passed through a solution of 2 g. of the monomer dissolved in 50 ml. of ethyl acetate until the reaction was complete. The reaction mixture was kept at Dry Ice temperatures to prevent the loss of any formaldehyde which might be liberated during the course of the reaction. The reaction time of each experiment was approximately 45 minutes. Decomposition of the ozonide was carried out by a procedure similar to that of Hurd and Blanchard[21] in which the ozonide was poured into 50 ml. of water and 10 g. of zinc dust and the mixture mechanically shaken for 20 minutes. The zinc dust was collected on a filter and the water layer separated from the organic layer in a separatory funnel. To the former there was added a solution of 36.4 g. (0.026 mole) of methone dissolved in 25 ml. of 50% ethanol and to the latter there was added a solution of 2.57 g. (0.13 mole) of 2,4-dinitrophenylhydrazine dissolved in 20 ml. of concentrated sulfuric acid to which was added 20 ml. of water. Crystals separated almost immediately in all experiments. The methone derivatives were recrystallized from 95% ethanol and ethyl acetate mixtures. The melting points and yields of the derivatives of the ozonide decomposition products for the three monomers were as follows: α-ethylstyrene, methone derivative, m.p. 189°, 59%; 2,4-dinitrophenylhydrazone, m.p. 190–191°, 45% (formaldehyde dimethone, m.p. 189°; ethyl phenyl ketone 2,4-dinitrophenylhydrazone, 191°)[22]; α-*n*-propylstyrene, methone derivative m.p. 188.5–189°, 52%; 2,4-dinitrophenylhydrazone, m.p. 189–190°, 57% (*n*-propyl phenyl ketone, 2,4-dinitrophenylhydrazone, m.p. 188 or 190°)[22]; α-isopropylstyrene, methone derivative, m.p. 189°, 53%; 2,4-dinitrophenylhydrazone, m.p. 157–158°, 62% (isopropylphenyl ketone, 2,4-dinitrophenylhydrazone, m.p. 163°.[22]

A mixture of methone derivatives from the ozonide decomposition products of the α-ethyl, α-propyl and α-isopropylstyrenes were mixed together with formaldehyde dimethone, m.p. 189°, with no depression of the melting point.

Acknowledgment.—We wish to thank the Office of Naval Research, Contract No. NR-343 (00) for their generous support of this work.

BROOKLYN, N. Y.

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[21] C. D. Hurd and C. A. Blanchard, THIS JOURNAL, **72**, 1461 (1950).

[22] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941.

[CONTRIBUTION FROM INSTITUTE OF POLYTECHNICS, OSAKA CITY UNIVERSITY]

Absorption Spectra and Chemical Structures. I. Conjugated Polyenes and *p*-Polyphenyls

BY KENZÔ HIRAYAMA

RECEIVED JULY 16, 1953

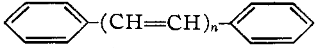
A study is presented of the dependence of spectral absorption on structure in polyene derivatives and *p*-polyphenyls. In this paper conjugation of similar chromophoric groups is considered. It is shown that the wave length of the first absorption maximum may be expressed by $(\lambda_{\max})^2 = A - BC^N$, where N is a proposed index defined by number of conjugated homochromophores, number and type of substituents, and of spectroscopically effective structures.

It has long been known that definite relationships exist between the structure of organic molecules and their visible and ultraviolet absorption spectra; empirical and theoretical formulas have been advanced relating the wave length of the first absorption maximum with the number of conjugated chromophoric groups.

But the values calculated by these formulas do not always agree satisfactorily with the observed values. However, we have found that the wave lengths predicted by equation 1,[1] in which n is the number of conjugated groups, agreed well with the observed wave lengths of the first absorption maximum.

$$(\lambda_{\max})^2 = a + B(1 - C^n) = A - BC^n \quad (1)$$
$$(A = a + B)$$

The adequacy of this functional relationship is shown in the following examples.

α,ω-Diphenylpolyenes: 

For benzene solutions, equation 2 holds

$$(\lambda_{\max}^{\text{benz}})^2 = (38.08 - 30.81 \times 0.934^n) \times 10^4 \text{ m}\mu^2 \quad (2)$$

The values in column *a* of Table I calculated by equation 2 are more satisfactory than those in column *b* calculated by Lewis and Calvin's formula 3[2]

$$(\lambda_{\max})^2 = A + Bn \quad (3)$$

or the values in columns *c* and *d* given by Dewar's LCAO MO method.[3]

In spite of the comparative agreement between the values in column *b* and those observed, equation 3 is not valid because the relation between λ^2 and n is obviously not linear[4] (see Fig. 1).

