

1969

The Dipole Moments, Molar Refractions and Ultraviolet Spectra of Several Substituted, β -Alkyl- β -Nitrostyrenes

K. W. Kraus
Loras College

R. J. Dolter
Loras College

G. E. Petrowski

R. T. Bogan

R. J. Buenker

See next page for additional authors

Copyright © Copyright 1969 by the Iowa Academy of Science, Inc.
Follow this and additional works at: <http://scholarworks.uni.edu/pias>

Recommended Citation

Kraus, K. W.; Dolter, R. J.; Petrowski, G. E.; Bogan, R. T.; Buenker, R. J.; Plamondon, J. E.; Miller, J. J.; Whalen, D. L.; and Koopman, D. J. (1969) "The Dipole Moments, Molar Refractions and Ultraviolet Spectra of Several Substituted, β -Alkyl- β -Nitrostyrenes," *Proceedings of the Iowa Academy of Science*: Vol. 76: No. 1, Article 19.
Available at: <http://scholarworks.uni.edu/pias/vol76/iss1/19>

This Research is brought to you for free and open access by UNI ScholarWorks. It has been accepted for inclusion in Proceedings of the Iowa Academy of Science by an authorized editor of UNI ScholarWorks. For more information, please contact scholarworks@uni.edu.

The Dipole Moments, Molar Refractions and Ultraviolet Spectra of Several Substituted, β -Alkyl- β -Nitrostyrenes

Authors

K. W. Kraus, R. J. Dolter, G. E. Petrowski, R. T. Bogan, R. J. Buenker, J. E. Plamondon, J. J. Miller, D. L. Whalen, and D. J. Koopman

The Dipole Moments, Molar Refractions and Ultraviolet Spectra of Several Substituted β -Alkyl- β -Nitrostyrenes

K. W. KRAUS¹, R. J. DOLTER¹, G. E. PETROWSKI,
R. T. BOGAN, R. J. BUENKER, J. E. PLAMONDON,
J. J. MILLER, D. L. WHALEN, AND D. J. KOOPMAN.

Abstract. The dipole moments, molar refractions, and some ultraviolet absorption data (λ_{\max} and ϵ_{\max}) are reported for β -methyl- β -nitrostyrene (4.25 D, 51.8 ml, 307 $m\mu$, 12,200), the *p*-methoxy (5.04 D, 59.2 ml), *p*-methyl (4.66 D, 54.8 ml), *p*-fluoro (2.82 D, 49.5 ml, 308 $m\mu$, 11,000), *p*-chloro (2.68 D, 54.5 ml, 310 $m\mu$, 14,200), *p*-bromo (2.71 D, 55.8 ml, 308 $m\mu$, 17,000), *p*-iodo (2.91 D, 62.8 ml, 318 $m\mu$, 15,500), *p*-nitro (1.12 D, 55.1 ml, 302 $m\mu$, 16,600), & *p*-cyano (1.15 D, 54.5 ml, 294 $m\mu$, 16,500) derivatives of β -methyl- β -nitrostyrene. The same data are reported for β -ethyl- β -nitrostyrene (4.15 D, 52.1 ml, 306 $m\mu$, 9,800), the *p*-methoxy (5.07 D, 63.3 ml, 346 $m\mu$, 15,600), *p*-methyl (4.73 D, 63.0 ml, 325 $m\mu$, 8,500), *p*-fluoro (2.77 D, 52.7 ml, 309 $m\mu$, 10,300), *p*-chloro (2.71 D, 60.6 ml, 312 $m\mu$, 12,300), *p*-bromo (2.77 D, 60.7 ml, 313 $m\mu$, 13,000), *p*-iodo (2.99 D, 69.1 ml, 320 $m\mu$, 15,100), *p*-nitro (1.12 D, 64.4 ml, 300 $m\mu$, 16,500) & *p*-cyano (1.31 D, 56.2 ml, 292 $m\mu$, 15,000) derivatives of β -ethyl- β -nitrostyrene. The ultraviolet absorptions are also reported for the *p*-fluoro (313 $m\mu$, 16,100), *p*-bromo (314 $m\mu$, 21,900), *p*-iodo (323 $m\mu$, 17,400), and the *p*-cyano (299 $m\mu$, 21,100) derivatives of *trans*- β -nitrostyrene.

