Synthesis and Halochromism of 4- and 6-Styryl-2-aminotropones

Kimiaki IMAFUKU and Hisashi MATSUMURA

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami, Kumamoto

(Received March 2, 1972)

The methylation of 4-styryltropolones with diazomethane afforded two isomers, 2-methoxy-4-styryltropones and 2-methoxy-6-styryltropones. Their reactions with ammonia gave the corresponding 2-amino-4-styryltropones and 2-amino-6-styryltropones, respectively, by normal nucleophilic substitution. Infrared and ultraviolet absorption spectra were measured. The halochromism of 2-aminotropones was also examined, the halochromic shifts being found to be linearly correlated with the Hammett substituent constants.

Investigations have been carried out by Nozoe,[1,2] Haworth,[3] Tarbell,[4,5] and Kuraoka[6] on styryltropolones with particular interest in them as a potential intermediate in the synthesis of colchicine and its analogues.

The chemical reactivities of 4- and 6-styryl-substituted 2-methoxytropones,[7] 2-chlorotropones,[7] and 2-tosyloxytropones[8,9] towards nucleophilic reagents such as ammonia, amines, and hydroxide ion were studied by one of us (H. M.). More quantitative treatments of the reactivity of the styryltropolones[10,11] were made by measuring their dissociation constants and by correlating them to the Hammett substituent constants. Thus, it was established that the electronic effects of the substituents in the benzene ring can be transmitted through an ethylenic linkage to the tropolone nucleus. The dissociation constants of 4- and 6-styryl-2-aminotropones were measured and found to obey the Hammett equation.[12]

This communication deals with the synthesis of 4- and 6-styryl-2-aminotropones, which are used for the measurements of the dissociation constants of their conjugate acids.[12] The infrared and ultraviolet absorption spectra of 2-methoxytropones and 2-aminotropones were also measured, and the halochromism of 2-aminotropones is discussed quantitatively.

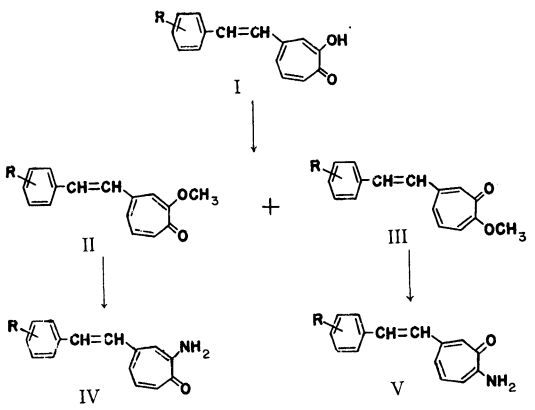

Fig. 1.

a R=H	e R=*m*-Cl
b R=*p*-OCH_3	f R=*p*-Br
c R=*p*-CH_3	g R=*p*-NO_2
d R=*p*-Cl	h R=*m*-NO_2

Results and Discussion

Synthesis. The starting materials, 4-styryltropolones (Ia—Ih) having substituent in the benzene ring, were prepared by the condensation of the corresponding benzaldehyde with 3-carboxy-4-carboxymethyltropolone[13] obtained from purpurogallin[14] and the decarboxylation of the condensation products.[15]

4-Styryltropolone (Ia) was methylated with diazomethane in ether to afford two isomers of methyl ether, 2-methoxy-4-styryltropone (IIa) and 2-methoxy-6-styryltropone (IIIa).[5,16] Similarly, seven 4-styryltropolone methyl ethers (IIb—IIh) and seven 6-styryltropolone methyl ethers (IIIb—IIIh) were obtained from seven 4-(substituted styryl)tropolones (Ib—Ih). These isomers could be readily and perfectly separated by means of preparative thin layer chromatography. The yields, melting points and analytical data are summarized in Table 1. The melting points of 6-isomers are higher than those of the corresponding 4-isomers.