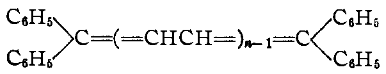
TABLE I

ABSORPTION MAXIMA OF α,ω-DIPHENYLPOLYENES IN BENZENE

n	Obsd.,[a] mμ	Calcd. *a*, mμ	*b*, mμ	*c*, mμ	*d*, mμ
1	306	305	310	311	256
2	334	335	334	357	294
3	358	360	358	412	339
4	384	382.5	380	445	366
5	403	402	400	480	395
6	420	420	420	505	416
7	435	435.5	438.5	532	438

[a] K. W. Hausser, R. Kuhn and A. Smakula, *Z. physik. Chem.*, **B29**, 384 (1935).

α,α,ω,ω-Tetraphenylpolyenes:



$$(C_6H_5)_2C{=}({=}CHCH{=})_{n-1}{=}C(C_6H_5)_2$$

Equation 4 holds for this series; the agreement between the values for the parameter C in equations 2 (C 0.934) and 4 (C 0.935) should be noted. The

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[1] One possible justification for the functional relation (1) will be demonstrated in the appendix.

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

[3] M. J. S. Dewar, *J. Chem. Soc.*, 3544 (1952).

[4] Nevertheless, since the numerical disagreement between the values obtained by equations 2 and 3 are so slight, it may be conceded that the results obtained with the Lewis and Calvin equation are superior in the sense that the latter was derived on the basis of a physically significant model. Thus far, our equation has been described merely as an empirical relation. In the appendix, however, a justification of the new relation is given.

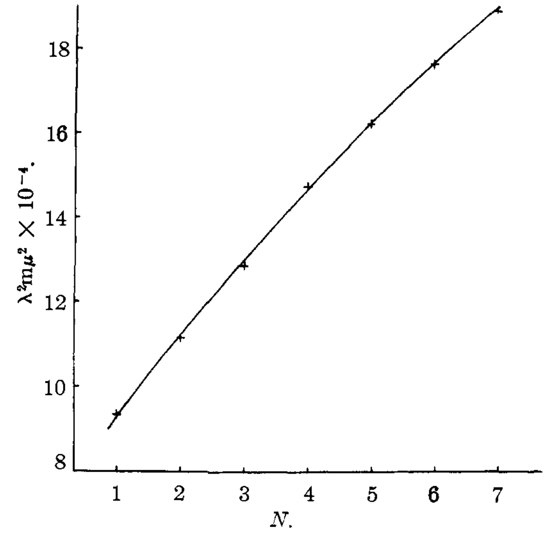


Fig. 1.—First absorption maxima of diphenylpolyenes: $(\lambda_{max}^{benz})^2 = (38.08–30.81 \times 0.934^n) \times 10^4$ mμ^2.

values for λ_{max} in Table II calculated from equation 4 are in excellent agreement with the experimental values.

$$(\lambda_{max}^{c\text{-}hex})^2 = (40.34 - 32.71 \times 0.935^n) \times 10^4 \text{ m}\mu^2 \quad (4)$$

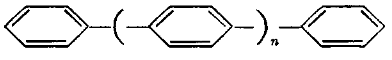
TABLE II

ABSORPTION MAXIMA OF $\alpha,\alpha,\omega,\omega$-TETRAPHENYLPOLYENES IN CYCLOHEXANE

n	Obsd.,[a] mμ	Calcd., mμ
1	312.5	312
2	342.5	343
3	. . .	369
4	392	392
5	411.5	412
6	430	430

[a] Observed wave lengths were calculated from wave numbers observed by G. Kortüm and G. Dreesen, *Chem. Ber.*, **84**, 182 (1951).

***p*-Polyphenyls:**



Equation 1 is also applicable to this conjugation series. The agreement between the experimental values for λ_{max} and those calculated (column *a*, Table III) from equation 5 is quite good.

$$(\lambda_{max}^{chlor})^2 = (10.97 - 4.66 \times 0.661^n) \times 10^4 \text{ m}\mu^2 \quad (5)$$

The values in column *b* were calculated by Dewar[3] by the LCAO MO method.

TABLE III

ABSORPTION MAXIMA OF *p*-POLYPHENYLS IN CHLOROFORM

n	Obsd.,[a] mμ	Calcd. *a*, mμ	Calcd. *b*, mμ
0	251.5	251	257
1	280	281	296
2	300	299	302
3	310	310	310
4	317.5	317.5	311

[a] Experimental data from E. A. Braude, *Ann. Repts. on Progr. Chem.* (*Chem. Soc. London*), **42**, 111 (1945).

