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

Absorption Spectra of Some Linear Conjugated Systems

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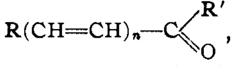
Introduction.—According to Senior's[2] generalized definition of homology, the interpolation of CH=CH groups gives a homologous series of compounds. The resulting series have been called vinylenic homologous series. The recognition of this type of homology is of value in the study of the relationship between the structure and the spectra of organic compounds, for in the spectra of such series one can often recognize bands whose wave lengths and extinction coefficients vary in a regular, and often simple, manner with the number of C_2H_2 groups. For example, in the vinylenic homologous diphenylpolyenes, λ^2_{max} of the longest waved length bands is a linear function of the number of C_2H_2 groups.

In this work we have studied the spectra of some vinylenic homologous series in which C_2H_2 groups have been interpolated conjugate to a CH=N group. These compounds have a heterogeneous conjugate system, like the series  $R(CH{=}CH)_n{-}C\genfrac{}{}{0pt}{}{R'}{O}$, but the valence of the nitrogen atom permits the conjugate system to be duplicated with the nitrogen atoms pointing inwards. This duplication can occur with the nitrogen atoms directly attached to each other or separated by aromatic nuclei, or saturated or unsaturated aliphatic chains.

We have obtained spectra of members of each of the homologous series $C_6H_5{-}(CH{=}CH)_n{-}CH{=}N{-}C_6H_5$, $C_6H_5(CH{=}CH)_n{-}CH{=}N{-}N{=}CH{-}(CH{=}CH)_m{-}C_6H_5$, p,p'-$O_2N{-}C_6H_4{-}(CH{=}CH)_n{-}CH{=}N{-}N{=}CH{-}(CH{=}CH)_m{-}C_6H_4{-}NO_2$, $C_6H_5{-}(CH{=}CH)_n{-}CH{=}N{-}CH_2{-}CH_2{-}N{=}CH{-}(CH{=}CH)_m{-}C_6H_5$, and p-$C_6H_5{-}(CH{=}CH)_n{-}CH{=}N{-}C_6H_4{-}N{=}CH{-}(CH{=}CH)_m{-}C_6H_5$. We have also obtained the spectra of several compounds related to the first members of some of these series.

Description of Compounds.—The compounds studied were prepared by the condensation of the appropriate aldehydes and amines. Unsymmetrical azines were prepared by condensing hydrazine with different aldehydes in succession. The last mentioned type of synthesis frequently fails, because of the difficulty of obtaining the intermediate in which only one of the amino groups has reacted with the aldehyde. The acetyl derivatives included were prepared by acetylating the corresponding hydroxy compound with hot acetic anhydride.

The identities of the compounds were assured by the methods of synthesis, the ultimate analyses and, when we found the compound in the literature, by the melting points. The identities of intermediates used in preparing unsymmetrical diimino compounds were confirmed by preparing known symmetrical diimino compounds from them.

The compounds, their analyses, and melting points are listed in Table I. The references appended to the table are to the earliest description of the compound that we have found, and to previously obtained absorption spectra. These spectra are in essential agreement with our measurements.

Measurements of Absorption Spectra.—All measurements of absorption spectra were made with a Beckman Quartz Spectrophotometer, Model D. The cells used were quartz tubes, 10 mm. square and 30 mm. tall, with lids to prevent evaporation of the solvent. For light sources, a hot cathode hydrogen discharge tube was used. The measurements at maximum absorption are accurate to about ±2% in ϵ_{max} and ±0.2% in $\bar{\nu}_{max}$. Measurements in this region were taken at intervals of about 10 Å.

The molar extinction coefficient, ϵ, is calculated according to the equation

$$\epsilon = \frac{1}{cd} \log I_0/I$$

where c is the concentration in moles per liter of solution, d, the width of the cell, equals 1 cm. and $\log I_0/I$ is the logarithm of the ratio of intensity of transmitted light of the solvent to that of the solution. Measurements were made at various concentrations for almost all compounds to verify the applicability of Beer's law.

The experimental results are shown in figures one to ten.

In general, ethyl alcohol is the solvent. Some of the compounds are inconveniently insoluble in this solvent. For this reason a few spectra were obtained in propyl alcohol, and some in glacial acetic acid. The spectra of the series $C_6H_5{-}(CH{=}CH)_n{-}CH{=}N{-}N{=}CH{-}(CH{=}CH)_n{-}C_6H_5$ were measured in propyl alcohol. Only one of these is too insoluble in ethyl alcohol. However, the frequencies of the principal bands of the other members of this series are, within experimental error, the same in ethyl alcohol as in propyl alcohol, and it may be assumed that this is true of all. In consequence the solvent effect may be ignored in the comparison between the frequencies given for the series in which propyl alcohol is the solvent and those in which ethyl alcohol is the solvent.

The spectra of all the nitro compounds were obtained in acetic acid. The spectra of these com-

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[1] Abstract from a thesis submitted to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1943.

[2] J. K. Senior, *J. Org. Chem.*, **3**, 1 (1938).

TABLE I

The analyses are means of duplicates and the figures in parentheses are calculated values.