Ammonolysis of 2-methoxy-4-styryltropone (IIa) and 2-methoxy-6-styryltropone (IIIa) with ammonia in absolute ethanol in a sealed tube afforded the corresponding 2-amino-4-styryltropone (IVa) and 2-amino-6-styryltropone (Va), respectively, by normal nucleophilic substitution.[7] 4-Styryl (IIb—IIh) and 6-styryl isomers (IIIb—IIIf) having substituent in the benzene ring were also aminated with ammonia to afford the corresponding seven 2-amino-4-styryltropones (IVb—IVh) and five 2-amino-6-styryltropones (Vb—Vf), re-

1) T. Nozoe, Y. Kitahara, K. Doi, and M. Endo, *Proc. Jap. Acad.*, **28**, 32 (1952).
2) T. Nozoe, Y. Kitahara, K. Doi, S. Masamune, M. Endo, M. Ishii, and J.-G. Shin, *Sci. Repts. Tohoku Univ., I*, **38**, 257 (1955).
3) W. D. Crow, R. D. Haworth, and P. R. Jefferies, *J. Chem. Soc.*, **1952**, 3705.
4) D. S. Tarbell, R. F. Smith, and V. Boeckelheide, *J. Amer. Chem. Soc.*, **76**, 2470 (1954).
5) D. S. Tarbell, K. I. H. Williams, and E. J. Sehm, *ibid.*, **81**, 3443 (1959).
6) T. Kuraoka, *Nippon Kagaku Zasshi*, **83**, 584, 587, 828, 831 (1962).
7) H. Matsumura, *ibid.*, **81**, 1763 (1960).
8) H. Matsumura, *ibid.*, **82**, 623 (1961).
9) H. Matsumura, *ibid.*, **82**, 774 (1961).
10) K. Imafuku, S. Nakama, and H. Matsumura, *Tetrahedron*, **26**, 1821 (1970).
11) K. Hamada, S. Nakama, K. Imafuku, K. Kurosawa, and H. Matsumura, *ibid.*, **27**, 337 (1971).
12) K. Imafuku and H. Matsumura, This Bulletin, in press.
13) R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, **1951**, 561.
14) J. D. Evans and M. M. Dehn, *J. Amer. Chem. Soc.*, **52**, 3647 (1930).
15) S. Nakama, K. Imafuku, and H. Matsumura, This Bulletin, **43**, 3265 (1970).
16) H. Matsumura, *Nippon Kagaku Zasshi*, **77**, 300 (1956).

TABLE 1. 4-AND 6-STYRYL-2-METHOXYTROPONES

Compound	R	Appearance[a]	Yield (%)	Mp (°C)	Formula	Found (%)			Calcd (%)		
						C	H	N	C	H	N
IIb	*p*-OCH_3	Y Nd	44.5	109—110	$C_{17}H_{16}O_3$	76.32	6.07		76.10	6.01	
IIc	*p*-CH_3	oil	35.9		$C_{23}H_{19}N_3O_9$[b]	57.56	4.08	8.38	57.38	3.98	8.73
IId	*p*-Cl	Y Pm	40.8	155—156	$C_{16}H_{13}ClO_3$	70.45	4.93		70.46	4.80	
IIe	*m*-Cl	Y Sc	45.5	146—148	$C_{16}H_{13}ClO_2$	70.36	4.84		70.46	4.80	
IIf	*p*-Br	Y Nd	48.8	141—142	$C_{16}H_{13}BrO_2$	60.88	4.39		60.59	4.13	
IIg	*p*-NO_2	Y Nd	22.8	224—225	$C_{16}H_{13}NO_4$	67.61	4.74	4.77	67.84	4.63	4.95
IIh	*m*-NO_2	Y Nd	22.8	175—176	$C_{16}H_{13}NO_4$	67.77	4.97	4.66	67.84	4.63	4.95
IIIb	*p*-OCH_3	Y Pl	30.3	146—148	$C_{17}H_{16}O_3$	75.91	6.12		76.10	6.01	
IIIc	*p*-CH_3	Y Pl	49.1	164—166	$C_{17}H_{16}O_2$	80.68	6.40		80.92	6.39	
IIId	*p*-Cl	Y Pl	39.8	160—161	$C_{16}H_{13}ClO_2$	70.39	4.88		70.46	4.80	
IIIe	*m*-Cl	L-Y Nd	42.7	160—161	$C_{16}H_{13}ClO_2$	70.57	4.74		70.46	4.80	
IIIf	*p*-Br	Y Sc	32.5	172—174	$C_{16}H_{13}BrO_2$	60.73	4.40		60.59	4.13	
IIIg	*p*-NO_2	L-Y Pd	13.3	253—255	$C_{16}H_{13}NO_4$			5.15			4.95
IIIh	*m*-NO_2	L-Y Pd	26.6	227—229	$C_{16}H_{13}NO_4$	68.00	4.44	4.84	67.84	4.63	4.95

a) Abbreviations: Y=yellow; L=light; Nd=needles; Pm=prisms; Sc=scales; Pl=plates; Pd=powder.
b) Picrate.

