beaker of hot water. The excess iodine was determined by titration with thiosulfate solution.

TABLE IV

THE DETERMINATION OF THE HEAVY PHASE $SnBr_4$–SO_2; QUADRUPLE POINT, 16.55°

Wt., $SnBr_4$	Wt., SO_2	Moles, $SnBr_4$	Moles, SO_2	Moles, SO_2 / Moles, $SnBr_4$
1.5420	0.1153	0.003518	0.001801	0.512
2.0675	.1520	.004717	.002355	.499
2.2427	.1643	.005117	.002567	.501
1.7934	.1314	.004092	.002051	.501

TABLE V

THE DETERMINATION OF THE HEAVY PHASE $TiCl_4$–SO_2; QUADRUPLE POINT, −31.4°

Wt., $TiCl_4$	Wt., SO_2	Moles, $TiCl_4$	Moles, SO_2	Moles, SO_2 / Moles, $TiCl_4$
0.6240	0.1056	0.003297	0.001650	0.501
.8342	.1413	.004393	.002207	.502
.7642	.1276	.004028	.001994	.495
.7284	.1235	.003839	.001930	.502

The results in each case show that at a temperature slightly above the quadruple point the lower layer has the same composition as that of the solvate determined previously as shown in Tables IV, V and VI.

As a further check on the molten material, portions of the crystalline solvates were separated, dried by decanting the liquid phase and allowed to stand until no evidence of liquid could be seen. The melting points were then determined. Results were consistently accurate and coincided within experimental accuracy with the temperature at which the liquid phases appeared.

TABLE VI

THE DETERMINATION OF THE HEAVY PHASE $TiBr_4$–SO_2; QUADRUPLE POINT, 29.4°

Wt., $TiBr_4$	Wt., SO_2	Moles, $TiBr_4$	Moles, SO_2	Moles, SO_2 / Moles, $TiBr_4$
1.1961	0.1050	0.00325	0.00164	0.502
0.9620	.0845	.00261	.00132	.504
1.2500	.1095	.00340	.00171	.502
1.3520	.1185	.00368	.00185	.503
0.7230	.0633	.00199	.00099	.496

Summary

The systems titanium tetrachloride–sulfur dioxide, tin tetrachloride–sulfur dioxide and titanium tetrabromide–sulfur dioxide have been investigated and solvates have been found.

The composition of the solvates has been determined and each has been found to contain one-half molecule of sulfur dioxide per molecule of the tetrahalide.

Comparison of the properties of the heavy layers with those of the solvated tetrahalides at temperatures slightly above the quadruple point indicates that within experimental error they are the same.

IOWA CITY, IOWA RECEIVED JUNE 9, 1945

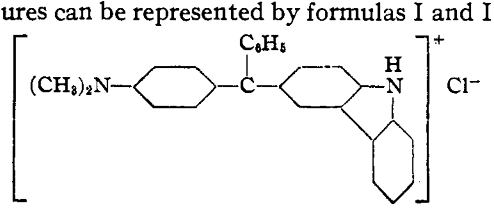
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

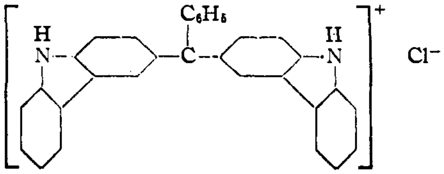
Spectra of Two Diaminotriphenylmethane Dyes Derived from Carbazole

BY G. E. K. BRANCH, B. M. TOLBERT AND WARREN LOWE

Brooker, Sprague and co-workers[1] have shown that the wave length of the principal band of a cyanine dye in which the two amino groups have very different basicities is less than the arithmetic or harmonic mean of the wave lengths of the principal bands of the two symmetrical dyes of which the dye in question is a structural hybrid. Phenylation of one of the amino groups of diaminotriphenylmethane dyes gives small deviations.[2] Thus λ_x for N-phenyl-N′-dimethyl-*p*,*p*′-diaminotriphenylmethyl chloride is only 6 mμ less than the arithmetic mean of the λ_x values of the parent dyes, viridine green and malachite green.

The above unsymmetrical dye is a derivative of diphenylamine and dimethylaniline, the former base being a weaker base than the latter. But carbazole is a weaker base than diphenylamine, so one might expect the Brooker deviation for a dye derived from carbazole and dimethylaniline to be much greater than 6 mμ. To test this prediction we prepared N-dimethyl-*p*-aminophenyl-3-carbazylphenylmethyl chloride and 3,3′-dicarbazylphenylmethyl chloride, the former being the structural hybrid of the latter and malachite green. Throughout this article we have called the two carbazyl derivatives the monocarbazyl dye and the dicarbazyl dye, respectively. Their structures can be represented by formulas I and II


I


II

The monocarbazyl dye was prepared by condensing N-dimethyl-*p*-aminobenzophenone with carbazole using phosphorus oxychloride as the condensing agent. The dicarbazyl dye was pre-

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(1) For a summary see L. G. S. Brooker, *Rev. Mod. Phys.*, **14**, 275 (1942).

(2) Tolbert, Branch and Berlenbach, THIS JOURNAL, **67**, 887 (1945).

pared by condensing two molecules of carbazole with one of benzotrichloride, using aluminum chloride as the condensing agent. That the products obtained from the condensations have structures I and II was verified in several ways.

Ultimate analyses of the methyl ethers of the dyes correspond to condensations in which one molecule of carbazole and one of dimethylaminobenzophenone are coupled, and in which two molecules of carbazole are coupled with one of benzotrichloride.

The absorption spectra of the colorless methyl ethers confirmed the presence of one and two carbazyl nuclei, respectively, both the methyl ethers giving the characteristic bands of carbazole, the molecular extinctions being respectively approximately equal to and twice as great as for carbazole. In the visible spectra of the dyes the strong x-bands and the weaker y-bands characteristic of p,p'-diaminotriphenylmethane dyes were found.

The condensations did not take place at the nitrogen atoms because the monocarbazyl dye has a proton that is reversibly removed by alkali, and the dicarbazyl dye has two such protons. When the monocarbazyl dye in acetone solution is treated with an alkali one obtains a solution of a colored anhydro base which reacts with methyl alcohol to form the methyl ether, and with hydrochloric acid to re-form the dye. When an acetone solution of the dicarbazyl dye is treated with a weak or dilute base it forms a red anhydro base, but when the solution of the dye or of the anhydro base is treated with a concentrated solution of a strong base a green solution is obtained. This solution reacts with methyl alcohol to form the methyl ether, with a very weak acid (triethylammonium chloride) to form the anhydro base, and with stronger acids to form the dye. It is evident that the green color is due to the negative ion of the anhydro base.