Formula	Analyses, % C	H	N	M. p., °C.	Ref.
$C_6H_5CH=N-C_6H_5$	86.0 (86.2)	6.1 (6.1)	7.7 (7.5)	52	3
$C_6H_5-CH=CH-CH=N-C_6H_5$	87.2 (87.0)	6.3 (6.3)	6.8 (6.8)	109	4
$C_6H_5(CH=CH)_2-CH=N-C_6H_5$	87.4 (87.6)	6.5 (6.4)	6.0 (6.0)	109	5
$p\text{-}O_2N-C_6H_4-CH=N-C_6H_5$	68.9 (69.0)	4.6 (4.4)	12.3 (12.3)	91	6
$p\text{-}HO-C_6H_4-CH=N-C_6H_5$	79.3 (79.2)	5.6 (5.6)	7.1 (7.1)	190	7
$o\text{-}HO-C_6H_4-CH=N-C_6H_5$	79.1 (79.2)	5.6 (5.6)	7.2 (7.1)	51	8
$C_6H_5-CH=N-N=CH-C_6H_5$	80.6 (80.8)	5.7 (5.8)	13.4 (13.5)	94	9
$[C_6H_5-CH=CH-CH=N-]_2$	83.1 (83.1)	6.4 (6.2)	10.6 (10.8)	167	10
$[C_6H_5-(CH=CH)_2-CH=N-]_2$	84.4 (84.6)	6.3 (6.4)	9.3 (9.0)	208	11
$[p\text{-}O_2N-C_6H_4-CH=N-]_2$				303	12
$[p\text{-}O_2N-C_6H_4-CH=CH-CH=N-]_2$	61.7 (61.7)	4.0 (4.0)		229	
$[p\text{-}O_2N-C_6H_4-(CH=CH)_2-CH=N-]_2$	64.2 (65.7)	4.5 (4.5)	13.9 (12.9)	210	[a]
$C_6H_5-CH=CH-CH=N-N=CH-C_6H_5$	82.4 (82.1)	5.8 (6.0)	11.8 (12.0)	113	
$C_6H_5-CH=CH-CH=N-N=CH-(CH=CH)_2-C_6H_5$	84.2 (84.0)	6.5 (6.3)	9.4 (9.8)	170	
$o\text{-}HO-C_6H_4-CH=N-N=CH-CH=CH-C_6H_5$	76.8 (76.8)	5.5 (5.6)	11.2 (11.2)	100	
$[o\text{-}O_2N-C_6H_4-CH=N-]_2$	55.9 (56.4)	3.0 (3.35)	18.6 (18.8)	207	13
$[m\text{-}O_2N-C_6H_4-CH=N-]_2$	56.5 (56.4)	3.2 (3.4)	18.6 (18.8)	195	13
$[p\text{-}HO-C_6H_4-CH=N-]_2$	69.9 (70.0)	5.2 (5.0)	11.0 (11.67)	260	14
$[p\text{-}AcO-C_6H_4-CH=N-]_2$				185	15
$[o\text{-}AcO-C_6H_4-CH=N-]_2$	66.6 (66.7)	4.9 (4.9)	8.5 (8.7)	187	15
$[o\text{-}HO-C_6H_4-CH=N-]_2$				216	16
$[C_6H_5-CH=N-CH_2-]_2$	81.5 (81.4)	6.5 (6.8)	12.2 (11.9)	53	17
$[C_6H_5-CH=CH-CH=N-CH_2-]_2$	83.4 (83.4)	6.7 (7.0)	10.2 (9.7)	109	18
$[o\text{-}HO-C_6H_4-CH=N-CH_2-]_2$				125	19
$p\text{-}C_6H_5-CH=N-C_6H_4-N=CH-C_6H_5$	84.1 (84.5)	5.4 (5.6)	9.9 (9.9)	139	20
$p\text{-}C_6H_5-CH=CH-CH=N-C_6H_4-N=CH-CH=CH-C_6H_5$	86.0 (85.5)	6.0 (6.0)	8.3 (8.3)	220	21
$p\text{-}C_6H_5(CH=CH)_2-CH=N-C_6H_4-N=CH-(CH=CH)_2-C_6H_5$	86.4 (86.6)	6.1 (6.2)	7.3 (7.2)	195	
$o\text{-}C_6H_5-CH=N-C_6H_4-N=CH-C_6H_5$	84.0 (84.5)	5.6 (5.6)	9.9 (9.9)	135	22
$m\text{-}C_6H_5-CH=N-C_6H_4-N=CH-C_6H_5$	84.2 (84.5)	5.5 (5.6)	9.9 (9.9)	109	23

[a] This analysis is poor; however, as the method of preparation is very general, and the spectrum of the compound fits well with those of its homologs, we have no doubt that the substance is di-(ω-p-nitrophenylbutadienal)-hydrazine.

pounds in alcohol and in acetic acid are markedly different. A comparison between the frequencies of the principal bands of the nitro compounds and those of the other compounds includes a solvent effect.

When one compares the spectra of the members of any of the homologous series shown in Figs. 1–6, it is possible by picking out a strong absorption band from each spectrum to obtain a series of bands that increase in extinction coefficient and in the wave length of the peak with each addition of a C_2H_2 group. We have assumed these to be corresponding bands due to a conjugated imino group, and have called them the principal bands. The wave numbers and extinction coefficients of the peaks of the bands are shown in Table II under the headings $\nu_{\max}$ and $\epsilon_{\max}$.

Except those for the nitro compounds and for $C_6H_5-CH=N-C_6H_5$ these principal bands are also those of greatest wave length. The peaks can be located within 20 Å. The spectra of the p,p'-dinitrophenylpolyeneazines have two bands that increase in wave length and extinction coefficient with increase of C_2H_2 groups. But that with the longer wave length is the smaller, and is often only a shoulder on the other band. For this series $\bar{\nu}_{\max}$ could not be determined with much accuracy, and we have used the stronger but shorter waved length band as the principal band.

In the spectra of some of the other imino compounds the strongest band is that with the greatest wave length, and there seems little doubt that

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(3) Hinsberg, *Ber.*, **20**, 1587 (1897). Abs. spectra: Baly, Tuck and Marsden, *J. Chem. Soc.*, **97**, 590 (1910).

(4) Doebner and Miller, *Ber.*, **16**, 1665 (1883).

(5) Vorländer and Doehn, *ibid.*, **62**, 542 (1929).

(6) Fischer, *ibid.*, **14**, 2525 (1881).

(7) Herzfield, *ibid.*, **10**, 1271 (1877).

(8) Emmerich, *Ann.*, **241**, 344 (1887). Abs. spectra: Pope, *J. Chem. Soc.*, **93**, 537 (1908).

(9) Thiele, *Ann.*, **336**, 244 (1904). Abs. spectra: Rădulescu and Aleza, *Ber.*, **64**, 2230 (1931).

(10) Knopfer, *Monatsh.*, **32**, 760 (1911). Abs. spectra: Rădulescu and Aleza, ref. 9.

(11) Fischer and Kunze, *Ber.*, **58**, 1284 (1925). Abs. spectra: Rădulescu and Aleza, ref. 9.

(12) Curtis and Pflug, *J. prakt. Chem.*, [2] **44**, 537 (1891).

(13) Curtis and Lublin, *Ber.*, **33**, 2640 (1900).

(14) Vorländer, *ibid.*, **39**, 807 (1906).

(15) Vorländer, *Chem. Zentr.*, **77**, 1, 1246 (1906).

(16) Knopfer, *Monatsh.*, **32**, 755 (1911).

(17) Mason, *Ber.*, **20**, 270 (1887). Abs. spectra: Tsuchida and Tsumaki, *Bull. Chem. Soc. Japan*, **13**, 527 (1938).

(18) Mason, ref. 17.

(19) Tsuchida and Tsumaki, ref. 17.

(20) Ladenburg, *Ber.*, **11**, 599 (1878).

(21) Vorländer, *ibid.*, **40**, 4536 (1907).

(22) Hensberg and Koller, *ibid.*, **29**, 1499 (1896).

(23) Myer and Gross, *ibid.*, **32**, 2366 (1899).