TABLE 2. 4- AND 6-STYRYL-2-AMINOTROPONES

Compound	R	Appearance[a]	Yield (%)	Mp (°C)	Formula	Found (%)			Calcd (%)		
						C	H	N	C	H	N
IVb	*p*-OCH_3	Y-O Pm	60.9	194—196	$C_{16}H_{15}NO_2$	75.61	5.98	5.58	75.87	5.97	5.53
IVc	*p*-CH_3	Y-B Ct	63.8	190—193	$C_{16}H_{15}NO$	81.09	6.41	5.95	80.98	6.37	5.90
IVd	*p*-Cl	Y-B Pm	58.2	211—213	$C_{15}H_{12}ClNO$	70.16	4.68	5.26	69.91	4.69	5.43
IVe	*m*-Cl	Y-O Pm	90.0	170—171	$C_{15}H_{12}ClNO$	69.82	4.77	5.71	69.91	4.69	5.43
IVf	*p*-Br	Y-O Ct	94.5	215—216	$C_{15}H_{12}BrNO$	59.52	4.10	4.62	59.62	4.00	4.64
IVg	*p*-NO_2	B Pd	63.4	265—267	$C_{15}H_{12}N_2O_3$	67.24	4.60	10.44	67.15	4.51	10.44
IVh	*m*-NO_2	B Ct	58.1	222—225	$C_{15}H_{12}N_2O_3$			10.29			10.44
Vb	*p*-OCH_3	Y-O Ct	90.0	151—153	$C_{16}H_{15}NO_2$			5.26			5.53
Vc	*p*-CH_3	Y-O Pm	95.7	175—176	$C_{16}H_{15}NO$	80.69	6.20	6.12	80.98	6.37	5.90
Vd	*p*-Cl	O Pl	68.8	183—184	$C_{15}H_{12}ClNO$	69.96	4.68	5.48	69.91	4.69	5.43
Ve	*m*-Cl	Y-O Pm	95.2	202—204	$C_{15}H_{12}ClNO$	69.63	4.66	5.35	69.91	4.69	5.43
Vf	*p*-Br	O Pl	99.7	199—201	$C_{15}H_{12}BrNO$	59.63	4.13	4.88	59.62	4.00	4.64

a) Abbreviations: Y=yellow; O=orange; B=brown; Pm=prisms; Ct=crystal; Pd=powder; Pl=plates.

spectively. However, the ammonolysis of both 2-methoxy-6-(*p*- and *m*-nitrostyryl)tropones (IIIg and IIIh) did not give the corresponding 2-aminotropones (Vg and Vh). The yields, melting points and analytical data are summarized in Table 2. In contrast to the case of methyl ethers, it was found that the melting points of 4-isomers are higher than those of the corresponding 6-isomers except for 2-aminotropones having *m*-chloro substituent.

These 2-aminotropones were hydrolyzed in alkali solution to give the corresponding original 4-styryltropolones.

Infrared Absorption Spectra. The infrared absorption spectra of the 2-methoxytropones (IIa—IIh and IIIa—IIIh) and 2-aminotropones (IVa—IVh and Va—Vf) were measured in chloroform. As characteristic bands, both of them have $\nu_{C=O}$ and δ_{CH} (in *trans* –CH=CH–) bands. 2-Aminotropones exhibit two ν_{NH} bands. These data are listed in Tables 3 and 4.

The geometry of the ethylenic linkage is *trans*, since the δ_{CH} bands are observed at 955—960 cm^{-1}. The carbonyl stretching bands of 6-isomers are observed in a lower wave number band than those of 4-isomers by *ca.* 10 cm^{-1}, if examined in detail. This might be due to the fact that the distance between the carbonyl group and the styryl group, which may conjugate with the former, is smaller in 6-isomers than in 4-isomers. It is found that, similar to 4-styryltropolones,[15] the $\nu_{C=O}$ bands of both 2-methoxytropones and 2-aminotropones are little affected by the substituents in the benzene ring.