Coupling at positions ortho and meta to the nitrogen atom of the carbazole nucleus can be eliminated on the basis of the much greater reactivity of the para position of an aromatic amine in reactions that yield triphenylmethane dyes. Hence only structures I and II satisfactorily represent the syntheses, analyses and properties of the two dyes.

The monocarbazyl dye is red-violet in aqueous solution, violet in methyl alcohol, and blue in chloroform. Normally the color of a diaminotriphenylmethane dye is very little affected by the solvent. The anhydro base of the monocarbazyl is blue in aqueous solution, and red-violet in chloroform.

The dicarbazyl dye is blue-green in all solvents. Its anhydro base varies from red-violet to red in alcohol, acetone and chloroform.

Experimental Method

In general the spectra were obtained by measuring the extinctions of solutions of known concentration using a Beckman quartz spectrophotometer and 1-cm. cells. From these measurements the molecular extinction coefficients were calculated and plotted against the wave lengths. Measurements were made from 900 to about 220 mμ. This lower limit was not reached in solvents that absorb strongly in this region.

The solutions of the dyes were made from weighed quantities of the methyl ethers and measured amounts of solvent containing enough hydrochloric acid to transform completely the methyl ether to the chloride. The molarities of the dyes ranged from 8×10^{-6} to 1.2×10^{-5}. In the case of the monocarbazyl dye in chloroform solution the spectrum is affected by small changes in the concentration of the hydrochloric acid. In this case measurements were made over a range of excess hydrochloric acid. Methyl alcohol, acetic acid, acetone and chloroform were used as solvents for both dyes. In addition the monocarbazyl dye was studied in water, mixtures of water and methyl alcohol, and of methyl alcohol and chloroform.

Methyl alcohol was used as the solvent for the methyl ethers.

Solutions of the anhydro bases were made by adding bases to solutions of the dyes in solvents in which the anhydro bases are sufficiently stable to permit measurement of the spectra.

Acetone was chosen as the solvent for the anhydro base, but we succeeded in measuring the spectrum of the anhydro base of the monocarbazyl dye in water as well, by extrapolating the extinctions to zero time. These extrapolations were made by plotting the logarithms of the extinctions against time. Since the extrapolations were small and the fading of the anhydro bases approximately first order reactions, very little error could have been introduced. For purposes of comparison the spectrum of the anhydro base of viridine green, $(C_6H_5NHC_6H_4)(C_6H_5)C{=}C_6H_4{=}NC_6H_5$, in acetone was measured.

The solutions of the anhydro bases contained unknown quantities of the carbinols. For this reason we did not calculate the molecular extinction coefficients, and confined the measurements to the visible, where the carbinols do not absorb.

Visible Spectra of the Dyes.—We shall first consider the spectra of the dyes in the visible. In this region both dyes have two absorption bands. The wave lengths and molecular extinction coefficients at the maxima of absorption for the two bands for both dyes dissolved in various solvents are given in Table I. Many of these spectra are also shown in the figures.

The spectra of malachite green, the monocarbazyl dye and the dicarbazyl dye all dissolved in methyl alcohol are shown in Fig. 1. The spectra of the monocarbazyl dye in chloroform, methyl alcohol and water are shown in Fig. 2. The spectra of the monocarbazyl dye in the series of mix-

TABLE I

ABSORPTION MAXIMA AND THEIR MOLECULAR EXTINCTION COEFFICIENTS

Dye	Solvent	Molarity of HCl	λ_x mμ	ϵ_x $\times 10^{-4}$	λ_y mμ	ϵ_y $\times 10^{-4}$	$\bar{\nu}_y - \bar{\nu}_x$ $\times 10^{-3}$
Monocarbazyl	H_2O	1.0×10^{-1}	562	3.5	408	1.16	6.72
Monocarbazyl	75% H_2O, 25% MeOH	1.0×10^{-2}	570	3.3	410	1.13	6.85
Monocarbazyl	50% H_2O, 50% MeOH	1.0×10^{-2}	575	4.3	413	1.39	6.82
Monocarbazyl	25% H_2O, 75% MeOH	1.0×10^{-2}	579	4.7	415	1.43	6.83
Monocarbazyl	MeOH	1.0×10^{-2}	585	5.0	416	1.52	6.94
Monocarbazyl	75% MeOH, 25% $CHCl_3$	1.0×10^{-2}	590	5.5	420	1.50	6.86
Monocarbazyl	50% MeOH, 50% $CHCl_3$	1.0×10^{-2}	599	6.0	425	1.59	6.83
Monocarbazyl	25% MeOH, 75% $CHCl_3$	1.0×10^{-2}	604	6.4	427	1.62	6.86
Monocarbazyl	$CHCl_3$	1.0×10^{-4}	629	6.6	440	1.42	6.83
Monocarbazyl	$CHCl_3$	2.0×10^{-2}	605	5.1	428	1.36	6.84
Monocarbazyl	CH_3COCH_3	1.0×10^{-2}	579	4.9	412	1.54	7.00
Monocarbazyl	AcOH	0	586	4.6	417	1.39	6.92
Dicarbazyl	MeOH	1.0×10^{-2}	606	6.0	445	1.32	5.97
Dicarbazyl	$CHCl_3$	1.0×10^{-4}	608	4.9	444	1.18	6.08
Dicarbazyl	$CHCl_3$	2.0×10^{-1}	614	6.0	450	1.54	5.94
Dicarbazyl	CH_3COCH_3	1.0×10^{-2}	601	6.2	444	1.48	5.88
Dicarbazyl	AcOH	0	607	5.9	445	1.36	6.00

tures of chloroform and methyl alcohol are shown in Fig. 3.

When the spectra of these dyes are compared with those of the corresponding dyes derived from diphenylamine, the principal variations are: (1) the larger Brooker deviation of the monocarbazyl dye in water, methyl alcohol, acetic acid and acetone; (2) the negative Brooker deviation of the monocarbazyl dye in chloroform; (3) the larger solvent effects on the spectra of the monocarbazyl dye; (4) the smaller value of λ_x for the dicarbazyl dye; and (5) the smaller difference of the wave numbers of the *x*- and *y*-bands ($\bar{\nu}_y - \bar{\nu}_x$) for the dicarbazyl dye. Usually λ_x increases $\bar{\nu}_y - \bar{\nu}_x$ decreases with phenylation.