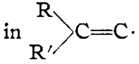
Polyenes with Auxochromic Substituents.—For polyenes with auxochromic substituents, the effect of the substituents must be considered. Although there are structural differences between chromophoric and auxochromic groups, experimentally the differences may be correlated with the amount of the wave length shift. Therefore for auxochromic substituted polyenes, the approximate value of λ_{max} may be calculated by adding the effect of the substituents to n. For this purpose, the ratio of the auxochromic substituent effect to the ethylene chromophore effect was determined for a number of substituted butadienes (Table VI, 2, 3, 9, 10 and 12–16), with the assumption that the curve λ^2–n is approximately a straight line for a small range of n, *e.g.*, $2 \leq n \leq 3$ (see Fig. 2). These ratios are given in Table IV.

TABLE IV

RATIOS OF BATHOCHROMIC EFFECTS OF ALKYL AND α-HYDROXYALKYL AUXOCHROMES TO THAT OF ETHYLENE CHROMOPHORE

Substituents[a]		Ratio
Alkyl	R	0.13
	R′	.17
	I	.09
α-Hydroxyalkyl	A	.15

[a] R = substituent in α- or ω-position; R′ = substituent in α- or ω-position in



$\begin{smallmatrix}R\\R'\end{smallmatrix}\!\!>\!C{=}C\cdots$; I = substituent in position other than α or ω; A = α-hydroxyalkyl group in α- or ω-position.

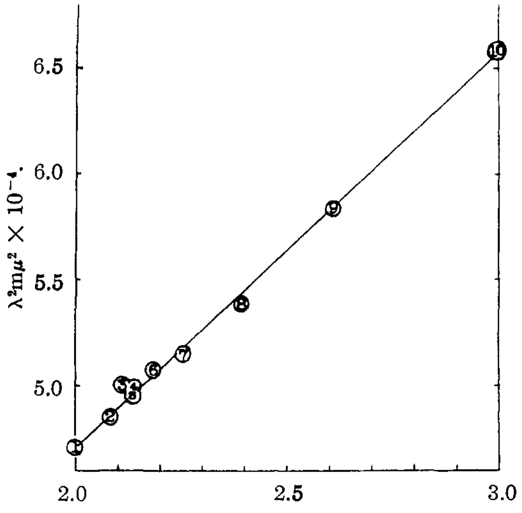


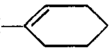
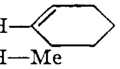
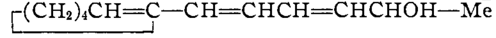
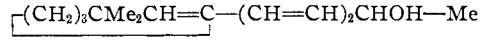
Fig. 2.—Auxochromic effect of alkyl substituents in butadiene derivatives.

Numbers as in Table VI

1.	Butadiene (BD)......	1
2.	2-MeBD............	10
3.	1-MeBD............	2
4.	1-CMe$_2$OH-BD......	16
5.	1-CH$_2$OH-BD........ 1-CHMeOH-BD.....	14 15
6.	2,3-DiMeBD........	13
7.	1,4-DiMeBD........	3
8.	1,1,3-TriMeBD......	12
9.	1,1,4,4-TetraMeBD...	9
10.	Hexatriene	

