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The Dipole Moments and Molar Refractions of Several *Trans*-Beta-Nitrostyrenes¹

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Abstract. The dipole moments and molar refractions are reported for p-nitrostyrene (4.24 D, 44.3 ml.), *trans*-beta-nitrostyrene (4.50 D, 45.7 ml.), the p-methoxy (5.45 D, 56.3 ml.), p-methyl (4.97 D, 52.0 ml.), p-fluoro (3.12 D, 45.5 ml.), p-chloro (2.90 D, 51.8 ml.), p-bromo (3.02 D, 54.4 ml.), p-iodo (3.26 D, 58.0 ml.), p-nitro (0.83 D, 52.0 ml.), and p-cyano (0.96 D, 47.9 ml.) derivatives of *trans*-beta-nitrostyrene. It is suggested that the large dipole moments obtained for the p-nitro and p-cyano-beta-nitrostyrenes may be due to unusually large atomic polarizations which would not be taken into consideration by the present method of measurement and calculation.

A previous paper from this laboratory (1) and other papers (2, 3, 4) have been concerned with the dipole moments and molar refractions of substituted styrenes. These properties have been of considerable importance in elucidating the geometrical and electronic structures of such compounds (1, 3, 4).

Several investigators in this laboratory have been interested in preparing pure *cis*-beta-nitrostyrenes for some time, however their efforts have met with only limited success. Although the dipole moments and spectral studies indicate that *cis* compounds have indeed been obtained, it appears that they are contaminated with significant amounts of the *trans* isomers. Attempts to purify the *cis* isomers are currently in progress.

Another area under investigation has been the observation of the effect of substitution of alkyl groups for hydrogen on the beta position by a comparison of the properties of beta-alkyl-beta-nitrostyrenes with the simple beta-nitrostyrenes. While this endeavor is also well under way, it is not finished.

However, the recent activity in this area and interest in this type of compound prompts the reporting of the dipole moments and molar refractions of eight *trans*-p-substituted-beta-nitrostyrenes, *trans*-beta-nitrostyrene and p-nitrostyrene. This informa-

¹ (a) R. J. Buenker was an N.S.F. Undergraduate Participant during the summers of 1961 and 1962, the 1961-62 academic year and the first semester of the 1962-63 academic year; (b) J. P. Plamondon was an N.S.F. Undergraduate Research Participant during the summers of 1961 and 1962 and the first semester of the 1962-63 academic year; (c) Dennis Koopman was an N.S.F. Undergraduate Research Participant during the summer of 1961 and the 1961-62 academic year.

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tion has been reported for some of these compounds and the published measurements have been compared to the current data.

The unusually large dipole moments obtained for the p-nitro and p-cyano-beta-nitrostyrenes are the only measurements obtained that are inconsistent with predicted values. However, this same type of anomalous behavior has been observed by others (5, 6) particularly with symmetrical compounds that contain two powerful electron withdrawing groups. Examples of such compounds are p-dinitrobenzene, p-cyanonitrobenzene, 4,4'-dicyanobiphenyl and 4,4'-dinitrobiphenyl. These authors and others (7) have concluded that the results may be due to an abnormally large atomic polarization in these compounds.

Since atomic polarizations are difficult to measure, dipole moments are usually calculated by assuming that the molar refraction is equal to the electronic polarization plus the atomic polarization (1). If however, the atomic polarization is very large this assumption is invalid and the dipole moment obtained will be too large.

$$R_D = P_e + P_a$$

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

The high dipole moments obtained for the p-nitro and p-cyano-beta-nitrostyrenes suggest that they may be additional examples of compounds with very large atomic polarizations.

Table 1. Slope-Intercept Data for Dilute Solutions of Styrenes in Benzene at 25°.