The dipole moments, molar refractions, and ultraviolet spectra have been useful properties for comparing geometric and electronic structures of substituted styrenes (2, 3, 4, 7, 10).

It has been shown previously that the presence of the β -methyl group exhibits a hindrance to resonance as evidenced by lower dipole moments for certain β -methyl- β -nitrostyrenes as compared to the simple β -nitrostyrenes (3, 10). The present data demonstrates that this behavior is general for a series of β -alkyl- β -nitrostyrenes.

The general bathochromic shift and hypochromic effect observed when β -alkyl- β -nitrostyrenes are compared to simple β -nitrostyrenes corroborate the ability of the β -alkyl group to offer steric inhibition to the resonance of the system.

A comparison of the observed dipole moments with values calculated from group moments confirm that the substituted phenyl group and the nitro group are *trans* to each other in these compounds.

The high dipole moments obtained for the *p*-nitro and *p*-cyano- β -alkyl- β -nitrostyrenes indicate that they are additional examples of compounds with very large atomic polarizations, as suggested for other similar compounds that contain two powerful electron withdrawing groups opposing each other (1, 7).

¹ Department of Chemistry, Loras College, Dubuque, Iowa—52001.

The dipole moments of the β -ethyl- β -nitrostyrenes are essentially the same values as those obtained for the corresponding β -methyl- β nitrostyrenes. The wavelength of ultraviolet absorption is also similar, but there is a general hypochromic effect observed in comparing the β -methyl derivatives to the β -ethyl compounds.

EXPERIMENTAL

Compounds. The β -alkyl- β -nitrostyrenes were prepared essentially by a method described by D. N. Robertson (9). The β -ethyl- β -nitrostyrene had a b.p. of 122-123° (5 mm); lit. b.p. 121° (6 mm) (5).

Table 1

Melting points, literature melting points and references for known compounds.

Compound	m.p.	m.p. (lit.)	Ref.
β -methyl- β -nitrostyrene	63-64°	64°	(10)
<i>p</i> -methoxy- β -methyl- β -nitrostyrene	44-45°	43-44°	(10)
<i>p</i> -methyl- β -methyl- β -nitrostyrene	54.5—55°	52.3°	(10)
<i>p</i> -chloro- β -methyl- β -nitrostyrene	81-83°	84°	(8)
<i>p</i> -nitro- β -methyl- β -nitrostyrene	114-115°	114-115°	(10)

Dipole Moments. The measurement and calculation of the dipole moments were carried out according to the method described by R. J. Dolter, et. al. (3). Table 3 lists the slope-intercept data for the β -methyl- β -nitrostyrenes. Table 4 lists the slope-intercept data for the β -ethyl- β -nitrostyrenes.

Table 5 contains the properties measured for the β -alkyl- β -nitrostyrenes and compares them with the corresponding β -nitrostyrenes.

Ultraviolet Spectra. The ultraviolet absorption data for the simple β -nitrostyrenes and the β -alkyl- β -nitrostyrenes are reported in Table 6.

ACKNOWLEDGEMENT

The authors wish to acknowledge the support of this work by the National Science Foundation Undergraduate Research Participation Program.

LITERATURE CITED

- DiCARLO, E. N. & C. P. SMYTH, *J. Am. Chem. Soc.*, **84**, 1128 (1962).
 DOLTER, R. J. & C. CURRAN, *J. Am. Chem. Soc.*, **82**, 4153 (1960).
 DOLTER, R. J., B. WINCH, J. KISSANE, G. JUNK, M. HOWIE, & P. McFADDEN, *Proc. Iowa Acad. Sci.*, **63**, 391 (1956).
 EVERARD, K. B., L. KUMAR, & L. E. SUTTON, *J. Chem. Soc.*, 2807 (1951).
 HASS, H. B., A. G. SUSIE & R. L. HEIDER, *J. Org. Chem.*, **15**, 8 (1950).