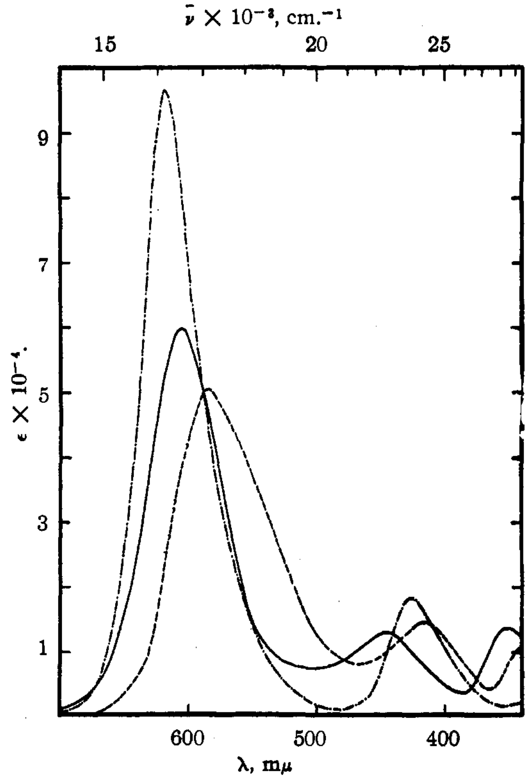


Fig. 1.—Absorption spectra of the two carbazyl dyes and malachite green, all in methyl alcohol solvent: ——— $[(C_{12}H_8N)C(C_6H_5)(C_{12}H_8N)]^+$; - - - $((C_{12}H_8N)C(C_6H_5)(C_6H_4N(CH_3)_2))^+$; —·—·—·— malachite green.

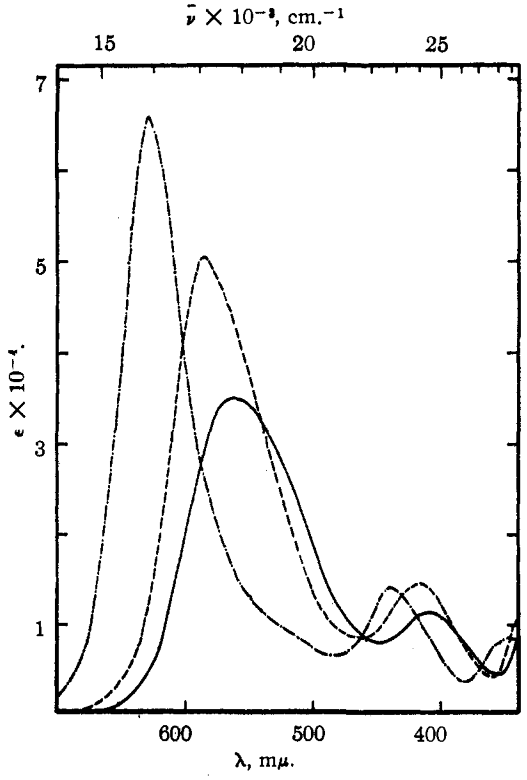


Fig. 2.—Spectra of the monocarbazyl dye $[(C_{12}H_8N)C(C_6H_5)(C_6H_4N(CH_3)_2)]^+$ in various solvents: ——— in water; - - - in methyl alcohol; —·—·—·— in chloroform.

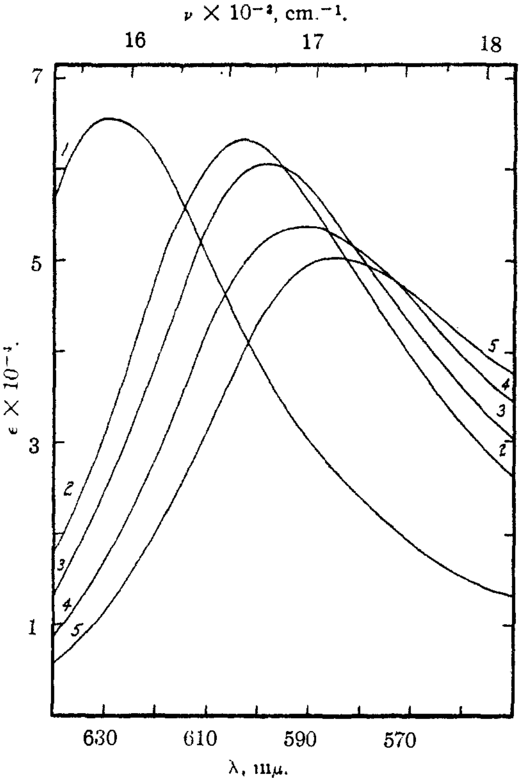


Fig. 3.—Spectra of the monocarbazyl dye $[(C_{12}H_8N)C(C_6H_5)(C_6H_4N(CH_3)_2)]^+$ in mixtures of chloroform and methyl alcohol: (1) in chloroform; (2) in 75% chloroform + 25% methyl alcohol; (3) 50% chloroform + 50% methyl alcohol; (4) 25% chloroform + 75% methyl alcohol; (5) methyl alcohol.

The following table compares the carbazyl dyes with those made in similar ways from dimethylaniline, diphenylamine, methyldiphenylamine and triphenylamine. In this table the first column gives the base that was condensed with benzotrichloride to form the symmetrical dye, and with N-dimethyl-*p*-aminobenzophenone to form the unsymmetrical dye. In the third column $\bar{\nu}_{x_0} - \bar{\nu}_x$ is given, $\bar{\nu}_{x_0}$ being $\bar{\nu}$ for the peak of the *x*-band of malachite green, and $\bar{\nu}_x$ being $\bar{\nu}$ for the peak of the symmetrical dye made from the base indicated in the first column. The fourth column shows the difference in wave numbers between the *x*- and *y*-bands of the symmetrical dye under the heading $\bar{\nu}_y - \bar{\nu}_x$. In the fifth column the difference between $\bar{\nu}_x$ for the hybrid dye of dimethylaniline and the base given in column one, and the arithmetic mean of $\bar{\nu}_x$ for malachite green and the symmetrical dye is shown. This quantity is as good a measure of the Brooker effect as $\lambda_{\text{mean}} - \lambda$. The values given in these columns are those found when acetic acid was used as the solvent. In the final column under the heading "Solvent Effect" the difference between $\bar{\nu}_x$ in acetic acid and in chloroform is shown for the hybrid dye of dimethylaniline and the indicated base.