TABLE V

ABSORPTION MAXIMUM OF POLYENES IN ALCOHOL

No.	Compound	*n*	Subst. and structure R	A	Ep	rl	*N*	$\lambda_{max}^{alc.}$, mμ Obsd.	Calcd.
1	$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$	3	0	0	0	0	3.0	257[a]	256
2	$CH_2{=}CMe{-}CH{=}CH{-}CH{=}CH_2$	3	1	0	0	0	3.1	257[a]	260.5
3	$Me{-}CH{=}CH{-}CH{=}CH{-}CMe{=}CH_2$	3	2	0	0	0	3.2	261[b]	265
4	$Me_2C{=}CH{-}CH{=}CH{-}CMe{-}CH_2$	3	3	0	0	0	3.3	270[b]	270
5	$Me{-}CH{=}CH{-}CH{=}CHCH{=}CHCH_2OH$	3	1	1	0	0	3.2	265[c]	265
6	$Me{-}CH{=}CH{-}CH{=}CHCH{=}CHCHOH{-}$ 	3	1	1	0	0	3.2	269[d]	265
7	$Me{-}CH{=}CH{-}CH{=}CHCH{=}CHCHOH{-}Ph$	3	1	1	0	0	3.2	269[c]	265
8	$Me{-}CH{=}CH{-}CH{=}CHCMe{=}CHCH_2OH$	3	2	1	0	0	3.3	268[c]	270
9	$Me{-}CH{=}CH{-}CH{=}CHCMe{=}CHCHOH{-}$ 	3	2	1	0	0	3.3	268[d]	270
10	 $(CH_2)_4CH{=}C{-}CH{=}CHCH{=}CHCHOH{-}Me$	3	2	1	0	0	3.3	270[d]	270
11	 $(CH_2)_3CMe_2CH{=}C{-}(CH{=}CH)_2CHOH{-}Me$	3	2	1	0	0	3.3	268[e]	270
12	$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$	4	0	0	0	0	4.0	302[a]	299.5
13	$Me{-}(CH{=}CH)_4{-}CH_2OH$	4	1	1	0	0	4.2	310[f]	307
14	$Me{-}(CH{=}CH)_5{-}Me$	5	2	0	0	0	5.2	343[g]	341
15	Dihydrobixin	8	6	0	0	0	8.6	425	423
16	Dihydromethylbixin	8	6	0	0	0	8.6	424	423
17	Dihydro-β-carotenone oxime	8	6	0	0	0	8.6	426	423
18	α-Apo-2-carotenol	8	5	1	0	0	8.6	423	423
19	5,6-Dihydro-α-carotene	9	6	0	0	0	9.6	443	441
20	Lycopene	11	8	0	0	0	11.8	472	473
21	Lycoxanthin	11	8	0	0	0	11.8	474	473
22	Lycophyll	11	8	0	0	0	11.8	474	473
23	Decapreno-ϵ_1-carotene	13	8	0	0	0	13.8	494[h]	496
24	Rhodoviolascin	13	8	0	0	0	13.8	491	496
25	Eloxanthin (xanthophyll epoxide?)	9	5	0	1	0	9.7	445	442
26	Cryptoxantin diepoxide	9	4	0	2	0	9.8	442	444
27	Violaxanthin (zeaxanthin diepoxide?)	9	4	0	2	0	9.8	442.5	444
28	Vitamin A_1	5	5	1	0	1	4.8	328[i]	328
29	β-Apo-2-carotenol	9	7	1	0	1	9.0	426	430
30	5,6-Dihydro-β-carotene	10	8	0	0	1	10.0	448	447
31	Lutein (xanthophyll)	10	8	0	0	1	10.0	446.5	447
32	Helenien (xanthophyll dipalmitate)	10	8	0	0	1	10.0	448	447
33	Capsanthol	10	7	1	0	1	10.0	448	447
34	Cryptoxanthin monoepoxide	10	7	0	1	1	10.1	449	449
35	Antheraxanthin	10	7	0	1	1	10.1	450	449
36	Gazaniaxanthin	11	9	0	0	1	11.1	462	463.5
37	Rubixanthin	11	9	0	0	1	11.1	463	463.5
38	Celaxanthin	13	10	0	0	1	13.2	488	490
39	Cryptoxanthin	11	10	0	0	2	10.4	452	453
40	Zeaxanthin	11	10	0	0	2	10.4	451.5	453
41	Decapreno-β-carotene	15	12	0	0	2	14.6	506[j]	504
42	Dodecapreno-β-carotene	19	14	0	0	2	18.8	536[k]	537
43	Tetradecapreno-β-carotene	23	16	0	0	2	23.0	...	559
44	Compound with $N = \infty$	∞	..	..	..	..	∞	...	608

Experimental data from P. Karrer and E. Jucker, "Carotenoids," Elsevier Publ. Co., Inc., Houston, Texas, 1950, unless otherwise indicated. [a] L. N. Ferguson, *Chem. Rev.*, **43**, 385 (1948). [b] E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 2007 (1950). [c] B. C. L. Weedon and R. J. Woods, *ibid.*, 2687 (1951). [d] E. A. Braude, T. Bruun, B. C. L. Weedon and R. J. Woods, *ibid.*, 1414 (1952). [e] E. A. Braude, T. Bruun, B. C. L. Weedon and R. J. Woods, *ibid.*, 1419 (1952). [f] K. Dimroth, *Angew. Chem.*, **52**, 545 (1939). [g] C. Bohlman, *Chem. Ber.*, **85**, 386 (1952). [h] P. Karrer, C. H. Eugster and M. Faust, *Helv. Chim. Acta*, **34**, 823 (1951). [i] A. E. Gillam and M. S. El Ridi, *Biochem. J.*, **32**, 820 (1938). [j] P. Karrer and C. H. Eugster, *Helv. Chim. Acta*, **34**, 28 (1951). [k] P. Karrer and C. H. Eugster, *ibid.*, **34**, 1805 (1951).

The difference in effect attributable to the chain length of the substituent is so slight that it can be ignored (see Table VI, 17–28). As Table IV shows, the position of the substituent also caused a slight difference which is always small compared with the effect of the chromophore; so that usually the rounded-off value for the ratio (0.1) is satisfactory for calculation purposes.