Table 2

Melting Points, Formulas and Analyses of New Compounds.

Compound	M.P.	Formula	Analysis			
			Calculated		Found	
			%C	%H	%C	%H
<i>p</i> -fluoro- β -methyl- β -nitrostyrene	65-66°	C ₉ H ₉ FNO ₂	59.67	4.45	59.88	4.57
<i>p</i> -bromo- β -methyl- β -nitrostyrene	89.5— 90.5°	C ₉ H ₈ BrNO ₂	44.65	3.33	44.90	3.48
<i>p</i> -iodo- β -methyl- β -nitrostyrene	126—127°	C ₉ H ₈ INO ₂	37.40	2.79	37.57	2.97
<i>p</i> -cyano- β -methyl- β -nitrostyrene	118.5— 119.5°	C ₁₀ H ₈ N ₂ O ₂	63.83	4.28	63.95	4.42
<i>p</i> -methoxy- β -ethyl- β -nitrostyrene	54.5—55.5°	C ₁₁ H ₁₃ NO ₃	63.76	6.32	63.95	6.39
<i>p</i> -methyl- β -ethyl- β -nitrostyrene	33—34°	C ₁₁ H ₁₃ NO ₂	69.09	6.85	68.89	7.02
<i>p</i> -fluoro- β -ethyl- β -nitrostyrene	70—71°	C ₁₀ H ₁₀ FNO ₂	61.53	5.16	61.42	5.14
<i>p</i> -chloro- β -ethyl- β -nitrostyrene	75—76°	C ₁₀ H ₁₀ ClNO ₂	56.75	4.76	56.91	4.89
<i>p</i> -bromo- β -ethyl- β -nitrostyrene	74.5—75°	C ₁₀ H ₁₀ BrNO ₂	46.90	3.94	46.95	4.03
<i>p</i> -iodo- β -ethyl- β -nitrostyrene	47-47.5°	C ₁₀ H ₁₀ INO ₂	39.63	3.33	39.73	3.40
<i>p</i> -nitro- β -ethyl- β -nitrostyrene	100—101°	C ₁₀ H ₁₀ N ₂ O ₄	54.06	4.54	54.27	4.62
<i>p</i> -cyano- β -ethyl- β -nitrostyrene	114—114.5°	C ₁₁ H ₁₀ N ₂ O ₂	65.34	4.98	65.26	4.92

Table 3
Slope-Intercept Data for Dilute Solutions of the β -methyl- β -nitrostyrenes in Benzene at 25°.
 p -XC₆H₄CH = C(NO₂)CH₃

X	ϵ_1	α	d_1	β	n_1	δ
H	2.2693	12.32	0.8730	0.213	1.4982	0.111
CH ₃ O	2.2710	14.65	0.8732	0.251	1.4971	0.118
CH ₃	2.2717	13.57	0.8733	0.195	1.4975	0.085
F	2.2722	4.97	0.8735	0.269	1.4985	0.071
Cl	2.2740	4.22	0.8732	0.292	1.4982	0.093
Br	2.2738	3.54	0.8729	0.404	1.4977	0.099
I	2.2714	3.51	0.8726	0.471	1.4980	0.111
NO ₂	2.2733	0.904	0.8723	0.314	1.4983	0.087
CN	2.2755	1.025	0.8735	0.254	1.4982	0.091

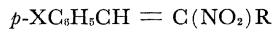
Table 4

Slope-Intercept Data for Dilute Solutions of the β -ethyl- β -nitrostyrenes in Benzene at 25°.