Table II

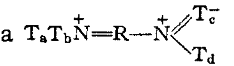
Effects of Phenyl and Carbazyl Groups

Base from which the dye is derived	No. of resonating forms in base	$\bar{\nu}_{x_0} - \bar{\nu}_x$ $\times 10^{-2}$, cm.$^{-1}$	$\bar{\nu}_y - \bar{\nu}_x$ $\times 10^{-3}$, cm.$^{-1}$	$\bar{\nu}_{x_{\text{mean}}} - \bar{\nu}_x$ $\times 10^{-3}$, cm.$^{-1}$	Solvent effect, cm.$^{-1}$
Dimethylaniline	4	0	7.24	0	52
Methyldiphenylamine	7	3.31	6.94	−1.40	129
Diphenylamine	7	4.30	6.67	−1.89	154
Triphenylamine	10	12.0	6.35	−3.71	224
Carbazole	13	−3.46	6.00	−7.63	1150

This table shows the quantities given in columns 3, 4, 5 and 6 to be regularly increasing or decreasing functions of the order chosen for the bases, except that λ_x for the dicarbazyl dye is less than λ_x for the malachite green, while for the other symmetrical dyes λ_x increases with the order chosen for the bases. If one assumes that the order of the bases is that of the resonance interaction of the nitrogen atoms with the other groups of the base, then in general for symmetrical dyes this interaction increases λ_x and diminishes the frequency difference of the *x*- and *y*-bands, and for the unsymmetrical dyes it increases the Brooker deviation and the solvent effect.

The value of λ_x for the dicarbazyl dye shows that the first of these rules must be qualified; the spectrum of the monocarbazyl dye in chloroform shows that the third also must be qualified. It is apparent that there is no simple relationship between the position of the absorption bands of the dyes and the resonance interaction of the nitrogen atoms with the groups attached to them, but that such interaction affects the spectra in many and even opposing ways.

The structure of the diaminotriphenylmethane dyes can be represented by the formula $T_aT_b{}^+N{=}R{-}NT_cT_d$, where T_a, T_b, T_c and T_d are the terminal groups that complete the valence of the nitrogen atoms, R is the conjugate system, $C_6H_4C(C_6H_5)C_6H_4$, and N is a nitrogen atom. In reality these ions are resonance hybrids of two structures, $T_aT_b{}^+N{=}R{-}NT_cT_d$ and $T_aT_bN{-}R{=}{}^+NT_cT_d$, which we shall call the *A*-structures, a number of structures in which the conjugate system is positively charged, which we shall call the *P*-structures and represent by the formula $T_aT_bN{-}{}^+R{-}NT_cT_d$, and a number of structures in which the conjugate system is negatively charged, which we shall call the *N*-structures and represent by the formula $T_aT_b{}^+N{=}{}^-R{=}{}^+NT_cT_d$. When a terminal group has a double bond or conjugate system adjacent to a nitrogen atom the resonance includes *T*-structures that can be represented by the formula



$T_aT_b\overset{+}{N}{=}R{-}\overset{+}{N}\begin{smallmatrix}{=}T_c^-\\ {-}T_d\end{smallmatrix}$

Structures that are combinations of those already given need not be included. Similar resonances exist in the cyanines and generalizations for the cyanines can be applied to the diaminotriphenylmethane dyes.

It has been observed that in the cyanine dyes terminal groups that produce or increase the number and stability of *T*-structures increases $\lambda_{max.}$ of the principal band. That this fact also applies to the diaminotriphenylmethane dyes can be seen by a comparison of the *x*-bands of the symmetrical dyes derived from dimethylaniline, diphenylamine and triphenylamine (see column 3, Table II).

However, secondary effects result from the formation of *T*-structures. One of these is that the basicities of the amino groups are reduced, thereby reducing the contribution of the *A*-structures to the resonance. Lewis[3] has assumed that the reduction of basicity of the amino group is hypsochromic. That this hypsochromic effect would be predominant in extreme cases can be seen from a consideration of the case in which the basicities are so small that the *A*-structures can be neglected. Then one would have a triphenylmethyl ion, a class of substances that does not absorb at the long wave lengths of the *x*-bands of the dyes. Hence structural changes that increase the resonance interaction between the nitrogen atoms and the terminal groups have two opposing actions, a primary bathochromic effect, and a hypsochromic one due to the decrease in the basicities of the amino groups. Apparently the latter effect is predominant only when the base strength is greatly reduced as in the case of the dicarbazyl dye.

When only one of the nitrogen atoms is attached to an unsaturated terminal group, the decrease of the basicity of only one of the nitrogen atoms destroys the degeneracy of the two *A*-structures. The resulting hypsochromic effect can be greater or less than the primary bathochromic one due to the introduction of *T*-structures into the resonance. Again the hypsochromic effect is predominant only when the base strength is greatly reduced. Thus $\lambda_{max.}$ for the dye made from diphenylamine and dimethylaniline is greater than that of malachite green, but $\lambda_{max.}$ for the monocarbazyl dye is less. As a first approximation one can use $\bar{\nu}_{x_{mean}}$ as the wave number that the dye would have were there no hypsochromic effect. Then $\bar{\nu}_{x_{mean}} - \bar{\nu}_x$ is a measure of the hypsochromic effect of lack of degeneracy of the two *A*-structures. Column five of Table II shows how the hypsochromic effect measured in this way increases as the basicity of the weaker component base is reduced, while the stronger base remains dimethylaniline.

In cases in which the lack of basicity of one of the parent dyes produces a marked increase in $\bar{\nu}_x$ it is doubtful that this factor should be included in obtaining $\bar{\nu}_{x_{mean}}$, for in the unsymmetrical dye the suppression of *A*-structures might not have reached the stage necessary to produce a large effect. In that case the value of $\bar{\nu}_x$ should be corrected before it is used to compute a mean. This correction would decrease $\bar{\nu}_x$ and the corrected mean would have a smaller frequency than the experimental one. The effect of this would be that the Brooker deviation minimizes the hypsochromic effect of lack of symmetry, especially when the base from which one of the parent dyes is made is very weak, as in the case of the carbazyl dyes. Therefore it would not be surprising to find cases in which lack of symmetry appears to have a bathochromic effect, when $\bar{\nu}_{x_{mean}} - \bar{\nu}_x$ is used as a measure of the effect. We believe that the bathochromic effect observed for the monocarbazyl dye in chloroform is not due to lack of symmetry but to the large increase of *T*-structures. If this is correct, the hypsochromic effect of lack of symmetry of the monocarbazyl dye in all solvents is grossly and equally underestimated when it is measured by $\bar{\nu}_{x_{mean}} - \bar{\nu}_x$. In chloroform the resulting error is greater than the effect itself.