If we define an index *N*, the homoconjugation index, as the value of the index *n*, corrected by substituent effects defined above, *N* will be in general non-integral and thus loses its meaning as the number of chromophores. Obviously, in the absence of auxochromic substituents, *e.g.*, in the α,ω-diphenylpolyenes, *N* and *n* are identical.

The values for 1–24, Table V, calculated by equation 6, which contains *N*, agree well with the observed values.

$$(\lambda_{max}^{alc})^2 = (36.98 - 39.10 \times 0.920^N) \times 10^4\ m\mu^2 \quad (6)$$

Table VI

Absorption Maximum of Compounds of 3 > N ≧ 2

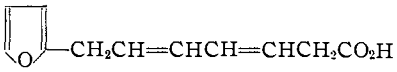
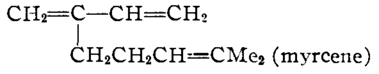
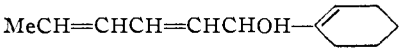
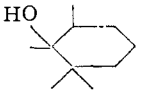
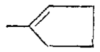
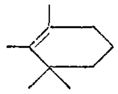
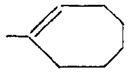
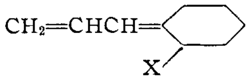
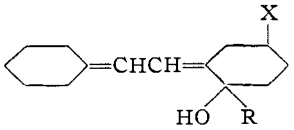
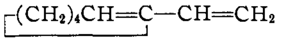
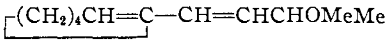
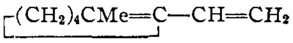
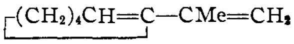
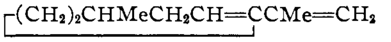
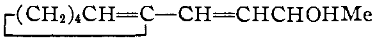
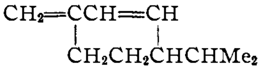
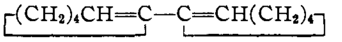
No.	Compound	Subst. and structure						N	λmax, mμ	
		E	E'	I	A	ex	en		Obsd.	Calcd.
1	$CH_2{=}CH{-}CH{=}CH_2$	0	0	0	0	0	0	2.00	217^{a}	(217)
2	$Me{-}CH{=}CH{-}CH{=}CH_2$	1	0	0	0	0	0	2.13	223.5^{b}	222
3	$Me{-}CH{=}CH{-}CH{=}CH{-}Me$	2	0	0	0	0	0	2.26	227^{c}	228
4	$Et{-}CH{=}CHCH{=}CHCH_2CO_2H$	2	0	0	0	0	0	2.26	228^{a}	228
5		2	0	0	0	0	0	2.26	226^{a}	228
6	$PhCH_2CH{=}CHCH{=}CHCH_2Ph$	2	0	0	0	0	0	2.26	235^{c}	228
7	$AcOCH_2CH{=}CHCH{=}CHCH_2OAc$	2	0	0	0	0	0	2.26	228^{c}	228
8	$EtOCH_2CH{=}CHCH{=}CHCH_2OEt$	2	0	0	0	0	0	2.26	228^{c}	228
9	$Me_2C{=}CHCH{=}CMe_2$	2	2	0	0	0	0	2.60	241^{d}	241
10	$CH_2{=}CMe{-}CH{=}CH_2$	0	0	1	0	0	0	2.09	220^{a}	221
11	 $CH_2{=}C(CH_2CH_2CH{=}CMe_2){-}CH{=}CH_2$ (myrcene)	0	0	1	0	0	0	2.09	224.5^{e}	221
12	$Me_2C{=}CH{-}CMe{=}CH_2$	1	1	1	0	0	0	2.39	232^{d}	233
13	$CH_2{=}CMe{-}CMe{=}CH_2$	0	0	2	0	0	0	2.18	225^{a}	224
14	$CH_2{=}CH{-}CH{=}CH{-}CH_2OH$	0	0	0	1	0	0	2.15	223^{f}	223
15	$CH_2{=}CH{-}CH{=}CH{-}CHOH{-}Me$	0	0	0	1	0	0	2.15	223^{f}	223
16	$CH_2{=}CH{-}CH{=}CH{-}CMe_2OH$	0	0	0	1	0	0	2.15	223.5^{f}	223
17	$MeCH{=}CHCH{=}CHCHOHMe$	1	0	0	1	0	0	2.28	227^{g}	228.5
18		1	0	0	1	0	0	2.28	228^{h}	228.5
19	$Me{-}CH{=}CH{-}CH{=}CH{-}CHOH{-}C{\equiv}CH$	1	0	0	1	0	0	2.28	230^{b}	228.5
20	$\{Me{-}CH{=}CH{-}CH{=}CH{-}CHOH{-}C{\equiv}\}_2$	1	0	0	1	0	0	2.28	229^{b}	228.5
21	$MeCH{=}CHCH{=}CHCMeOHCH{=}CHPh$	1	0	0	1	0	0	2.28	228^{i}	228.5
22	$MeCH{=}CHCH{=}CHCMeOHC{\equiv}CR$ R = H	1	0	0	1	0	0	2.28	227^{i}	228.5
23	R = 	1	0	0	1	0	0	2.28	229^{j}	228.5
24	R = 	1	0	0	1	0	0	2.28	228^{k}	228.5
25	R = 	1	0	0	1	0	0	2.28	227^{k}	228.5
26	R = 	1	0	0	1	0	0	2.28	230^{j}	228.5
27	R = 	1	0	0	1	0	0	2.28	229^{k}	228.5
28	$Me{-}CH{=}CH{-}CH{=}CH{-}CMe_2OH$	1	0	0	1	0	0	2.28	227^{f}	228.5
29	$Me_2C{=}CH{-}CH{=}CH{-}CH_2OH$	1	1	0	1	0	0	2.45	236^{f}	235
30	$Me_2C{=}CH{-}CH{=}CH{-}CHOH{-}Me$	1	1	0	1	0	0	2.45	236^{f}	235
31	$Me_2C{=}CH{-}CH{=}CH{-}CMe_2OH$	1	1	0	1	0	0	2.45	237^{d}	235
32	$Me{-}CH{=}CH{-}CMe{=}CH{-}CMe_2OH$	1	0	1	1	0	0	2.37	235^{d}	232
33	$Me_2C{=}CH{-}CMe{=}CH{-}CMe_2OH$	1	1	1	1	0	0	2.54	236^{d}	239
34	$PhCHOHCH{=}CHCH{=}CHCHOHPh$	0	0	0	2	0	0	2.30	240^{a}	229
35	 X = H	1	1	0	0	1	0	2.37	236.5^{c}	232
36	X = NMe_2	1	1	0	0	1	0	2.37	236^{e}	232
37	X = OH	0	1	0	1	1	0	2.39	233^{l}	233
38	 X = H, R = H	1	2	0	1	2	0	2.76	248^{a}	247
39	X = H, R = Me	1	2	0	1	2	0	2.76	245^{c}	247
40	X = OH, R = CH_2CO_2H	1	2	0	1	2	0	2.76	247^{e}	247
41	X = OAc, R = CH_2CO_2H	1	2	0	1	2	0	2.76	246^{e}	247
42	 $(CH_2)_4CH{=}C{-}CH{=}CH_2$	1	0	1	0	0	1	2.26	230^{c}	228
43	 $(CH_2)_4CH{=}C{-}CH{=}CHCHOMeMe$	2	0	1	0	0	1	2.39	232^{l}	233
44	 $(CH_2)_4CMe{=}C{-}CH{=}CH_2$	1	1	1	0	0	1	2.43	233^{c}	234
45	 $(CH_2)_4CH{=}C{-}CMe{=}CH_2$	1	0	2	0	0	1	2.35	242^{c}	231