Compound	ϵ_1	α	d_1	β	n_1	γ
p-nitrostyrene	2.2701	13.34	0.8733	0.218	1.4979	0.079
<i>trans</i> -beta-nitrostyrene	2.2760	15.08	0.8724	0.243	1.4969	0.113
<i>trans</i> -p-methoxy-beta-nitrostyrene	2.2764	18.45	0.8733	0.265	1.4976	0.141
<i>trans</i> -p-methyl-beta-nitrostyrene	2.2738	16.83	0.8729	0.217	1.4972	0.117
<i>trans</i> -p-fluoro-beta-nitrostyrene	2.2726	6.55	0.8735	0.283	1.4975	0.080
<i>trans</i> -p-chloro-beta-nitrostyrene	2.2821	5.34	0.8730	0.316	1.4972	0.119
<i>trans</i> -p-bromo-beta-nitrostyrene	2.2742	4.68	0.8731	0.417	1.4972	0.111
<i>trans</i> -p-iodo-beta-nitrostyrene ^a	2.2692	4.53	0.8748	0.483	1.4995	0.107
<i>trans</i> -p-nitro-beta-nitrostyrene	2.2733	0.705	0.8733	0.348	1.4973	0.114
<i>trans</i> -p-cyano-beta-nitrostyrene ^b	2.2693	0.873	0.8725	0.312	1.4971	0.109

^a Taken from the unpublished work of R. J. Dolter and T. J. Swift.

^b Taken from the unpublished work of R. J. Dolter and J. R. Tretter.

EXPERIMENTAL

Trans-beta-nitrostyrenes. The *trans*-beta-nitrostyrenes were prepared by condensing the appropriate aromatic aldehyde with nitromethane according to the procedure in Organic Syntheses for the preparation of *trans*-beta-nitrostyrene (8). Table 3 lists

the observed melting points, literature melting points and references.

Table 2. Observed Molar Polarizations, Molar Refractions and Dipole Moments; Literature Dipole Moments and Literature References.

Compound	∞P_2	R_D	μ	μ (lit)	Ref.
p-nitrostyrene	413.1	44.3	4.24	4.23	(2)
trans-beta-nitrostyrene	459.8	45.7	4.50	4.50 4.51 4.51	(2) (4) (4)
Trans-p-dimethylamino-beta-nitrostyrene	7.58 7.67 7.61	(1) (3) (4)
trans-p-methoxy-beta-nitrostyrene	663.8	56.3	5.45	5.43	(4)
trans-p-bromo-beta-nitrostyrene	558.6	52.0	4.97	5.00	(4)
trans-p-fluoro-beta-nitrostyrene	244.4	45.5	3.12
trans-p-chloro-beta-nitrostyrene	224.0	51.8	2.90
trans-p-methyl-beta-nitrostyrene	241.2	54.4	3.02	3.08	(1)
trans-p-iodo-beta-nitrostyrene ^a	275.6	58.0	3.26
trans-p-nitro-beta-nitrostyrene	65.9	52.0	0.83	1.00	(4)
trans-p-cyano-beta-nitrostyrene ^b	66.8	47.9	0.96

^a Taken from the unpublished work of R. J. Dolter and T. J. Swift.

^b Taken from the unpublished work of R. J. Dolter and J. R. Tretter.

Table 3.

Compound	m.p.	m.p. (lit)	Ref.
trans-beta-nitrostyrene	57.5-58.2°	57-58°	(8)
trans-p-methoxy-beta-nitrostyrene	87-88°	86-87°	(4,9)
trans-p-methyl-beta-nitrostyrene	103-103.5°	103-103.5°	(10)
trans-p-fluoro-beta-nitrostyrene	100-101°	100-101°	(a)
trans-p-chloro-beta-nitrostyrene	114-115°	112-112.5°	(11)
trans-p-bromo-beta-nitrostyrene	149-150°	149-150°	(1)
		156-158°	(12)
trans-p-iodo-beta-nitrostyrene	187°	183-184°	(12)
trans-p-nitro-beta-nitrostyrene	201-203°	203-204°	(13)
trans-p-cyano-beta-nitrostyrene	188-189°	186-188°	(14)

^a Taken from the unpublished work of R. J. Dolter and J. J. Miller.

p-Nitrostyrene prepared by a method described for the preparation of m-nitrostyrene (15), gave a m.p. 21.5-22°; literature m.p. 21.4° (16).

The measurement and calculation of the dipole moments were carried out according to the method described by Rev. R. J. Dolter, et. al. (1).

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