TABLE II

EXTINCTION COEFFICIENTS AND WAVE NUMBERS OF THE PRINCIPAL BANDS OF THE ABSORPTION SPECTRA OF CONJUGATED IMINO COMPOUNDS

Substance	Solvent	$\epsilon_{max} \times 10^{-2}$	$\bar{\nu}_{max} \times 10^{-3}$	Fig.
$[C_6H_5-CH=N-]_2$	n-PrOH	380	33.2	3
$[C_6H_5-CH=CH-CH=N-]_2$	n-PrOH	710	28.9	3
$[C_6H_5-(CH=CH)_2-CH=N-]_2$	n-PrOH	839	26.0	3
$C_6H_5-CH=N-N=CH-CH=CH-C_6H_5$	EtOH	520	29.5	4
$[C_6H_5-CH=CH-CH=N-]_2$	EtOH	650	28.9	4
$C_6H_5-(CH=CH)_2-CH=N-N=CH-CH=CH-C_6H_5$	EtOH	764	26.5	4
$C_6H_5-CH=N-C_6H_5$	EtOH	168	38.0	1
$C_6H_5-CH=CH-CH=N-C_6H_5$	EtOH	280	33.3	1
$C_6H_5-(CH=CH)_2-CH=N-C_6H_5$	EtOH	436	29.3	1
$[C_6H_5-CH=CH-CH=N-CH_2-]_2$	EtOH	552	35.5	2
$[C_6H_5-CH=N-CH_2-]_2$	EtOH	298	40.5	2
$C_6H_5-CH=N-CH_3$	EtOH	172	40.5	2
$C_6H_5-CH=N-C_2H_5$	EtOH	159	40.8	
p-$C_6H_5-CH=N-C_6H_4-N=CH-C_6H_5$	EtOH	254	28.9	6
p-$C_6H_5-CH=CH-CH=N-C_6H_4-N=CH-CH=CH-C_6H_5$	EtOH	465	26.8	6
p-$C_6H_5-(CH=CH)_2-CH=N-C_6H_4-N=CH-(CH=CH)_2-C_6H_5$	EtOH	699	26.3	6
m-$C_6H_5-CH=N-C_6H_4-N=CH-C_6H_5$	EtOH	338	37.4	7
[p-$HO-C_6H_4-CH=N-]_2$	EtOH	460	30.0	8
[p-$AcO-C_6H_4-CH=N-]_2$	EtOH	425	32.5	8
[o-$HO-C_6H_4-CH=N-]_2$	EtOH	246	28.0	8
[o-$AcO-C_6H_4-CH=N-]_2$	EtOH	324	33.0	8
[p-$O_2N-C_6H_4-CH=N-]_2$	AcOH	311	37.8	5
[p-$O_2N-C_6H_4-CH=CH-CH=N-]_2$	AcOH	362	32.0	5
[p-$O_2N-C_6H_4-(CH=CH)_2-CH=N-]_2$	AcOH	540	28.7	5

it corresponds to the other principal bands. The values of ν_{max} and ϵ_{max} of these bands have been included in the table of principal bands. The spectrum of *o,o'*-dihydroxybenzalazine shows two strong bands, that with the longer wave length has been chosen for the principal band; the choice is doubtful.

For many of the compounds no principal band has been chosen, either because the choice is too indefinite, or because the position of the band is not discussed later.

The spectrum of benzalethylamine is not shown, though its principal band is included in Table II.

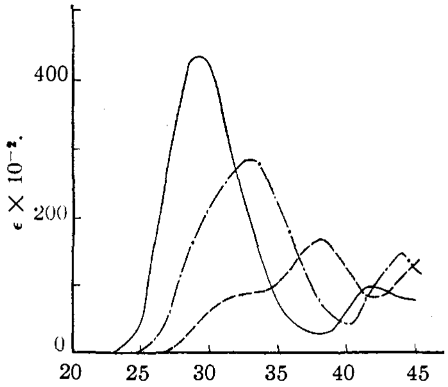

Fig. 1.—Absorption spectra in ethyl alcohol of: $C_6H_5-CH=N-C_6H_5$ — — — —; $C_6H_5-CH=CH-CH=N-C_6H_5$ —·—·—; $C_6H_5-(CH=CH)_2-CH=N-C_6H_5$ ———.

The spectrum of this compound is almost identical with that of benzalmethylamine (Fig. 2). The difference is adequately obtained by a comparison of the ϵ_{max} and $\bar{\nu}_{max}$ values given in Table II.

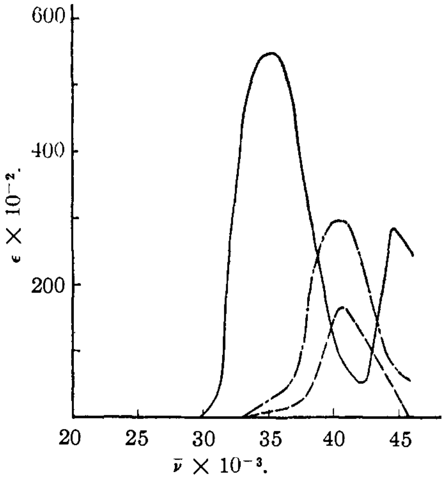

Fig. 2.—Absorption spectra in ethyl alcohol of: $C_6H_5-CH=N-CH_3$ — — — — —; $[C_6H_5-CH=N-CH_2-]_2$ —·—·—; $[C_6H_5-CH=CH-CH=N-CH_2-]_2$ ———.

Discussion

Among the purposes of comparing the spectra of structurally related compounds is the hope of obtaining methods of predicting the spectra of compounds from their structures and, conversely, of deducing their structures from their spectra. The problem has been approached in various

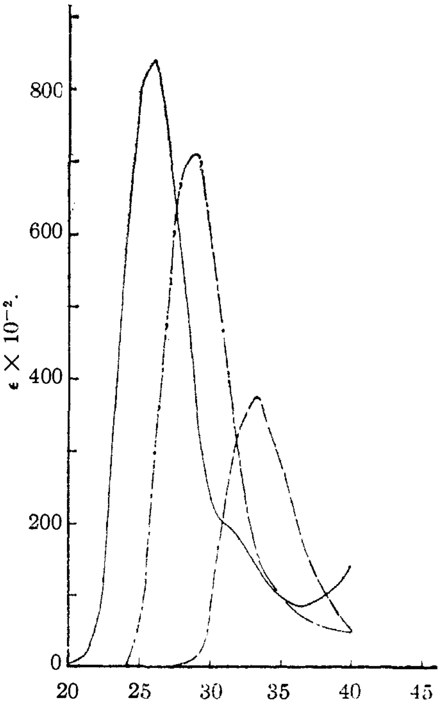

Fig. 3.—Absorption spectra in *n*-propyl alcohol of: $[C_6H_5—CH{=}N—]_2$ — — —; $[C_6H_5—CH{=}CH—CH{=}N—]_2$ —·—·—; $[C_6H_5—(CH{=}CH)_2—CH{=}N—]_2$ ——.

ways. The ideal way is to deduce the energy differences between ground and excited states from the axioms of quantum mechanics. The solution of the problem in this way is not satisfactory in the case of complicated molecules, and various short cuts have been attempted. Thus Lewis and Calvin[24] have compared structural features with certain types of oscillators. In their system a conjugated system of CH=CH groups is likened to a linear oscillator made up of similar parts that can oscillate in phase. From this point of view the present work is of interest in showing the variation of the type of oscillator produced by having CH=N groups as well as CH=CH groups in the conjugate chain and by having two such chains conjugated with each other, separated by a $CH_2—CH_2$ group or a benzene ring.