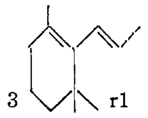
TABLE VI (*Continued*)

No.	Compound	Subst. and structure E	E′	I	A	ex	en	N	λ_{max}, mμ Obsd.	Calcd.
46	 $\text{(CH}_2)_2\text{CHMeCH}_2\text{CH}{=}\text{CCMe}{=}\text{CH}_2$	1	0	2	0	0	1	2.35	235[c]	231
47	 $\text{(CH}_2)_4\text{CH}{=}\text{C}{-}\text{CH}{=}\text{CHCHOHMe}$	1	0	1	1	0	1	2.41	235[l]	234
48	 $\text{CH}_2{=}\text{CCH}{=}\text{CH}$ / $\text{CH}_2\text{CH}_2\text{CHCHMe}_2$	1	0	1	0	1	1	2.33	232[c]	230.5
49	 $\text{(CH}_2)_4\text{CH}{=}\text{C}{-}\text{C}{=}\text{CH(CH}_2)_4$	2	0	2	0	0	2	2.52	236[e]	238

[a] K. Dimroth, *Angew. Chem.*, **52**, 545 (1939). [b] E. A. Braude, *Ann. Repts. Progr. Chem.*, **42,** 105 (1946). [c] L. N. Ferguson, *Chem. Revs.*, **43**, 385 (1948). [d] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1425 (1952). [e] R. B. Woodward, THIS JOURNAL, **64**, 72 (1942). [f] E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 2007 (1950). [g] E. A. Braude and J. A. Coles, *ibid.*, 2085 (1951). [h] L. Crombie, S. H. Harper and D. Thompson, *ibid.*, 2906 (1951). [i] B. C. L. Weedon and R. J. Woods, *ibid.*, 2687 (1951). [j] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen and T. Walker, *ibid.*, 1094 (1952). [k] T. Bruun, I. Heilbron, B. C. L. Weedon and R. J. Woods, *ibid.*, 633 (1950). [l] E. A. Braude and J. A. Coles, *ibid.*, 2014 (1950).

