60.7	5.59
<i>p</i> -Dimethylaminobenzalacetone	B	.7-3.2	18.9	.197	.164	725	73.2	5.64
<i>p</i> -Dimethylaminocinnamaldehyde	B	.5-3.0	26.4	.232	.176	918	70.6	6.43
<i>p</i> -Dimethylamino- $\beta$ -nitrostyrene	B	.2-0.7	34.1	.281	.259	1280	77	7.67

<sup>a</sup> Extrapolated values ( $wf_2 = 0$ ).

lyde was condensed in glacial acetic acid and H<sub>2</sub>SO<sub>4</sub>. Each product was purified by recrystallizing from a methanol-water mixture. The melting points were 82-84° on fast heating and 82-104° on slow heating. Rupe and Siebel<sup>9</sup> report a melting point of 81° on recrystallizing from this solvent. A portion of the product was recrystallized from benzene, m.p. 104-105°. Both high and low melting forms exhibited the same physical properties in solution.

Ethyl *p*-dimethylaminocinnamate was prepared from *p*-dimethylaminobenzaldehyde and malonic acid according to the preceding method, m.p. 77-78°.

*p*-Dimethylaminobenzalacetone was prepared by condensation<sup>10</sup> of *p*-dimethylaminobenzaldehyde and acetone in aqueous ethanol with NaOH. The product was recrystallized from 95% ethanol, m.p. 135-136°.

*p*-Dimethylaminocinnamaldehyde was prepared by the method of König,<sup>11</sup> *et al.* *p*-Dimethylaminobenzaldehyde was condensed at 0° with paraldehyde in concentrated H<sub>2</sub>SO<sub>4</sub>. The melting point on recrystallization from ethanol was 139-140°.

*p*-Dimethylamino- $\beta$ -nitrostyrene was prepared by the method of Drain and Wilson.<sup>12</sup> The product was recrystallized from nitromethane, m.p. 181°.

Solvents were purified as in previous studies; the dielectric constant of the dioxane at 25° varied from 2.207 to 2.212.

**Measurements and Calculations.**—Indices of refraction of solutions were measured with a Pulfrich refractometer, using the sodium D line. The molar refractions were calculated from the  $\Delta n/wf_2$  and  $\Delta d/wf_2$  ratios using an equation similar to that of Sutton and co-workers.<sup>13</sup> Measurements of dielectric constants and densities have been described previously.<sup>14</sup> In calculating the electric moments, the distortion polarizations were taken as  $R_D$ . Sutton<sup>8</sup> has pointed out that the dispersion,  $D = R_D - R_\infty$  for a substituted styrene is appreciably greater than the atomic polarization. He has chosen to calculate  $R_D$  from group refractions and has equated  $P_A$  to  $R_D$  (calcd.) -  $R_\infty$ . We have observed large exaltations in the values of  $R_D$  for disubstituted benzenes<sup>15</sup> having electron releasing groups conjugated with electron withdrawing groups and have attributed a portion of these exaltations to increased  $\pi$ -electron delocalization. More recently we have observed exaltations in  $R_\infty$  for *p*-aminocinnamionitrile and *p*-dimethylaminocinnamionitrile in ethanol of 6.8 and 6.0 m., respectively; for each of these compounds in this solvent,  $R_\infty$  is greater than  $R_D$  (calcd.). It is recognized that the distortion polarizations of the compounds studied are probably

somewhat less than  $R_D$ , but they appear also to be greater than  $R_D$  (calcd.).

The increases in dielectric constant, refractive index and density with weight fraction of solute for the compounds studied are listed in Table I along with the polarizations and electric moments.

### Discussion

The large moments obtained for the esters, ketones, aldehyde and  $\beta$ -nitro derivative indicate that these are *trans* compounds. The smaller moments found for the lower melting nitriles definitely establish them as the *cis* isomers. The difference in moment between the *trans* and *cis* nitrile isomers is the same for both the amino and dimethylamino compounds, 1.35 Debye units.