Organic chemists have in general approached the problem by seeking empirical relationships between structure and spectra. A quantitative relationship is then expressed as an empirical equation. The present discussion essentially follows this method.

The wave lengths of the principal bands in the spectra of the diphenylpolyenes, a class of compounds that are homologous in C_2H_2, are given as functions of the number of C_2H_2 groups by the equation

$$\lambda^2_{\max} = A + Bn$$

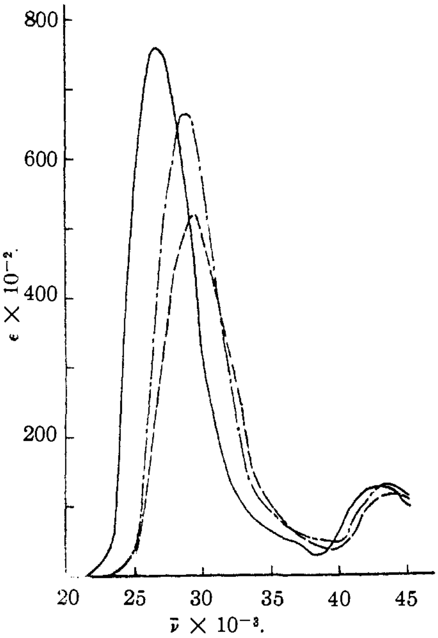

Fig. 4.—Absorption spectra in ethyl alcohol of: $C_6H_5—CH{=}CH—CH{=}N—N{=}CH—C_6H_5$ — — —; $C_6H_5—CH{=}CH—CH{=}N—N{=}CH—CH{=}CH—C_6H_5$ —·—·—; $C_6H_5—CH{=}CH—CH{=}N—N{=}CH—(CH{=}CH)_2—C_6H_5$ ——.

where $\lambda_{\max}$ is the wave length at the maximum of absorption of the principal band, n is the number of C_2H_2 groups and A and B are constants having the values 8.3×10^6 and 1.9×10^6, respectively. By making the phenyl group equivalent to 2.35 double bonds this equation can be deduced from the Lewis–Calvin model.

Any set of compounds having the general for-

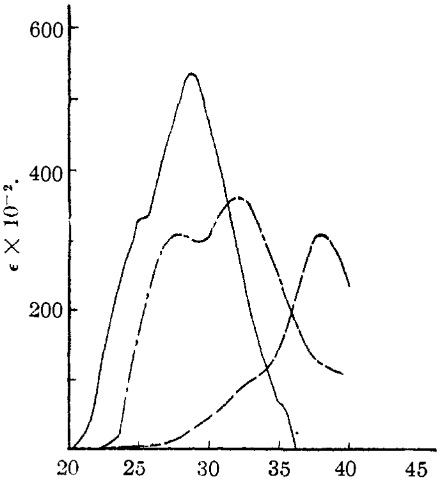

Fig. 5.—Absorption spectra in glacial acetic acid of: $[p\text{-}O_2N—C_6H_4—CH{=}N—]_2$ — — —; $[p\text{-}O_2N—C_6H_4—CH{=}CH—CH{=}N—]_2$ —·—·—; $[p\text{-}O_2N—C_6H_4—(CH{=}CH)_2—CH{=}N—]_2$ ········.

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[24] G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

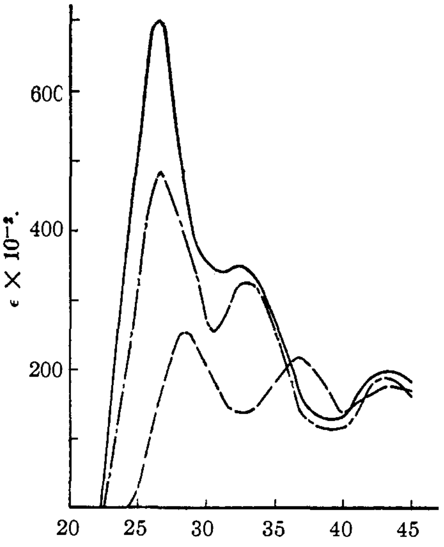
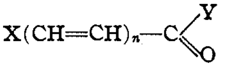


Fig. 6.—Absorption spectra in ethyl alcohol of: p-$C_6H_5{-}CH{=}N{-}C_6H_4{-}N{=}CH{-}C_6H_5$ — — —; p-$C_6H_5{-}CH{=}CH{-}CH{=}N{-}C_6H_4{-}N{=}CH{-}CH{=}CH{-}C_6H_5$ —·—·—; p-$C_6H_5{-}(CH{=}CH)_2{-}CH{=}N{-}C_6H_4{-}N{=}CH{-}(CH{=}CH)_2{-}C_6H_5$ ———.

mula  $X(CH{=}CH)_n{-}C\begin{matrix}\diagup Y\\ \diagdown O\end{matrix}$ is a vinylenic homologous series. For many of these series the squares of the wave lengths of the principal bands are approximately linear with the number of C_2H_2 groups. That is, $\lambda^2_{max} = A + Bn$. The values of the constants A and B are not the same as those in the similar equation for the diphenylpolyenes. Variation of the X and Y groups produces more change in A than in B. So that as a first approximation we can put this equation in the form

$$\lambda^2_{max} = A + B(n + \beta + \gamma)$$

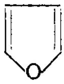
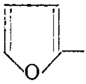
in which the effects of the groups X and Y are put as equivalent to those of β and γ double bonds, respectively. For example, for the four series methylpolyene aldehydes and acids and α-furylpolyene aldehydes and acids,[25] we have taken $A = 2.65 \times 10^6$, $B = 2.3 \times 10^6$, $\beta_{CH_3} = 0$, $\beta_{\alpha\text{-furyl}} = 2.05$, $\gamma_H = 0$ and $\gamma_{OH} = -0.38$, and calculated the λ_{max} for those members of the series whose spectra have been obtained. Calculated and observed values are compared in Table III.