As a first approximation one can represent one of these dyes by the function $\Psi = a_1\psi_{A_1} + a_2\psi_{A_2}$ where ψ_{A_1} and ψ_{A_2} are functions for the *A*-structures qualified by the effects of the terminal groups. When the dye is not symmetrical with respect to the terminal groups a_1 is not equal to a_2, but the *A*-structure in which the more basic nitrogen atom is doubly bonded to the conjugate system is favored. In that case the charge on the ion is distributed more on one end of the molecule than on the other, and the electrical capacity of the ion is smaller than it is in a more symmetrical dye. Hence a large difference between the coefficients a_1 and a_2 is attained more readily in a solvent of high than in one of low dielectric constant. Thus in chloroform solution the ion is more symmetrical than it is in water. If the Brooker deviation is associated with the inequality of a_1 and a_2, as Brooker, Sprague and co-workers[1] assume, the deviation is larger in water than it is in chloroform. Since the spectra of the symmetrical dyes are little affected by the solvent there is a large solvent effect on the spectrum of the unsymmetrical dye. The way in which the solvent effect and the Brooker deviation go hand in hand can be seen in Table II. However this correlation should not be perfect. If the basicity of one of the nitrogen atoms is continuously reduced while that of the other is kept constant, eventually the charge of the ion would be located entirely on one of the nitrogen atoms, no matter how low the dielectric constant of the solvent, and the solvent effect would be small.

We have described the solvent effect as if it were due to the dielectric constant of the liquid. Actually it depends on the molecules of the solvent that are very near the ions, and these molecules can be affected by the ions in a way that can greatly increase their effective dielectric constant. Thus the experimentally found solvent effect of acetic acid, which has a dielectric constant of 9.7, is about the same as that of methyl alcohol. The low dielectric constant of acetic acid

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(3) G. N. Lewis, This Journal, 67, 770 (1945).

is due to the formation of a cyclic dimer with no dipole moment. Acetic acid molecules very near to the ions are largely dissociated, and in consequence behave like molecules of a solvent having a much higher dielectric constant than 9.7.

The wave lengths of the x- and y-bands of the monocarbazyl dye in chloroform solutions are reduced by excess hydrochloric acid. This is probably a solvent effect. In that case hydrochloric acid in chloroform behaves as a solvent with a very high effective dielectric constant, because its effect is much greater than that which would be produced by the same concentration of methyl alcohol.

If it is assumed that in Table II the bases are ordered according to the resonance interaction of the constituent groups and the nitrogen atoms, the value of $\bar{\nu}_y - \bar{\nu}_x$ of the symmetrical dye decreases as the resonance interaction increases. This is a quantitative measure of the energy difference between the x- and y-excited states. The decrease of $\bar{\nu}_y - \bar{\nu}_x$ shows that the resonance interaction tends to favor the y- over the x-state. These resonance interactions produce T-structures, which have dipoles in which the nitrogen atoms are positive and the terminal groups negative. These dipoles repel the charge of the ion toward the center of the ion and the extra phenyl group. Hence it may be assumed that these parts of the ion carry a greater part of the charge in the y- than in the x-state. This is in agreement with Lewis and Calvin[4] who assume that the x-band is due to a vibration of the charge between the nitrogen atoms, and the y-band to a vibration in the perpendicular axis, which includes the extra phenyl group.

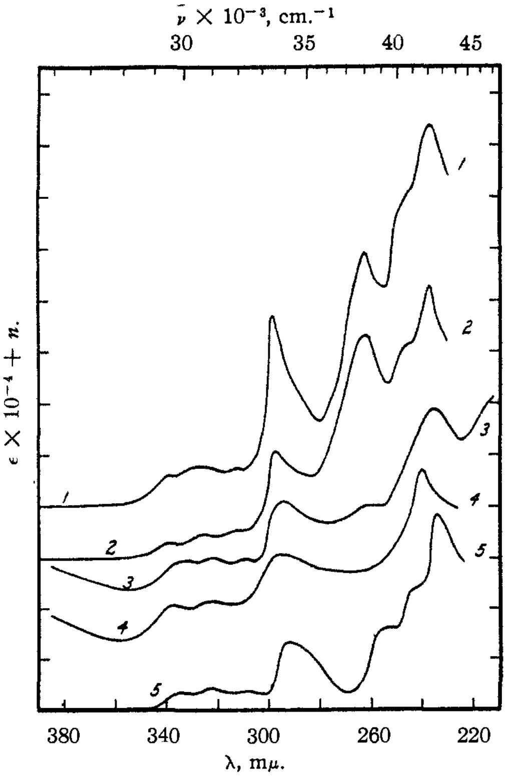

Fig. 4.—Ultraviolet spectra of some compounds containing carbazyl nuclei: (1) dicarbazyl methyl ether in methyl alcohol, n = 4; (2) monocarbazyl methyl ether in methyl alcohol, n = 3; (3) monocarbazyl dye in water, n = 2; (4) monocarbazyl dye in methyl alcohol, n = 1; (5) carbazole in methyl alcohol, n = 0.

Ultraviolet Spectra of the Dyes.—The ultraviolet spectrum of the monocarbazyl dye varies considerably with the solvent, the extreme variation being that between water and chloroform. In the latter solvent the spectrum of the monocarbazyl dye is not unlike that of the dicarbazyl dye in any solvent, but in water the spectrum of the monocarbazyl dye is almost the same as that of carbazole in methyl alcohol. The spectra of the methyl ethers of both the mono- and dicarbazyl dyes are also almost the same as that of carbazole. The similarities of these spectra are shown in Fig. 4 where they are plotted one above the other by changing the point of zero extinction coefficient but retaining the same units. The spectrum of the monocarbazyl dye in methyl alcohol is also shown in this figure. It resembles, but not very closely, the other spectra.