Whereas in this investigation *cis* isomers were isolated only for the nitriles, *cis* isomers have been reported for a number of unsubstituted cinnamyl derivatives, for example, cinnamic acid and benzalacetone. This suggests that the increased  $\pi$ -electron delocalization in *p*-amino- and *p*-dimethylaminocinnamyl compounds, resulting in greater single bond character for the vinyl carbon-to-carbon bond, allows the sterically less stable *cis* compounds (or intermediates) to be completely converted to the *trans* isomers. The *cis* nitriles are sterically less strained than the other *cis* derivatives, so their isolation is not surprising. On standing for six months at room temperature, 20% of crystalline *cis-p*-dimethylaminocinnamionitrile isomerized.

As indicated in Table II, the ultraviolet spectra of the *cis* and *trans* nitriles in ethanol are very similar. In contrast, the transition probabilities for the long wave length absorption by cinnamic acid in ethanol<sup>16</sup> and benzalacetophenone in iso-octane<sup>17</sup> are appreciably greater for the *trans* than for the *cis* isomers. This illustrates the much greater effect on light absorption of non-planarity than the mere bending back of a planar conjugated chain.

The moment obtained for *p*-dimethylaminocinnamaldehyde is 0.79 unit higher than that of *p*-dimethylaminobenzalacetone, compared to the difference, 0.32 Debye, obtained by Sutton and co-workers for cinnamaldehyde and benzalacetone.

(16) E. A. Braude, *Ann. Reports of Chem. Soc. (London)*, **42**, 105 (1945).

(17) R. E. Lutz and R. H. Jordan, *This Journal*, **72**, 1010 (1950).

(9) H. Rupe and O. Siebel, *Z. Farbenindustrie*, **5**, 301 (1906); *Chem. Zentr.*, **77**, II, 1324 (1906).

(10) N. Picus and P. E. Spoerri, *This Journal*, **70**, 3072 (1948).

(11) W. König, W. Schramek, G. Rosch and H. Arnold, *Ber.*, **61B**, 2074 (1928).

(12) D. Drain and W. Wilson, *J. Chem. Soc.*, 767 (1949).

(13) K. B. Everard, R. A. W. Hill and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

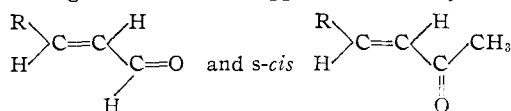
(14) C. Curran, P. A. McCusker and H. S. Makowski, *This Journal*, **79**, 5188 (1957).

(15) C. Curran and F. M. Palermi, *ibid.*, **73**, 3733 (1951).

TABLE II  
ULTRAVIOLET ABSORPTION CHARACTERISTICS

		$\lambda_{\max},$ m $\mu$	$\epsilon \times 10^{-2}$	$\lambda'_{\max},$ m $\mu$	$\epsilon \times 10^{-2}$
Cinnamic acid	<i>cis</i>	264	9.5	214	10.5
	<i>trans</i>	273	20.0	215	15.0
Benzalacetophenone	<i>cis</i>	290	9.0	248	14.0
	<i>trans</i>	298	23.6	227	12.0
<i>p</i> -Aminocinnamo- nitrile	<i>cis</i>	344	20.1	238	9.0
	<i>trans</i>	344	24.3	235	9.1
<i>p</i> -Dimethylamino- cinnamonnitrile	<i>cis</i>	364	28.6	244	10.3
	<i>trans</i>	364	31.0	243	10.6

This large difference suggests not only *s-trans*



conformations for the aldehyde and ketone but also that there is less resonance interaction between the electron releasing and electron withdrawing groups in the ketone. This latter conclusion is supported by the large interaction polarizability,<sup>15</sup> 10.6 ml., for the aldehyde compared to the value 8.8 ml. for the ketone.