Inspection of the following table shows that B is not quite invariant to change of the substituent groups, but is sufficiently so to justify the use of the empirical equation $\lambda^2_{max} = A + B(n + \beta + \gamma)$ as a first approximation. Except for α-$C_4H_3O{-}(CH{=}CH)_2{-}COOH$, whose spectrum is obviously anomalous, the mean deviation between calculated and observed values is less than 45 Å. This is about the same as the mean deviation of the observed values of λ_{max} for diphenylpolyenes from those calculated from the equation $\lambda^2_{max} = A + B(n)$.

TABLE III

CALCULATED AND OBSERVED WAVE LENGTHS OF THE PEAKS OF THE PRINCIPAL BANDS OF ABSORPTION SPECTRA OF ACYL COMPOUNDS AND THEIR VINYLENE HOMOLOGS

Type I: $CH_3{-}(CH{=}CH)_n{-}CHO$. $\lambda^2 = 2.65 \times 10^6 + 2.3 \times 10^6(n)$

n	λ_{max} Calcd., Å.	λ_{max} Obs., Å.	Diff., Å.
1	2225	2170	55
2	2693	2700	7
3	3090	3160	70
Type II: $CH_3{-}(CH{=}CH)_n{-}COOH$. $\lambda^2 = 2.65 \times 10^6 + 2.3 \times 10^6\ (n - 0.38)$			
1	2017	2040	23
2	2524	2540	16
3	2945	2940	5
4	3312	3270	42
Type III:  $-(CH{=}CH)_n{-}CHO$. $\lambda^2 = 2.65 \times 10^6 + 2.3 \times 10^6\ (n + 2.05)$			
0	2711	2720	9
1	3106	3140	24
2	3443	3500	57
3	3822	3730	92
Type IV:  $-(CH{=}CH)_n{-}COOH$. $\lambda^2 = 2.65 \times 10^6 + 2.3 \times 10^6\ (n + 2.05 - 0.38)$			
0	2548	2480	68
1	2965	3010	45
2	3330	3200	130
3	3659	3630	29

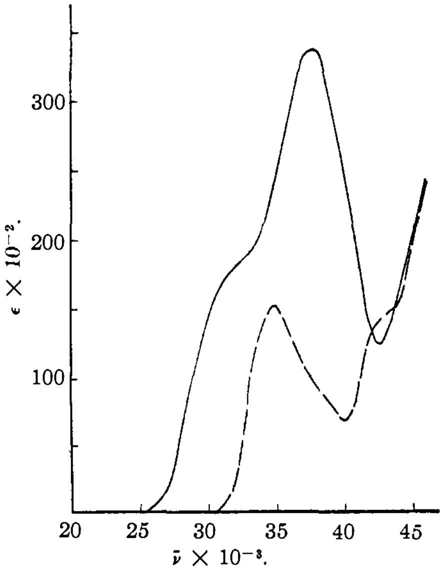


Fig. 7.—Absorption spectra in ethyl alcohol of: o-$C_6H_5{-}CH{=}N{-}C_6H_4{-}N{=}CH{-}C_6H_5$ — — —; m-$C_6H_5{-}CH{=}N{-}C_6H_4{-}N{=}CH{-}C_6H_5$ ———.

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(25) K. W. Hauser, R. Kuhn, *et al.*, *Z. physik. Chem.*, **B29**, 363–417 (1935).

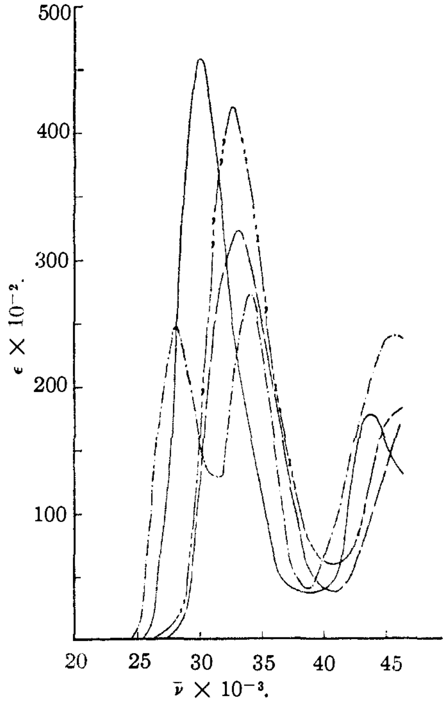

Fig. 8.—Absorption spectra in ethyl alcohol of: $[p\text{-}HO{-}C_6H_4{-}CH{=}N{-}]_2$ ————; $[p\text{-}AcOC_6H_4{-}CH{=}N{-}]_2$ — ··· — ··· —; $[o\text{-}HO{-}C_6H_4{-}CH{=}N{-}]_2$ — · — · —; $[o\text{-}AcOC_6H_4{-}CH{=}N{-}]_2$ — — —.

The equation $\lambda^2_{\max} = 2.65 \times 10^6 + 2.3 \times 10^6 (n + \beta + \gamma)$ does not hold for all homologous series of the class $X(CH{=}CH)_n{-}C\begin{smallmatrix}\diagup Y\\ \diagdown O\end{smallmatrix}$ For instance, in the series $p\text{-}(CH_3)_2NC_6H_4(CH{=}CH)_n{-}CHO$, the increment in $\lambda^2_{\max}$ per C_2H_2 group is greater than 2.3×10^6 when n is small but less when n is large.[26]

Imino Compounds.—We have obtained the spectra of three members of the homologous series $C_6H_5{-}(CH{=}CH)_n{-}CH{=}N{-}C_6H_5$, and two members of the series $C_6H_5(CH{=}CH)_n{-}CH = N{-}CH_2{-}CH_2{-}N = CH{-}(CH = CH)_n\text{-}C_6H_5$. In the former the increment of $\lambda^2_{\max}$ per C_2H_2 group was found to be about 2×10^6, in the latter one-half of this amount. However, in the latter series the two conjugated systems are insulated from each other, and one might expect that except for an increase in the extinction coefficients the spectrum would be that of a compound of the type $C_6H_5(CH{=}CH)_n{-}CH{=}N{-}R$, where R is an aliphatic radical. This was found to be true of $C_6H_5{-}CH{=}N{-}CH_2{-}CH_2{-}N{=}CH{-}C_6H_5$ and $C_6H_5{-}CH{=}N{-}C_2H_5$. For these compounds $\lambda_{\max}$ and $\epsilon_{\max}$ are 2470 Å. and 2.98×10^4 for the former and 2452 Å. and 1.59×10^4 for the latter. One should, therefore, compare the increment $\lambda^2_{\max}$ per C_2H_2 group in $C_6H_5{-}(CH{=}CH)_n{-}CH{=}N{-}C_6H_5$ with the increment of $\lambda^2_{\max}$ per two C_2H_2 groups in $C_6H_5{-}(CH{=}CH)_n{-}CH{=}N{-}CH_2{-}CH_2{-}N{=}CH)CH{=}CH)_n{-}C_6H_5$. These increments are approximately equal.

