Proceedings of the Iowa Academy of Science

Volume 76 | Annual Issue Article 19

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

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. KRAUS[1], R. J. DOLTER[1], 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 mμ, 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 mμ, 11,000), *p*-chloro (2.68 D, 54.5 ml, 310 mμ, 14,200), *p*-bromo (2.71 D, 55.8 ml, 308 mμ, 17,000), *p*-iodo (2.91 D, 62.8 ml, 318 mμ, 15,500), *p*-nitro (1.12 D, 55.1 ml, 302 mμ, 16,600), & *p*-cyano (1.15 D, 54.5 ml, 294 mμ, 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 mμ, 9,800), the *p*-methoxy (5.07 D, 63.3 ml, 346 mμ, 15,600), *p*-methyl (4.73 D, 63.0 ml, 325 mμ, 8,500), *p*-fluoro (2.77 D, 52.7 ml, 309 mμ, 10,300), *p*-chloro (2.71 D, 60.6 ml, 312 mμ, 12,300), *p*-bromo (2.77 D, 60.7 ml, 313 mμ, 13,000), *p*-iodo (2.99 D, 69.1 ml, 320 mμ, 15,100), *p*-nitro (1.12 D, 64.4 ml, 300 mμ, 16,500) & *p*-cyano (1.31 D, 56.2 ml, 292 mμ, 15,000) derivatives of β-ethyl-β-nitrostyrene. The ultraviolet absorptions are also reported for the *p*-fluoro (313 mμ, 16,100), *p*-bromo (314 mμ, 21,900), *p*-iodo (323 mμ, 17,400), and the *p*-cyano (299 mμ, 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)
p-methoxy-β-methyl-β-nitrostyrene	44-45°	43-44°	(10)
p-methyl-β-methyl-β-nitrostyrene	54.5—55°	52.3°	(10)
p-chloro-β-methyl-β-nitrostyrene	81-83°	84°	(8)
p-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
p-fluoro-β-methyl-β-nitrostyrene	65-66°	$C_9H_8FNO_2$	59.67	4.45	59.88	4.57
p-bromo-β-methyl-β-nitrostyrene	89.5—90.5°	$C_9H_8BrNO_2$	44.65	3.33	44.90	3.48
p-iodo-β-methyl-β-nitrostyrene	126—127°	$C_9H_8INO_2$	37.40	2.79	37.57	2.97
p-cyano-β-methyl-β-nitrostyrene	118.5—119.5°	$C_{10}H_8N_2O_2$	63.83	4.28	63.95	4.42
p-methoxy-β-ethyl-β-nitrostyrene	54.5—55.5°	$C_{11}H_{13}NO_3$	63.76	6.32	63.95	6.39
p-methyl-β-ethyl-β-nitrostyrene	33—34°	$C_{11}H_{13}NO_2$	69.09	6.85	68.89	7.02
p-fluoro-β-ethyl-β-nitrostyrene	70—71°	$C_{10}H_{10}FNO_2$	61.53	5.16	61.42	5.14
p-chloro-β-ethyl-β-nitrostyrene	75—76°	$C_{10}H_{10}ClNO_2$	56.75	4.76	56.91	4.89
p-bromo-β-ethyl-β-nitrostyrene	74.5—75°	$C_{10}H_{10}BrNO_2$	46.90	3.94	46.95	4.03
p-iodo-β-ethyl-β-nitrostyrene	47-47.5°	$C_{10}H_{10}INO_2$	39.63	3.33	39.73	3 40
p-nitro-β-ethyl-β-nitrostyrene	100—101°	$C_{10}H_{10}N_2O_4$	54.06	4.54	54.27	4.62
p-cyano-β-ethyl-β-nitrostyrene	114—114.5°	$C_{11}H_{10}N_2O_2$	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-$XC_6H_5CH = C(NO_2)CH_3$

X	ϵ_1	α	d_1	β	n_1	ϑ
H	2.2693	12.32	0.8730	0.213	1.4982	0.111
CH_3O	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°.

p-$XC_6H_5CH = C(NO_2)C_2H_5$

X	ϵ_1	α	d_1	β	n_1	γ
H	2.2669	10.74	0.8734	0.200	1.4982	0.062
CH_3O	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 = CH_3 or C_2H_5).

p-$XC_6H_5CH = C(NO_2)R$

X	R = H (Ref. 7)		R = CH_3				R = C_2H_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_3O	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 and $\epsilon \times 10^{-4}$ for the simple β-nitrostyrenes (R = H) and λ and $\epsilon \times 10^{-4}$ for the β-alkyl-β-nitrostyrenes (R = CH_3 or C_2H_5).

$$p\text{-}XC_6H_3CH = C(NO_2)R$$

X	R = H		R = CH_3		R = C_2H_5	
	λ_{max} (mμ)	$\epsilon \times 10^{-4}$ (Ref.)	λ_{max} (mμ)	$\epsilon \times 10^{-4}$	λ_{max} (mμ)	$\epsilon \times 10^{-4}$
H	310	1.65 (6)	307	1.22	306	0.98
CH_3O	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).