Ultraviolet Absorption Spectra. The ultraviolet absorption spectra of 4- and 6-styryl-substituted 2-methoxytropones (IIa—IIh and IIIa—IIIh) and 2-aminotropones (IVa—IVh and Va—Vf) were measured in methanol, and are shown in Tables 3 and 4, respectively.

There is a remarkable difference between the spectra of 4-styryl- and 6-styryl-2-methoxytropones. On the other hand, the spectra of 4- and 6-styryl-2-aminotropones are very similar and hardly distinguishable, as shown in Fig. 2. However, when these 2-aminotropones are dissolved in acidic medium, they show different patterns. The spectra of 4- and 6-styryl-2-

Table 3. Spectral data for 4- and 6-styryl-2-methoxytropones

Compound	R	IR (cm^{-1})			UV: λ_{max} (log ε)			
		$\nu_{C=O}$	$\nu_{C=C}$	δ_{CH}				
IIa	H	1596	1576	958	242(4.04)	310(4.22)	355(4.15)	
IIb	*p*-OCH_3	1588	1572	959	250(4.20)	281(4.10)	332(4.09)	400(4.39)
IIc	*p*-CH_3	1592	1572	959	248(4.12)	280(4.12)	318(4.10)	386(4.24)
IId	*p*-Cl	1586	1570	959	248(4.15)	283(4.28)	314(4.27)	398(4.36)
IIe	*m*-Cl	1596	1571	958	247(4.16)	294(4.31)	392(4.30)	
IIf	*p*-Br	1594	1571	960	249(4.15)	285(4.27)	315(4.27)	393(4.36)
IIg	*p*-NO_2	1598	1578	954	261(4.13)	322(4.34)	400(4.39)	
IIh	*m*-NO_2	1596	1577	959	277(4.34)	294(4.32)	359(4.17)	391(4.20)
IIIa	H	1584	1559	960	233(4.04)	308(4.51)		
IIIb	*p*-OCH_3	1583	1554	962	237(4.24)	314(4.55)	350(4.48)	
IIIc	*p*-CH_3	1582	1553	962	251(4.27)	317(4.24)	363(4.17)	
IIId	*p*-Cl	1582	1556	963	234(4.17)	313(4.52)		
IIIe	*m*-Cl	1583	1559	960	234(4.17)	307(4.55)		
IIIf	*p*-Br	1581	1554	961	233(4.18)	314(4.54)		
IIIg	*p*-NO_2	1584	1556	960	225(4.17)	341(4.54)		
IIIh	*m*-NO_2	1586	1560	961	231(4.22)	303(4.57)		

Table 4. Spectral data for 4- and 6-styryl-2-aminotropones

Compound	R	IR (cm^{-1})					UV: λ_{max} (log ε)			
		ν_{NH_1}	ν_{NH_2}	$\nu_{C=O}$	$\nu_{C=C}$	δ_{CH}				
IVa	H	3500	3360	1584	1559	960	233(3.84)	323(4.56)	425(4.00)	
IVb	*p*-OCH_3	3500	3360	1586	1560	959	245(4.11)	337(4.57)	370(4.32)	429(4.11)
IVc	*p*-CH_3	3500	3360	1588	1560	960	239(3.98)	327(4.50)	430(3.94)	
IVd	*p*-Cl	3500	3360	1590	1560	959	238(4.06)	327(4.63)	432(4.03)	
IVe	*m*-Cl	3500	3360	1592	1562	955	236(4.13)	320(4.60)	432(3.98)	
IVf	*p*-Br	3500	3360	1592	1562	959	238(4.11)	327(4.60)	432(3.95)	
IVg	*p*-NO_2	3500	3360	1594	1560	960	222(4.06)	282(4.11)	337(4.53)	444(3.95)
IVh	*m*-NO_2	3500	3360	1588	1558	950	231(4.14)	314(4.59)	435(3.95)	
Va	H	3510	3360	1582	1558	960	235(4.02)	320(4.66)	425(4.00)	
Vb	*p*-OCH_3	3510	3360	1580	1558	958	249(4.19)	331(4.79)	428(4.19)	
Vc	*p*-CH_3	3510	3360	1581	1559	960	245(4.10)	328(4.62)	430(3.98)	
Vd	*p*-Cl	3510	3360	1581	1559	961	240(4.15)	324(4.67)	432(4.01)	
Ve	*m*-Cl	3510	3360	1581	1559	959	240(4.12)	320(4.62)	431(3.96)	
Vf	*p*-Br	3510	3360	1580	1559	960	246(4.11)	326(4.64)	432(4.00)	