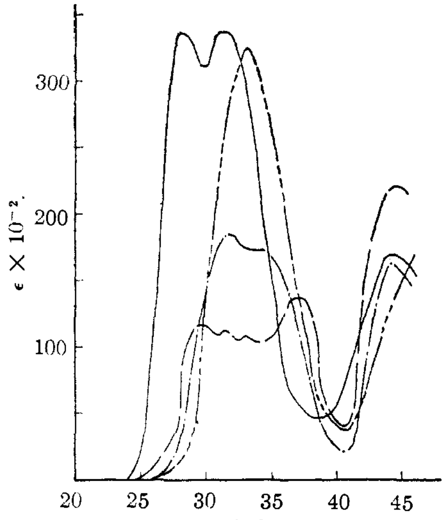

Fig. 9.—Absorption spectra in ethyl alcohol of: $p\text{-}HO{-}C_6H_4{-}CH{=}N{-}C_6H_5$ — · — · —; $o\text{-}HO{-}C_6H_4{-}CH{=}N{-}C_6H_5$ — — — ; $o\text{-}HO{-}C_6H_4{-}CH{=}N{-}N{=}CH{-}CH{=}CH{-}C_6H_5$ ————; $o,o'\text{-}HO{-}C_6H_4{-}CH{=}N{-}CH_2{-}CH_2{-}N{=}CH{-}C_6H_4{-}OH$ — ··· — ··· —.

In view of the likeness between $X(CH{-}CH)_n{=}C\begin{smallmatrix}\diagup O\\ \diagdown Y\end{smallmatrix}$ and $X(CH{=}CH)_n{-}CH{=}N{-}Y$, these few examples suggest that for the latter type of compounds, $\lambda^2_{\max} = A + B(n)$ is a fair approximation when n is small and there are no complicating factors. The value of B is between those found

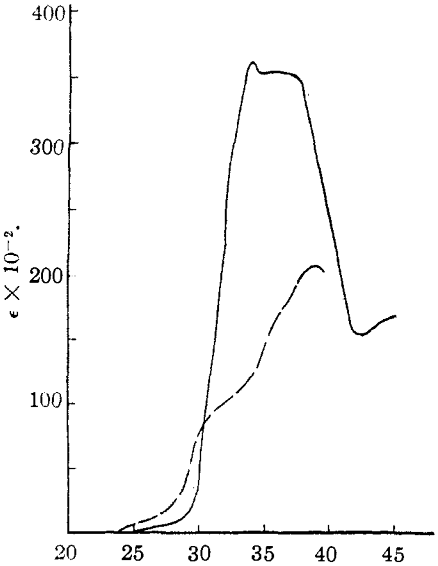

Fig. 10.—Absorption spectra in glacial acetic acid of: $[o\text{-}O_2N{-}C_6H_4{-}CH{=}N{-}]_2$ — — —; $[m\text{-}O_2N{-}C_6H_4{-}CH{=}N{-}]_2$ ————.

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(26) Konig, Schramek and Rosch, *Ber.*, **61**, 2074 (1928).

for diphenylpolyenes and for $X(CH{=}CH)_n{-}C\begin{smallmatrix}{\nearrow}O\\{\searrow}Y\end{smallmatrix}$.

However, the main purpose of this research was to study the spectra of conjugated systems in which the homogeneity is broken in the middle. Three series of this type were investigated, C_6H_5—(CH=CH)$_n$—CH=N—N=CH—(CH=CH)$_m$—C_6H_5, p,p′-O_2N—C_6H_4(CH=CH)$_n$—CH=N—N=CH—(CH=CH)$_m$—C_6H_4—NO_2, and p-C_6H_5—(CH=CH)—CH=N—C_6H_4—N=CH—(CH=CH)$_m$—C_6H_5. The number of members obtained in any series was not great, being five, three, and three, respectively. In these homologous series the relationships between λ_{max} and the number of C_2H_2 groups are not those of the simple conjugate systems.

In the series C_6H_5—(CH=CH)$_n$—CH=N—N=CH—(CH=CH)$_m$—C_6H_5, and p,p′-$O_2NC_6H_4$—(CH=CH)$_n$—CH=N—N=CH—(CH=CH)$_m$—$C_6H_4NO_2$, λ^2_{max} is linear with $n + m$ when $n = m$, and the slopes of the two lines are the same, but the increment per C_2H_2 group is markedly less than that for the simple conjugated imino compounds and markedly greater than the increment per C_2H_2 group for the case of two simple conjugated systems insulated from each other by a CH_2—CH_2 group. Further, in the two cases in which n is not equal to m, λ^2_{max} is markedly greater than the value obtained from the plot of λ^2_{max} against $n + m$ for the symmetrical compounds. In the series p-C_6H_5—(CH=CH)$_n$—CH=N—C_6H_4—N=CH—(CH=CH)$_m$—C_6H_5, λ^2_{max} is not linear with $n + m$, even though $n = m$ in all of our examples.

The compound C_6H_5—CH=CH—CH=N—N=CH—CH=CH—C_6H_5 is a combination of the classical structure and internally ionized forms. The latter include structures of type I, C_6H_5—$^+$CH—CH=CH—N$^-$—N=CH—CH=CH—C_6H_5, and type II, C_6H_5—$^+$CH—CH=CH—N=N—CH=CH—$^-$CH—C_6H_5. Type I is similar to structures involved in the resonance of C_6H_5—CH=CH—CH=N—C_6H_5 and C_6H_5—CH=CH—CH=N—CH_2—CH_2—N=CH—CH=CH—C_6H_5, but type II has no analog in the simple or insulated conjugated imino compounds. The energy level of type II is higher than that of type I, since the negative charge is more readily located on a nitrogen atom than on a carbon atom, and the C=N bond is probably more stable than the N=N bond. The contributions of type II structures are, therefore, less than those of type I. The conjugate system (C=C)$_n$—C=N—N=C—(C=C)$_m$ belongs to a type that is intermediate between the simple system (C=C)$_n$—C=N and one composed of two insulated conjugate systems, *e. g.*, C=C$_n$—C=N—C—C—N=C—(C=C)$_n$. It is, therefore, not surprising that the increment in λ^2_{max} produced by the symmetrical interpolation of two C_2H_2 groups in C_6H_5—CH=CH—CH=N—N=CH—CH=CH—C_6H_5 is greater than that resulting from a similar interpolation in C_6H_5—CH=CH—CH=N—CH_2—CH_2—N=CH—CH=CH—C_6H_5, but less than that resulting from the interpolation of two C_2H_2 groups in C_6H_5—CH=CH—CH=N—C_6H_5. The effect of interpolating C_2H_2 groups in only one-half of the molecule would be expected to be similar to that of interpolating C_2H_2 groups in C_6H_5—CH=CH—CH=N—C_6H_5, as our measurements show.