On the other hand, except for a band between 290 and 295 mμ, the spectra of the dicarbazyl dye

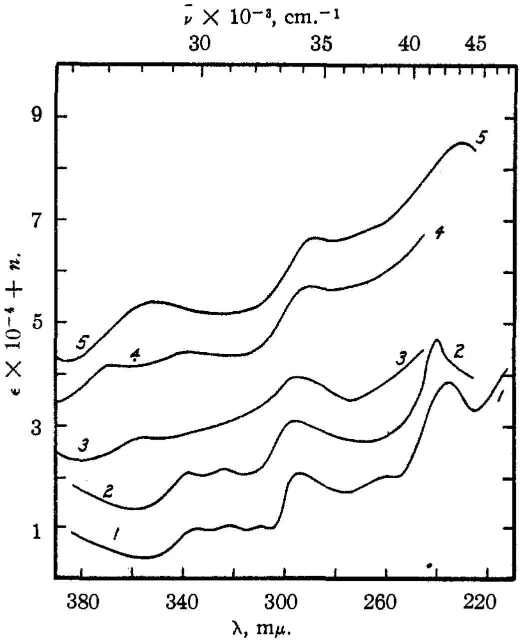

Fig. 5.—Ultraviolet spectra of the two carbazyl dyes in various solvents: (1) monocarbazyl dye in water, n = 0; (2) monocarbazyl dye in methyl alcohol, n = 1; (3) monocarbazyl dye in chloroform, n = 2; (4) dicarbazyl dye in chloroform, n = 3; (5) dicarbazyl dye in methyl alcohol, n = 4.

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[4] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

in any solvent and of the monocarbazyl dye in chloroform are unlike those of carbazole and the methyl ethers. This is illustrated in Fig. 5, which shows the spectra of the dicarbazyl dye in chloroform and in methyl alcohol, and the somewhat similar spectrum of the monocarbazyl dye in chloroform. For contrast Fig. 5 also shows the carbazole-like spectrum of the monocarbazyl dye in water, and the intermediate type of spectrum obtained with this dye when the solvent is methyl alcohol. The wave lengths of the ultraviolet absorption bands found in all the spectra measured are given in Table III.

TABLE III

ABSORPTION MAXIMA OF THE CARBAZYL DYES IN THE ULTRAVIOLET

In the table dashes indicate the absence of absorption maxima and blank spaces that measurements were not made at these wave lengths.

Compound	Solvent	Wave lengths, mμ						
Dicarbazyl dye	$CHCl_3$	369	..	317	290	..		
Dicarbazyl dye	AcOH	355	..	..	290	..		
Dicarbazyl dye	CH_3OH	353	..	..	290	..	..	230
Monocarbazyl dye	$CHCl_3$	355	..	..	295	..		
Monocarbazyl dye	AcOH	340	325	..	295	..		
Monocarbazyl dye	CH_3OH	340	325	..	295	..	..	240
Monocarbazyl dye	H_2O	335	325	310	295	260	..	235
Dicarbazyl methyl ether	CH_3OH	338	325	312	296	265	245	237
Monocarbazyl methyl ether	CH_3OH	340	325	312	294	263	245	237
Carbazole	CH_3OH	335	324	309	293	255	243	234

In the methyl ethers of the mono- and dicarbazyl dyes there are one or two carbazyl nuclei which are insulated by single bonds from the other parts of the molecule. In consequence the spectra of these compounds should show the characteristics of that of carbazole, and in any region in which bands due to other structural units have low molecular extinction coefficients their spectra should closely resemble that of carbazole. Thus if small adjustments of the positions of the bands are made, the molecular extinction coefficients of the monocarbazyl and the dicarbazyl dyes are respectively only slightly greater than once and twice the corresponding coefficients of carbazole.

The carbazyl nucleus in the monocarbazyl dye is not insulated from the rest of the molecule, and the spectrum of the dye should not be very much like that of carbazole. But the carbinol of a dye can form two ions, the quinoidal ion and an ion formed by the addition of hydrogen ion to one of the nitrogen atoms, $(R_2\overset{+}{N}HC_6H_4)(C_6H_5)$-$(R_2NC_6H_4)COH$. The group $R_2NC_6H_4$ is insulated, and, if it is a carbazyl nucleus, the spectrum of the ion should be similar to that of carbazole. Hence the spectra show that the carbinol ion of the monocarbazyl dye exists in water solution to an extent that makes its spectrum predominant in the region of 360 to 220 mμ. But in chloroform solution the benzenoidal ion does not exist to so great an extent. The spectrum of the dicarbazyl dye is not like that of carbazole, and this spectrum would not obscure the carbazole bands at 335, 324, 309, 255 and 243 mμ if they were present. Hence the carbinol ion of the dicarbazyl dye exists in very small concentrations.

In a benzenoidal ion the charge is concentrated on one nitrogen atom, but it is distributed over a larger portion of the molecule in the quinoidal form. The benzenoidal ion is, therefore, favored by water more than it is by chloroform. Further, in chloroform the solvent itself does not add to a quinoidal ion, and the formation of the benzenoidal ion depends on the hydroxylated molecules added with the color base, or present as impurities.

The equilibrium ratio of the benzenoidal and quinoidal ions of a dye equals the ratio of the base constant for the carbinol forming a benzenoidal ion and that for the formation of the quinoidal ion. The former should approximately equal $K_b + K_{b'}$, where K_b is the base constant for the stronger of the two bases from which the dye is derived, and $K_{b'}$ the constant for the other base. For the monocarbazyl dye, the base constant for the formation of the benzenoidal ion would be approximately that of dimethylaniline, and for the dicarbazyl dye, the corresponding constant would be approximately twice the base constant of carbazole. So, as a true base, the carbinol of the monocarbazyl dye is very much stronger than that of the dicarbazyl dye. On the other hand, the formation of the quinoidal ion depends on its resonance energy. The resonance of the dicarbazyl ion is one between two equivalent structures but in the monocarbazyl dye the degeneracy is far from complete, especially in water where there is a large Brooker deviation. In consequence the formation of the quinoidal ion of the dicarbazyl dye is assisted by resonance more than the corresponding reaction of the monocarbazyl dye. This compensates for the fact that the average strength of the bases from which the dicarbazyl dye is derived is much less than the average strength of the bases from which the monocarbazyl dye is derived. So, as a pseudobase, the carbinol of the monocarbazyl dye is not much stronger than that of the dicarbazyl dye. Hence K_1/K_2, where K_1 is the base constant of a carbinol or ether forming a benzenoidal ion and K_2 that for the formation of the quinoidal ion is much greater for the monocarbazyl than for the dicarbazyl dye, and at equilibrium the former dye contains a greater proportion of the benzenoidal ion than the latter does.