In the case of carotenoids, an α,β-epoxyalkyl substituent (Ep) has a larger bathochromic effect ($N_{\text{Ep}} = +0.2$) than an alkyl substituent.[5] Thus, $N_{\text{Ep}} = +0.2$ was used in the calculation of N for compounds 25–27, Table V.

It is known that a ring structure like (rl) exerts a



hypsochromic effect.[5] The values for compounds 28, 29, 30, 41 and 42 Table V, were calculated with the assumption that $N_{\text{rl}} = -0.8$; a ring with a hydroxyl group at position 3 of rl has the same value for N as N_{rl} (see Table V, 31–40).

Our method is illustrated by the following calculation of λ_{max} of tetradecapreno-β-carotene, which is still to be synthesized. The number of conjugated ethylene linkages n is 23, the number of alkyl substituents R is 16 and the number of conjugated rings rl is 2; then with $N_{\text{R}} = 0.1$ and $N_{\text{rl}} = -0.8$

$$N = 23 + (0.1 \times 16) - (0.8 \times 2) = 23.0$$

Therefore

$$(\lambda^{\text{alc}}_{\text{max}})^2 = (36.98 - 39.10 \times 0.920^{23}) \times 10^4 \text{ m}\mu^2;\ \lambda^{\text{alc}}_{\text{max}}\ 559 \text{ m}\mu$$

Substituted Butadienes.—Although equation 6 is quite satisfactory for compounds where $N \geqq 3$, the error becomes considerable when $N < 3$. The observed λ^2–N curve has a point of inflection at $N \doteqdot 3$, while the curve plotted according to equation 6 has no such point. However, as the observed line shows only a slight curvature and is almost linear in the region $2 \leqq N < 3$, λ_{max} can also be calculated for this range from the homoconjugation index N according to equation 7. This expression was obtained from the straight line connecting the λ_{max} for $N = 3$ calculated by equation 6 and the observed λ_{max} for $N = 2$; the observed line is assumed to be straight for $2 \leqq N < 3$.

$$(\lambda_{\text{max}})^2 = (1.061 + 1.824 \times N) \times 10^4 \text{ m}\mu^2 (2 \leqq N < 3) \quad (7)$$

Since in this case N is small, the effect of the substituents is relatively large; therefore, the values given in Table IV for the contribution of auxochromic substituents to N should be used rather than 0.1. The values of λ_{max} of compounds 1–34, Table VI, calculated in this way show good agreement with those observed.

Equation 7 is applicable to methanol, hexane, petroleum ether, ether, alcohol and light ligroin solutions, because the effect of these solvents is about the same in the range $2 \leqq N < 3$ (see Part II).

The good agreement between the observed and calculated values for compounds 4, 5, 7, 8 and 18–27, Table VI, shows that a chromophore or auxochrome, other than an alkyl and hydroxyl group, at the α-position of an alkyl substituent has little bathochromic effect. The considerable discrepancy in compounds 6 and 34, Table VI, is probably due to overlapping of the absorption of the phenyl chromophore (*ca.* 220–270 mμ) with that of the diene chromophore.

The effect of the exocyclic ethylene group (35–41, Table VI) is $N_{\text{ex}} = +0.07$.

The observed absorption maxima of compounds 42–49, Table VI, are generally larger than the calculated values unless the endocyclic ethylene (en) is taken into account; the effect of this linkage is $N_{\text{en}} = +0.04$.

The above values ($N_{\text{Ep}} = +0.18$, $N_{\text{ex}} = +0.07$, and $N_{\text{en}} = +0.04$) are used for compounds $2 \leqq N < 3$, but for compounds $N > 3$ the rounded-off values (+0.2, +0.1 and 0, respectively) are sufficiently accurate.

Calculation with these factors gives satisfactory results except for compound 45, Table VI; this large deviation may be due to an incorrect observed value, since good agreement was obtained for the analogous compounds (Table VI, 42, 44, 46, 47 and 49).

Steroid.—Equations 6 and 7 can be used without modification for conjugated unsaturated steroids; see Table VII, 1–13.

It has also been shown that the 1,2-dihydrobenzene ring (db) exerts a bathochromic effect,[6] and the value of which is $N_{\text{db}} = +0.83$ (+0.8); the values calculated with this factor (Table VII, 14–22, 25–29 and 31) are satisfactory.