In terms of the Lewis–Calvin model C_6H_5—(CH=CH)$_n$—CH=N—N=CH—(CH=CH)$_m$—C_6H_5 is a linear oscillator in which the double bonds on one side of the nitrogen atoms are fully effective but those on the other side only partially so. When the two sides are not equal, the fully effective double bonds are those in the longer part of the molecule.

One can express these qualitative ideas by the empirical equation $\lambda^2_{max} = A + B(n + Cm)$, where C is a constant fraction, and $n \geq m$. This equation can be considered as a special case of a general equation $\lambda^2_{max} = A + B(n + \beta + \gamma)$ for compounds of the type X(CH=CH)$_n$—CH=NY. C_6H_5—CH=N—N=CH—C_6H_5 has been chosen as the reference compound. The λ^2_{max} for this compound (9.06 × 10^6 Å.^{2}) has been chosen for the constant A, $\beta_{C_6H_5}$ is arbitrarily fixed at zero, while γ for all groups of the general form N=CH—(CH=CH)$_m$—C_6H_5 have been made equal to Cm. Special variants of the general equation $\lambda^2_{max} = A + B(n + \beta + \gamma)$ can be given for various series of the general formula X(CH=CH)$_n$—CH=NY by giving special values to the constants β and γ.

The special equation for the series p,p′-O_2N—C_6H_4—(CH=CH)$_n$—CH=N—N=CH—(CH=CH)$_m$—$C_6H_4NO_2$ would include the term Cm, but further constants would be necessary to give the effects of the nitro groups. However, we used acetic acid as the solvent in obtaining the spectra of these compounds, and some correction is needed for the effect of changing the solvent. It is probable that this correction can be made by considering the solvent effect as equivalent to a number of C_2H_2 groups, in which case, we can put $\lambda^2_{max} = A + B(n + Cm + \delta)$ where δ is a correction for the effects of the solvent and the two nitro groups.

The special equation for C_6H_5—(CH=CH)$_n$—C_6H_5 would be $\lambda^2_{max} = A + B(n + \gamma_{C_6H_5})$. But this equation would also be approximately correct for m-C_6H_5—CH=CH$_n$—CH=N—C_6H_4—N=CH—(CH=CH)$_n$—C_6H_5, because in the meta diimino compounds two conjugated systems are insulated from each other, and inductive effects of meta N=CH(CH=CH)$_n$—C_6H_5 groups would be small.

The equation for C_6H_5—(CH=CH)$_n$—CH=N—CH_2—CH_2—N=CH—(CH=CH)$_n$—C_6H_5 would be $\lambda^2_{max} = A + B(n + \gamma_R)$ where γ_R is the value of γ for an alkyl group. In this insulated system the effect of one conjugate system on the other is purely inductive, and presumably very small. Hence γ can be taken as determined by the CH_2 groups, which as a first approximation can be taken as equal to that of a saturated alkyl group.

By choosing the constants, λ_{max} for many of the imino groups can be calculated. The comparisons of calculated and observed values are shown in Table IV. The constants used are $A = \lambda^2_{max}$ for $C_6H_5—CH═N—N═CH—C_6H_5 = 9.06 \times 10^6$ Å.^{2}. $B = 2.15 \times 10^6$, $C = 0.35$, $\delta = -1.05$, $\gamma_{C_6H_5} = -0.99$, and $\gamma_R = -1.4$. That the phenyl group becomes equivalent to a negative number of double bonds is due to its effect being compared to that of $N═CH—C_6H_5$ and not to that of a saturated group. The negative value of δ can be due to the fact that in the nitro compounds we may be comparing a band that does not correspond to that chosen for the other compounds.

TABLE IV

CALCULATED AND OBSERVED WAVE LENGTHS OF THE PEAKS OF THE PRINCIPAL BANDS OF ABSORPTION SPECTRA OF IMINO COMPOUNDS AND THEIR VINYLENIC HOMOLOGS

Type I: $C_6H_5—(CH═CH)_n—CH═N—N═CH—(CH═CH)_m—C_6H_5$. $\lambda^2 = 9.06 \times 10^6 + 2.15 \times 10^6 (n + 0.35\,m)$

n	m	λ_{max} Calcd., Å.	λ_{max} Obs., Å.	Diff., Å.	Additional compounds
0	0	(3011)	3011	(0.)	
1	1	3458	3460	2	
2	2	3855	3850	5	
1	0	3348	3390	42	
2	1	3756	3760	4	

Type II: $C_6H_5—(CH═CH)_n—CH═N—C_6H_5$. $\lambda^2 = 9.06 \times 10^6 + 2.15 \times 10^6 (n - 0.99)$

0	..	2632	2632	0	
1	..	3007	3005	2	
2	..	3351	3414	63	
0	..	2632	2670	38	m-$C_6H_5—CH═N—C_6H_4—N═CH—C_6H_5$

Type III: $C_6H_5—(CH═CH)_n—CH═N—CH_2—CH_2—N═CH—(CH═CH)_m—C_6H_5$. $\lambda^2 = 9.06 \times 10^6 + 2.15 \times 10^6 (n - 1.4)$

0	0	2460	2470	10	
1	1	2864	2841	23	
0	..	2460	2470	10	$C_6H_5—CH═N—CH_3$
0	..	2460	2452	8	$C_6H_5—CH═N—C_2H_5$

Type IV: p,p-$O_2N—C_6H_4—(CH═CH)_n—CH═N—N═CH—(CH═CH)_m—C_6H_4—NO_2$. $\lambda^2 = 9.06 \times 10^6 + 2.15 \times 10^6 (n + .35\,m - 1.05)$

0	0	2610	2650	40	
1	1	3116	3130	14	
2	2	3550	3480	70	

In Table IV, the member with $n = 0$ has been included in each series, whereas in the carbonyl compounds this was done for some of the series but not for others. The general principle has been to include the member with $n = 0$, when it is a conjugated system with one double bond that is not part of a ring, but not to include the first member of the series when it is not a conjugate system, nor when the conjugated bonds all belong to rings. On this principle CH_3CHO and CH_3COOH have not been considered as the first members of the unsaturated aldehydes and acids. When this principle is applied to the diphenylpolyenes, biphenyl is not included in the series, but *sym*-diphenylethylene is taken as the first member.