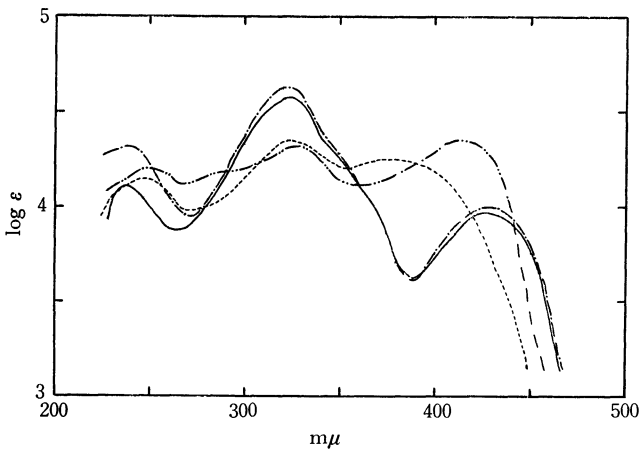

Fig. 2. The absorption spectra of 4- and 6-styryl-2-aminotropones.
——: IVa in neutral solution
------: IVa in acidic solution
——: Va in neutral solution
——: Va in acidic solution

aminotropones are shown in Fig. 2, as an example. Although their visible absorption bands show hypsochromic shifts, the 4-isomers show stronger shifts than the 6-isomers. The positions of the longest absorption bands in neutral and in acidic media are shown in Table 5, in terms of λ_B and λ_{BH^+} values, respectively.

The effects of the substituents in the benzene ring on the spectra can be seen from Tables 3 and 4. In general, the visible bands are shifted toward longer wavelength by *para* substituents, and the effect is roughly proportional to the Hammett substituent constants with the exception of electron-donating methoxy group. However, *meta* substituents cause little or none. A similar substituent effect is found in 4-aminostilbenes,[17] since the 2-aminotropone ring can be regarded as a non-benzenoid analogue of aniline and the spectroscopic properties of styryl-substituted 2-aminotropones can be directly compared with aminostilbenes. The longest absorption bands of the protonated ions are

17) H. Veschambre and A. Kergomard, *Bull. Soc. Chim. Fr.*, **1966**, 336.

TABLE 5. DISSOCIATION CONSTANTS AND VISIBLE SPECTRAL DATA FOR 4- AND 6-STYRYL-2-AMINOTROPONES

	No.[a]	R	σ	pK_a	λ_B	ν_B	λ_{BH^+}	ν_{BH^+}	$\Delta\nu$
4-Styryl	1	*p*-OCH_3	−0.268	2.71	428	23360	397	25190	1830
	2	*p*-CH_3	−0.170	2.64	428	23360	381	26250	2890
	3	H	0	2.54	428	23360	374	26740	3380
	4	*p*-Cl	0.227	2.39	430	23260	371	26950	3690
	5	*p*-Br	0.232	2.34	430	23260	374	26740	3480
	6	*m*-Cl	0.373	2.33	432	23150			
	7	*m*-NO_2	0.710	2.14	432	23150			
	8	*p*-NO_2	0.778	2.08	440	22730	364	27470	4740
6-Styryl	9	*p*-OCH_3	−0.268	2.69	429	23310	421	23750	440
	10	*p*-CH_3	−0.170	2.65	430	23260	420	23810	550
	11	H	0	2.57	429	23310	414	24150	840
	12	*p*-Cl	0.227	2.51	432	23150	415	24100	950
	13	*p*-Br	0.232	2.50	431	23200	415	24100	900
	14	*m*-Cl	0.373	2.42	430	23260	412	24270	1010

a) Numbers refer to those given in Figs. 3 and 4.

also sensitive to substituent effects in a manner parallel to the neutral species.

Halochromism and Substituent Effects. Rapoport *et al.*[18] measured the absorption spectra of 4-substituted 2-nitrophenols in neutral and in alkaline solutions, and showed theoretically that the difference between the longest absorption bands in two media are quantitatively related with the dissociation constants. These wavenumber shifts are also proportional to the Hammett substituent constants. This phenomenon is well-known in a number of azobenzene series such as 4-phenylazophenols[19] and 4-phenylazoanilines[20] as halochromism. It was found to hold in 5-phenylazotropolones which are non-benzenoid aromatic compounds.[21] The degree of halochromism of a compound can be defined as the frequency difference between the visible bands of the neutral and its conjugate acid or base.