Spectra of the Anhydro Bases.—The wave lengths of the maxima of the absorption bands found in the spectra of the anhydro bases in the various solvents are given in Table IV; which includes a column for the drying agent. Three of the absorption spectra are given in Fig. 6.

In the spectra of the anhydro bases of the monocarbazyl dye two bands were obtained in the visible. We shall call these two bands the x- and y-bands. Whether in this dye λ_x is greater for the ion or the anhydro base depends on the solvent. In acetone the x-bands of the ion and of the

TABLE IV

ABSORPTION MAXIMA OF THE ANHYDRO BASES

The anhydro base of	Solvent	Drying agent	λ_x, mμ	λ_y, mμ
Viridine Green	C_6H_6	Na_2SO_4	440[5]	
Viridine Green	60% CH_3OH, 40% C_6H_6	0.5% H_2O	489[5]	
Viridine Green	CH_3COCH_3	K_2CO_3	459	
Dicarbazyl dye	CH_3COCH_3	K_2CO_3	496	
Monocarbazyl dye	CH_3COCH_3	K_2CO_3	574	415
Monocarbazyl dye	H_2O	....	618	430

anhydro base have maxima at almost the same wave length, and this is also true for the *y*-bands. In water the anhydro base absorbs at a much longer wave length than the ion does, λ_x = 618 mμ for the anhydro base, and 562 mμ for the ion. In chloroform the ion is blue and the anhydro base a red-violet. A comparison of the color brings out in a very striking way the difference in the effects of solvents on the spectra of the monocarbazyl dye and its anhydro base. Dissolved in water the dye is a red-violet that is very like the color of a solution of the anhydro base in chloroform; while in water the anhydro base is blue, and so also is a solution of the dye in chloroform.

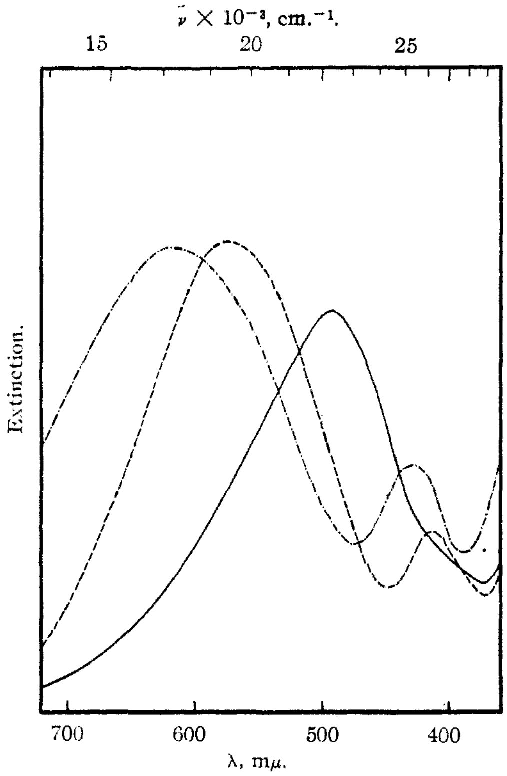

Fig. 6.—Absorption spectra of the anhydro bases of the carbazyl dyes: ——— $(C_{12}H_8N)(C_6H_5)C{=}(C_{12}H_7N)$ in acetone; - - - $(CH_3)_2NC_6H_4(C_6H_5)C{=}(C_{12}H_7N)$ in acetone; -.-.-.- $(CH_3)_2NC_6H_4(C_6H_5)C{=}(C_{12}H_7N)$ in water.

One may represent a molecule having amidine or amidinium type resonance by the function $\Psi = a_1\psi_{A_1} + a_2\psi_{A_2}$ where ψ_{A_1} and ψ_{A_2} are the functions for the two *A*-structures. For an anhydro base ψ_{A_1} and ψ_{A_2} represent the structures

$$T_aT_bN{-}C_6H_4(C_6H_5)C{=}C_6H_4{=}NT_c \text{ and } T_aT_b{}^{+}N{=}C_6H_4{=}C(C_6H_5)C_6H_4N^{-}T_c,$$

respectively. The latter is the less stable structure, so $a_1 > a_2$ and there is a large Brooker deviation and λ is smaller than it is for the positive ion. Since the smaller coefficient (a_2) refers to the structure with much the greater dipole moment, the dipole moment is greater the more nearly equal the coefficients are. Hence in a solvent with a high dielectric constant, *e.g.*, water, the molecule is at a minimum energy with the coefficients more nearly equal than they are in a solvent with a low dielectric constant. In consequence λ is greater in water solution than it is in the less polar solvents.

In order that the anhydro base should have a large value of λ one must enhance the acidity of the amino group from which the hydrogen ion is lost in the formation of the anhydro base, and retain the basicity of the other amino group. That is, the negative ion of one of the amines from which the dye is derived must be a base that is not overwhelmingly stronger than the other base. Then in a solvent with a high dielectric constant the anhydro base will give a spectrum not unlike that of a symmetrical dye. Carbazole is a much stronger acid than most amines. One may therefore expect λ for the anhydro base of the monocarbazyl dye to have a high value, especially in water solution.

Brooker and Sprague[6] have found that phenol blue, *p,p'*-$(CH_3)_2NC_6H_4NC_6H_4O$, has the spectrum of a very unsymmetrical dye in acetone, but of a nearly symmetrical dye in water, and in consequence has a high value of λ in the latter solvent. This is similar to our observations on the spectrum of the anhydro base of the monocarbazyl dye, and our explanation is essentially theirs. In both explanations the solvent effect of water is assumed to be due to the equalization of the coefficients of the *A*-structures; but they attributed this equalization to the stabilization of the polar component structure by water, but we have attributed it to the stabilization of the molecule itself.