Table IV shows a surprising agreement between calculated and observed values, the average deviation being about 20 Å. Part of this agreement is due to the freedom of choice for the values of the constants. The significance or lack of significance of the agreement between observed and calculated values can be evaluated best by considering the constant C. If λ^2_{max} is linear with respect to n for the simple conjugated system and for the symmetrical diphenylpolyeneazines, then by a proper choice of constants one can express λ^2_{max} for both series as the same linear function of a quantity $(n + Cm + \beta + \gamma)$, and the agreement between calculated and observed values is only significant in the fact that it indicates a linear relationship between λ^2_{max} and n for both homologous series. However, C is fixed by using a single equation for both series. There is, therefore, additional significance when this value of C can be used to obtain agreement between calculated and observed values for λ^2_{max} of the unsymmetrical diphenylpolyeneazines. This further signifies that the anomalous increment of λ^2_{max} per C_2H_2 group in the symmetrical azines and the lack of linearity of λ^2_{max} as a function of the number of C_2H_2 groups when symmetrical and unsymmetrical azines are included in the same series are due to the same fundamental cause. Naturally, our theory cannot be an adequate description of this cause, nor can the empirical equations we have used be anything but approximations.

N,N′-Phenylenediamine Derivatives.—The application of these assumptions must be limited to certain simple types of structural changes. The insertion of a phenyl group might be expected to produce an anomalous effect even though formally a completely conjugated system results. When a phenyl ring is placed between the two opposed linear oscillators of the azines we obtain the system p-$C_6H_5—(CH═CH)_n—CH═NC_6H_4$-$N═CH—(CH═CH)_m—C_6H_5$. The wave length of the first absorption band of this series has been measured for the first three members where $n = m = 0, 1, 2$. For $n = m = 0$, the insertion of the phenyl group greatly shifts the λ_{max} toward the red, less so when $n = m = 1$ and toward the blue when $n = m = 2$. This is shown in Table V.

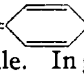
TABLE V

COMPARISON OF THE PEAKS OF THE PRINCIPAL BANDS OF THE ABSORPTION SPECTRA OF CORRESPONDING PHENYLPOLYENEAL HOMOLOGS OF HYDRAZINE AND p-PHENYLENEDIAMINE

	$C_6H_5—(CH═CH)_n—CH═N—N═CH—(CH═CH)_n—C_6H_5$	p-$C_6H_5—(CH═CH)_n—CH═N—C_6H_4—N═CH—(CH═CH)_n—C_6H_5$	
n	λ_{max}, Å.	λ_{max}, Å.	Diff., Å.
0	3010	3510	400
1	3460	3730	270
2	3850	3800	−50

It appears that the phenyl group has two effects. It acts as an auxochrome (C_6H_5—CH=N—C_6H_5 absorbs at higher wave length than C_6H_5—CH=N—CH_3) and also as a partial insulator between the two conjugated systems. If it is assumed that the insulating effect of the phenyl group increases with n, the insertion of a phenyl group would have the effect described above, and a plot of $\lambda^2_{\max}$ against $n + m$ would not be linear, but convex upward.

The insulating effect of the phenyl group is to be attributed to the fact that interaction between two conjugated systems through an aromatic nucleus involves a quinoidal structure of the ring and a consequent decrease in its Kekulé[27] resonance. When two unsaturated systems are separated by an aromatic nucleus there are certain resonating forms of the unsaturated systems that are capable of interaction with each other in spite of the resistance of the Kekulé resonance. When the complexity of the unsaturated systems is increased, the fraction of these interacting forms is decreased. The aromatic nucleus, therefore, acts more and more as an insulator as the complexity of the two unsaturated systems is increased. At the limit the benzene ring would completely insulate the unsaturated systems. A compound *p*-C_6H_5—$(CH{=}CH)_n$—CH=N—C_6H_4—N=CH—$(CH{=}CH)_n$—C_6H_5 with n a large number would then have its principal band at approximately the same wave length as that of C_6H_5—$(CH{=}CH)_n$—CH=N—C_6H_5.

Hydroxy Derivatives.—A hydroxyl group interacts with an *ortho* or *para* unsaturated group. The interaction can be attributed to the contribution of a quinoidal structure of the type $HO^+{=}$$=$ A—B^- to the resonance of the molecule. In general, when the unsaturated group is a chromophore, the hydroxyl group is an auxochrome. When the hydrogen atom of the hydroxyl group is replaced by an acyl group the importance of the quinoidal structure is reduced, and the auxochromic effect of the oxygen atom is decreased but not eliminated.

The spectra of 4,4′-dihydroxybenzalazine and its acetyl derivative is an example of the above rule. In both spectra there is a strong band at the long wave length limit of absorption, which corresponds without doubt to the principal band of dibenzalazine. The para hydroxyl group increases $\lambda_{\max}$ and $\epsilon_{\max}$. The *p*-acetoxy group does the same but to a much smaller extent.

The spectra of the ortho compounds are somewhat anomalous. That of the *o*-acetoxy compound has a band which can be identified as the principal band. $\lambda_{\max}$ is a little greater, but $\epsilon_{\max}$ is less than the corresponding values for the principal band of dibenzalazine. The spectrum of *o,o*′-dihydroxybenzalazine is very different from that of the para isomer. There are two large bands in the near ultraviolet. If it is realized that the bands chosen as the principal bands of the phenylpolyeneazines might show structure at low temperatures, the choice of a principal band from the two bands of the ortho compound is not certain. However, we have chosen the one of longest wave length. With this choice, $\lambda_{\max}$ for the ortho compound is greater than that for the para, but $\epsilon_{\max}$ is smaller than that for the unsubstituted compound. The spectra of the ortho and para hydroxy and acetoxy compounds are shown in Fig. 8.

Summary

The spectra of some aromatic conjugated imino compounds were obtained. Many of these compounds belong to vinylenic homologous series.

The spectra of these homologous series show certain bands that appear to be related to each other. The ways in which the values of $\lambda_{\max}$ for these bands vary with the number of CH=CH groups have been discussed and compared with the variation of $\lambda_{\max}$ for the diphenylpolyenes and for some similarly conjugated homologous series containing a C=O group.

A reduction of the effect of the conjugate system beyond the first nitrogen atom in diphenylpolyeneazines is observed. The interpolation of a CH_2—CH_2 group between two benzalimino groups completely insulates the groups. When a benzene ring is interpolated so that the benzalimino groups are meta to each other insulation is indicated. If the benzene ring is interpolated so that the conjugate systems are para to each other partial insulation is observed. This insulation becomes more complete as the number of ethylene groups in the conjugate systems are increased.

The expected auxochromic effects of para hydroxyl groups were observed. In the ortho position the hydroxyl group shows somewhat anomalous effects.

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[27] Compare Lewis and Calvin's discussion of the spectra of para-polyphenyls obtained by Gillam and Hey (*J. Chem. Soc.*, 1170 (1939)).