We measured absorption spectra of 4- and 6-styryl-2-aminotropones in 50% aqueous methanol (pH *ca.* 6) and in 50% aqueous methanol containing hydrochloric acid (pH *ca.* 1). That only one species exists in each solution was checked by the pH changes of solution. The longest absorption spectra of both of these 2-aminotropones are shifted to shorter wavelength. The degree of shifts is larger in 4-styryl than in 6-styryl isomers as mentioned above. The wavelengths and wave numbers are listed in Table 5 as λ_B and ν_B for the neutral species and λ_{BH^+} and ν_{BH^+} for the protonated species, respectively. The $\Delta\nu$ values in the same Table give the difference between ν_B and ν_{BH^+} values. The dissociation constants (pK_a)[12] of these 2-aminotropones are also shown in Table 5.

When the $\Delta\nu$ values of 4- and 6-styryl-2-aminotropones are plotted against their pK_a values, the plots define the two lines for 4- and 6-isomers as shown in Fig. 3. The following equations are obtained by the least square method.

(4-styryl) $\Delta\nu = 12868 - 3891\text{p}K_a$ (r=0.905)

(6-styryl) $\Delta\nu = 6434 - 2211\text{p}K_a$ (r=0.961)

The magnitude of the pK_a values for suitable equilibria in phenyl derivatives is directly proportional to the Hammett substituent constants of substituent in the benzene ring. Thus, the $\Delta\nu$ values should be proportional to the substituent constants. Several examples of this type of correlation have been reported.[18-27]

When the $\Delta\nu$ values are plotted against the σ constants, two lines for 4- and 6-styryl-2-aminotropones are obtained as shown in Fig. 4. However, the $\Delta\nu$

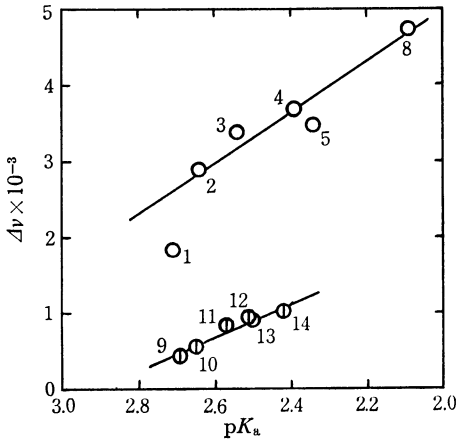

Fig. 3. The relationship between $\Delta\nu$ and pK_a.
○: 2-Amino-4-styryltropones
ⓘ: 2-Amino-6-styryltropones

18) M. Rapoport, C. K. Hancock, and E. A. Meyers, *J. Amer. Chem. Soc.*, **83**, 3489 (1961).
19) W. R. Brode and V. E. Cheyney, *J. Org. Chem.*, **6**, 341 (1941).
20) L. M. Yagupol'skii and L. Z. Gandel'sman, *Zh. Obshch. Khim.*, **35**, 1252 (1965); **37**, 2101 (1967).
21) J. Griffins, *J. Chem. Soc., B*, **1971**, 801.
22) L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960).
23) C. K. Hancock and A. D. Clague, *J. Amer. Chem. Soc.*, **86**, 4942 (1964).
24) W. Bartok, P. J. Lucchesi, and N. S. Snider, *ibid.*, **84**, 1842 (1962).
25) H. H. Jaffé, D. L. Beveridge, and H. L. Jones, *ibid.*, **86**, 2932 (1964).
26) H. H. Jaffé, H. L. Jones, and M. Isaks, *ibid.*, **86**, 2934 (1964).
27) E. L. Wehring and L. B. Rogers, *ibid.*, **87**, 4234 (1965).