The insertion of the vinyl group between the benzene ring and the electron withdrawing group in *para* disubstituted benzenes has the following effects on the electric moments in benzene solution:

1. The moments of the *p*-dimethylamino ester<sup>18</sup> nitrile,<sup>19</sup> aldehyde<sup>5</sup> and nitro compound<sup>20</sup> are in-

(18) J. J. Downs, M.S. Thesis, University of Notre Dame, 1952.

(19) E. Hertel and E. Dumont, *Z. physik. Chem.*, **B30**, 139 (1935); value recalculated.

creased by 0.40, 0.78, 0.85 and 0.80 unit, respectively.

2. The moments of the *p*-amino<sup>5</sup> ester, nitrile and ketone are increased by 0.42, 0.34 and 0.46 units, respectively. These results suggest about equal contributions of highly polar structures to the corresponding benzene and styrene derivatives, the greater charge separation in the latter structures accounting for the greater moments.

The insertion of the vinyl group also brings about a greater change in dipole moment,  $\Delta\mu$ , from benzene to dioxane solution for the *p*-amino derivatives. The values of  $\Delta\mu$  for the ester, nitrile and ketone in the benzene series<sup>5</sup> are 0.39, 0.50 and 0.46 Debye and in the styrene series 0.53, 0.67 and 0.65, respectively. This suggests that the increased stabilization of highly polar resonance structures in dioxane by O---H---N hydrogen bonding is about the same for the corresponding members of the two series, the greater charge separation in the styrene derivatives accounting for the larger values of  $\Delta\mu$ .

These data offer conclusive evidence that the vinyl group does not impede resonance between an electron-releasing group on the benzene ring and a beta electron withdrawing substituent. Such impedence might be inferred from the predominantly *ortho*, *para* substitution in alkyl cinnamates by electrophilic groups, which has led some authors to propose electron migration from the vinyl group to the ring in the activated state. It may well be that the vinyl group in reacting molecules is significantly affected by a constituent of the reaction mixture before substitution occurs.

(20) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 599 (1936).

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

## The Heat Capacity and Thermodynamic Functions of Mercurous Sulfate Between 4 and 20°K.<sup>1</sup>

BY T. E. BRACKETT, E. W. HORNUNG AND T. E. HOPKINS

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The heat capacity of mercurous sulfate has been measured from 4 to 20°K. The results, together with available heat capacity data at higher temperatures, have been used to calculate the entropy at 298.15°K., which is found to be 47.96 gibbs mole<sup>-1</sup>.<sup>2</sup> This value along with the third law values of other compounds is used to compute the change in entropy of two reactions. The change in entropy computed in this way is then compared with the results of cell measurements on these reactions. The comparisons indicate that the cell measurements are in error.

This paper reports the results of an investigation of the heat capacity of mercurous sulfate in the temperature region 4 to 20°K. Measurements of its heat capacity between 15 and 300°K. have been made by Papadopoulos and Giauque.<sup>3</sup> The combined results establish accurate values of the thermodynamic properties of mercurous sulfate from 4 to 300°K.

For substances with a very small heat capacity

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(2) 1 gbs. (gibbs) = 1 defined cal./defined deg. K. See, W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *THIS JOURNAL*, **82**, 62 (1960).

(3) M. N. Papadopoulos and W. F. Giauque (to be published).

at 15°K., or substances which obey a Debye  $T^3$  expression near that temperature, it is usually sufficient to extrapolate the heat capacity vs. temperature graph to 0°K. and still retain a high accuracy for the thermodynamic functions of the compound. Mercurous sulfate, however, has the high heat capacity of 3.308 gibbs mole<sup>-1</sup> at 15°K. and it departs considerably from a  $T^3$  function; therefore it was considered desirable to extend the measurements on this salt to lower temperatures, thereby obtaining as accurate values as possible for its thermodynamic functions.

**Apparatus.**—The apparatus was a calorimeter designed to operate in the region from 4 to 20°K. In general the apparatus was not dissimilar to those used in this Laboratory at higher temperatures. A few differences are noted below.