Preparations

N-Dimethyl-*p*-aminophenyl-3-carbazylphenylmethyl Methyl Ether.—One mole of N-dimethyl-*p*-aminobenzophenone, one mole of carbazole and two moles of phosphorus oxychloride were mixed in a flask fitted with a reflux condenser and a drying tube. The flask was heated for two hours in an oil-bath at 140 to 150°. The reaction product was dissolved in methanol and the solution added to a large excess of aqueous 2 *N* hydrochloric acid solution. The precipitated dye was dissolved in acetone and converted to the carbinol with sodium hydroxide. The resulting solution of the carbinol was filtered and the filtrate was added to a mixture of benzene and water. The benzene layer was separated, washed, and dried with sodium sulfate. The chloride of the dye, free from any other salt, was precipitated from the benzene solution of the carbinol with an ethereal solution of hydrochloric

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(5) Hill, Branch and Patapoff, THIS JOURNAL, **67**, 454 (1945).

(6) Brooker and Sprague, *ibid.* **63**, 3214 (1941).

acid. The chloride was purified by repeatedly precipitating it from chloroform solutions by adding hexane and later by adding ether. At the end of this treatment the chloride was a fine crystalline powder with a metallic luster.

The chloride was dissolved in methanol and converted to the methyl ether by adding sodium methylate. After it had stood sufficiently long to allow all of the anhydro base to change to the methyl ether, the methyl ether was precipitated with water. The methyl ether was dissolved in chloroform. The solution was boiled with nuchar 00 and filtered. The chloroform was evaporated off. The resulting methyl ether was further decolorized by dissolving in methanol and boiling the solution with nuchar 00. This was repeated until the solution was quite colorless. Finally the methyl ether was precipitated from the solution with water, and dried *in vacuo*. The product was a white powder, m. p. 102–104°.

Anal. Calcd. for $C_{28}H_{26}N_2O$: C, 82.7; H, 6.45; N, 6.89. Found: C, 82.5, 82.4; H, 6.30, 6.27; N, 6.95, 7.02.

3,3'-Dicarbazylphenylmethyl Methyl Ether.—Two moles of carbazole, two moles of aluminum chloride, a mole of hydrochloric acid in saturated ethereal solution and 800 ml. of isoöctane were mixed in a vessel fitted with a stirrer, a dropping funnel and a reflux condenser equipped with a drying tube. The flask was placed on a steam-bath and one mole of benzotrichloride added through the dropping funnel. The stirring and the heating were continued for eight hours. The isoöctane was decanted and the reaction product dissolved in methanol. After filtration, the solution was added to a large excess of aqueous 2 *N* hydrochloric acid solution. The precipitated chloride of the dye was purified by repeated precipitation from chloroform solutions with ether. The purified chloride was a fine crystalline powder with a red metallic luster.

The chloride was dissolved in methanol and converted to the methyl ether with sodium methylate, allowing it to stand until all the anhydro base had disappeared. The methyl ether was precipitated from the solution with water. The precipitated methyl ether was dissolved in benzene and the solution filtered. The benzene was removed by evaporation *in vacuo*. The methyl ether was decolorized by boiling a methanol solution of it with nuchar 00. Finally the methyl ether was precipitated from the solution with water, filtered and dried *in vacuo*. The product was a white powder; m. p. 160–165°.

Anal. Calcd. for $C_{32}H_{24}N_2O$: C, 84.9; H, 5.35. Found: C, 84.7, 84.7; H, 5.30, 5.34.

Summary

The two dyes, N-dimethyl-*p*-aminophenyl-3-carbazylphenylmethyl chloride and 3,3'-dicarbazylphenylmethyl chloride, have been prepared and their absorption spectra measured. The spectrum of the former dye was found to vary considerably with the solvent; thus λ_x was 629 mμ in chloroform and 562 mμ in water.

The spectrum of the symmetrical dye was found to be nearly independent of the solvent. The value of λ_x was found to be less and that of λ_y greater than for the corresponding bands of malachite green.

The ultraviolet spectrum of the monocarbazyl dye in water showed the existence of a benzenoidal ion in equilibrium with the quinoidal ion.

The spectra of the anhydro bases of both dyes were also measured. In water solution the anhydro base of the monocarbazyl dye absorbs at a longer wave length than the dye itself.

The relationships between these spectra and those of malachite green and phenylated diaminotriphenylmethane dyes have been discussed.

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Copolymerization. II. The Copolymerization of Acrylonitrile, Methyl Methacrylate, Styrene and Vinylidene Chloride

BY FREDERICK M. LEWIS, FRANK R. MAYO AND WILLIAM F. HULSE[1]

A previous paper from this Laboratory[2] showed that the composition of the copolymer being formed, d [S]/d [M], from two monomers at concentrations [S] and [M] should be represented by the copolymerization equation

$$\frac{d[S]}{d[M]} = \frac{[S]}{[M]} \cdot \frac{\sigma[S] + [M]}{\mu[M] + [S]}$$

where σ and μ are the *monomer reactivity ratios* for radicals ending in S and M units, respectively.[3] Each monomer reactivity ratio was defined as the ratio of the rate constants for the reaction of the chosen radical type with the corresponding monomer and with the other monomer of the pair, respectively. The use of an integrated form of this equation was described and the equation was shown to account for the copolymerization of styrene and methyl methacrylate by a free radical mechanism over a wide range of monomer mixtures, conversions, and rates of polymerization. The present paper describes a study of other binary systems of the monomers acrylonitrile, methyl methacrylate, styrene and vinylidene chloride and shows how monomer reactivity ratios of radicals may be used to compare reactivities of various ethylene bonds with free radicals.

Experimental

Monomers.—The styrene and methyl methacrylate samples were like those used for most of the experiments in the previous paper.[2] Acrylonitrile was a commercial product which had been carefully fractionated; b. p. 77.0° (760 mm.), $n^{20}{}_{D}$ 1.3931. Vinylidene chloride was

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(1) Ensign, U. S. N. R.

(2) F. R. Mayo and F. M. Lewis, THIS JOURNAL, **66**, 1594 (1944).

(3) Similar equations have been derived independently by T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 205, 322 (1944), and by F. T. Wall, THIS JOURNAL, **66**, 2050 (1944). The *A* and *B* of Alfrey and Goldfinger in their second paper correspond to our *S* and *M*, their $1/\alpha$ and $1/\beta$ to our σ and μ. The *X*, *Y*, σ, and ρ of Wall correspond to our *S*, *M*, σ, and μ. R. Simha and H. Branson, *J. Chem. Phys.*, **12**, 253 (1944), have presented more complicated and detailed treatments of copolymerization.