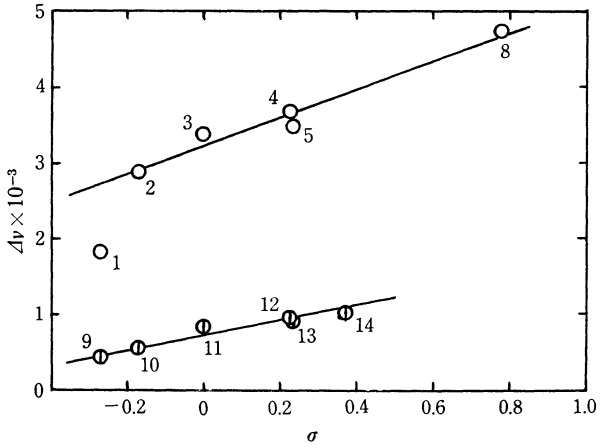

Fig. 4. The relationship between $\Delta\nu$ and σ.
○: 2-Amino-4-styryltropones
ⓘ: 2-Amino-6-styryltropones

value for 2-amino-4-(*p*-methoxystyryl)tropone having strongly electron-donating group considerably deviates from the regression line. The value is, therefore, not included in a calculation of the regression line. When an electrophilic substituent constants[28] ($\sigma^+ = -0.778$ for *p*-methoxy) is introduced, the plot of *p*-methoxy group is found to lie on the line. The regression equations are as follows.

$$\text{(4-styryl)}\quad \Delta\nu = 1879\sigma + 3235 \quad (r=0.984)$$

$$\text{(6-styryl)}\quad \Delta\nu = 882\sigma + 724 \quad (r=0.963)$$

The effect of substituents in the benzene ring on the electronic spectra is larger in 4-styryl than in 6-styryl isomers. This is consistent with the Hammett type analysis of both their dissociation constants.[12] Thus, it is found that the effect of resonance should not be neglected in the 4-isomers, since the effect in 4-isomers is about twice as much as in 6-isomers and σ^+ value fits better than the unmodified σ value for electron-donating *p*-methoxy group.

The excellent linear correlation between $\Delta\nu$ and pK_a or σ for 4- and 6-styryl-2-aminotropones suggests that similar relationships should hold for the other types of equilibria in troponoids having styryl group.

28) H. C. Brwon and Y. Okamoto, *ibid.*, **80**, 4980 (1958).

Experimental

All the melting points were measured on a Yanagimoto micro-melting point apparatus and uncorrected. The infrared and ultraviolet absorption spectra were taken on a JASCO IRA-1 and a Hitachi EPS-3T spectrophotometer, respectively.

4-Styryltropolones (Ia—Ih). The starting materials, 4-(substituted styryl) tropolones (Ia—Ih), were prepared according to a previous work.[15]

The corresponding benzaldehydes were treated with 3-carboxy-4-carboxymethyltropolone[13] obtained from purpurogallin[14] by sodium iodate oxidation, to give 3-carboxy-4-styryltropolones. The latter were sublimed at elevated temperature to afford 4-styryltropolones (Ia—Ih) with the elimination of carbon dioxide.

2-Methoxy-4-styryltropones (IIa—IIh) and 2-Methoxy-6-styryltropones (IIIa—IIIh). An excess of diazomethane in ether was added to a solution of 4-styryltropolones (Ia—Ih) (1 g, 3.3—4.2 mmole) in chloroform (20 ml), and the mixture was allowed to stand in a refrigerator (at *ca.* 5°C). After two days, the solvent was evaporated off under reduced pressure. The residue was dissolved in a small amount of chloroform and separated on silica gel plates (Wakogel B-10) with ethyl acetate as a developing solvent. Two bands of isomers of methyl ethers from 4-styryltropolones appeared. Each band was scraped out and extracted with chloroform. 2-Methoxy-4-styryltropones (IIa—IIh) and 2-methoxy-6-styryltropones (IIIa—IIIh) were obtained from the upper and the lower bands, respectively. Each methyl ether was recrystallized from benzene.

2-Amino-4-styryltropones (IVa—IVh) and 2-Amino-6-styryltropones (Va—Vf). A solution of 4- and 6-styryl-2-methoxytropones (IIa—IIh and IIIa—IIIh) (200 mg, 0.7—0.9 mmol) in absolute ethanol (10 ml), saturated with ammonia at ice-cooled temperature, was heated in a sealed tube for 3 hr at 100°C. The dark red solution was evaporated to give a reddish oil. The residue was crystallized by treating with a small amount of chloroform to afford 4- and 6-styryl-2-aminotropones (IVa—IVh and Va—Vf), respectively. These 2-aminotropones were recrystallized from either benzene or ethanol.