X	ϵ_1	α	d_1	β	n_1	δ
H	2.2669	10.74	0.8734	0.200	1.4982	0.062
CH ₃ O	2.2764	13.82	0.8725	0.239	1.4978	0.108
CH ₃	2.2674	12.97	0.8713	0.170	1.4981	0.102
F	2.2766	4.44	0.8734	0.254	1.4975	0.054
Cl	2.2701	3.99	0.8729	0.246	1.4982	0.079
Br	2.2741	3.47	0.8732	0.371	1.4982	0.077
I	2.2771	3.49	0.8739	0.420	1.4981	0.094
NO ₂	2.2744	0.877	0.8739	0.256	1.4980	0.092
CN	2.2725	1.061	0.8733	0.226	1.4986	0.050

Table 5

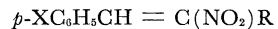
Literature Molar Refractions, Dipole Moments and References for the simple β -nitrostyrenes (R = H) and the Observed Molar Polarizations, Molar Refractions, Dipole Moments, Literature Dipole Moments and Literature References for the β -alkyl- β -nitrostyrenes (R = CH₃ or C₂H₅).



X	R = H (Ref. 7)		R = CH ₃				R = C ₂ H ₅		
	R _D	μ	∞P_2	R _D	μ	μ (Ref. 10)	∞P_2	R _D	μ
H	45.7	4.50	421.1	51.8	4.25	4.14	405.6	52.1	4.15
CH ₃ O	56.3	5.45	580.2	59.2	5.04	5.09	590.0	63.3	5.07
CH ₃	52.0	4.97	499.6	54.8	4.66	4.55	521.5	63.0	4.73
F	45.5	3.12	211.9	49.5	2.82	—	210.0	52.7	2.77
Cl	51.8	2.90	201.9	54.5	2.68	—	210.9	60.6	2.71
Br	54.4	3.02	206.5	55.8	2.71	—	217.6	60.7	2.77
I	58.0	3.26	236.5	62.8	2.91	—	252.7	69.1	2.99
NO ₂	52.0	0.83	80.9	55.1	1.12	0.41	90.3	64.4	1.12
CN	47.9	0.96	81.8	54.5	1.15	—	91.5	56.2	1.31

Table 6

U.V. λ_{\max} and $\epsilon \times 10^{-4}$ for the simple β -nitrostyrenes ($R = H$) and λ_{\max} and $\epsilon \times 10^{-4}$ for the β -alkyl- β -nitrostyrenes ($R = CH_3$ or C_2H_5).



X	R = H		R = CH ₃		R = C ₂ H ₅	
	λ_{\max} (m μ)	$\epsilon \times 10^{-4}$ (Ref.)	λ_{\max} (m μ)	$\epsilon \times 10^{-4}$	λ_{\max} (m μ)	$\epsilon \times 10^{-4}$
H	310	1.65 (6)	307	1.22	306	0.98
CH ₃ O	350	2.04 (6)	—	—	346	1.56
CH ₃	—	—	—	—	325	0.85
F	313	1.61	308	1.10	309	1.03
Cl	315	1.91 (6)	310	1.42	312	1.23
Br	314	2.19	308	1.70	313	1.30
I	323	1.74	318	1.55	320	1.51
NO ₂	301	2.11	301	1.66	300	1.65
CN	299	2.11	294	1.65	292	1.50

- KAMLET, M. J. & D. J. GLOVER, *J. Am. Chem. Soc.*, 77, 5696 (1955).
KRAUS, K. W., G. N. SCHULTE, R. J. DOLTER, R. J. BUENKER, J. E.
PLAMONDON, & D. KOOPMAN, *Proc. Iowa Acad. Sci.*, 71, 208 (1964).
PELLEGRINI, M. J. T., *C.A.*, 50, 10667 i (1956)
ROBERTSON, D. N., *J. Org. Chem.*, 25, 47 (1960).
VASIL'eva, V. N., V. V. PERAKLIN, & V. G. VASIL'ev, *Zhur Obshchei
Khim*, 31, 2175 (1961); *C.A.*, 56, 9558 g (1962).