The 1,2,5,6-tetrahydronaphthalene ring (tn), which is considered as two fused dihydrobenzene rings, should exert a bathochromic effect equivalent to more than one and less than two db rings; N_{tn} calculated from the observed values for the compounds 30 and 32, Table VII, was +1.12 (+1.1).

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(5) L. F. Fieser, *J. Org. Chem.*, **15**, 930 (1950).

(6) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1949.

TABLE VII

ABSORPTION MAXIMUM OF STEROIDAL POLYENES

No.	Compound	Subst. and structure										λ_{max}, mμ	
		n	E	E′	I	A	ex	en	db	tn	N	Obsd.[a]	Calcd.[b]
1	7-Methylenecholesterol	2	1	1	1	0	2	1	0	0	2.57	236	240
2	3,5-Cholestadiene	2	2	0	1	0	1	2	0	0	2.50	240	237
3	5-Cholestene-3-one enol acetate	2	2	0	1	0	1	2	0	0	2.50	240	237
4	Testosterone diacetate	2	2	0	1	0	1	2	0	0	2.50	240	237
5	4,6-Cholestadiene	2	2	0	1	0	1	2	0	0	2.50	238	237
6	Ergosterol D	2	2	1	2	0	1	2	0	0	2.76	242	247
7	4,6-Chloestadien-3-ol	2	1	0	1	1	1	2	0	0	2.52	238	238
8	Cholestadienol B_3	2	2	0	2	0	2	2	0	0	2.66	248	243
9	Cholestadienol B_3 acetate	2	2	0	2	0	2	2	0	0	2.66	246	243
10	Ergosterol B_3	2	2	0	2	0	2	2	0	0	2.66	242	243
11	7,9(11)-Cholestadien-3-ol acetate	2	2	0	2	0	2	2	0	0	2.66	245	243
12	6,8(14)-Cholestadien-3,9-diol	2	2	1	0	1	2	2	0	0	2.80	248	248
13	6,8(14)-Cholestadien-3,9-diol 3-acetate	2	2	1	0	1	2	2	0	0	2.80	245	248
14	2,4-Cholestadiene	2	2	1	0	0	1	0	1	0	3.31	275	270
15	Ergostatriene	2	2	2	0	0	2	0	1	0	3.55	280	281
16	5,7-Androstadien-3,17-diol	2	2	2	0	0	2	0	1	0	3.55	280	281
17	7-Dehydrocholesterol	2	2	2	0	0	2	0	1	0	3.55	281	281
18	Ergosterol	2	2	2	0	0	2	0	1	0	3.55	280	281
19	Lumisterol	2	2	2	0	0	2	0	1	0	3.55	280	281
20	Pyrocalciferol	2	2	2	0	0	2	0	1	0	3.55	280	281
21	6,8-Cholestadien-3-ol	2	2	1	1	0	0	1	1	0	3.37	275	273
22	6,8-Coprostadien-3-ol	2	2	1	1	0	0	1	1	0	3.37	270	273
23	Vitamin D_2	3	1	1	2	0	3	0	0	0	3.69	265	287
24	Tachysterol$_2$	3	2	1	2	0	0	2	0	0	3.69	280	287
25	4,6,22-Ergostatrien-3-one enol acetate	3	2	0	1	0	1	1	1	0	4.27	304	310
26	3,5,7,22-Ergostatetraene	3	2	1	1	0	2	1	1	0	4.51	316	318
27	5,7,22-Ergostatrien-3-one enol acetate	3	2	1	1	0	2	1	1	0	4.51	316	318
28	5,7,9(11)-Cholestatrien-3-ol	3	2	1	2	0	3	1	1	0	4.67	320	324
29	Dehydroergosterol	3	2	1	2	0	3	1	1	0	4.67	320	324
30	6,8,11-Cholestatrien-3-ol	3	2	0	2	0	0	0	0	1	4.56	325	320
31	5,7,9(11),22-Ergostatetraen-3-one enol acetate	4	2	0	3	0	3	2	1	0	5.67	356	355
32	4,6,8,11-Cholestatetraen-3-ol	4	2	0	3	0	1	2	0	1	5.80	355	359

[a] Experimental data from L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd. Ed., Reinhold Publishing Corp., New York, N. Y., 1949; K. Dimroth, *Angew. Chem.*, **52**, 545 (1939); E. A. Braude, *Ann. Repts. Progr. Chem.*, **42**, 105 (1946). [b] Calculated by $(\lambda_{max})^2 = 36.98 - 39.10 \times 0.920^n$ dμ^2 when $N \geqq 3$, or by $(\lambda_{max})^2 = 1.061 + 1.824N$ dμ^2 when $3 > N \geqq 2$.

Since N is usually a small number in the case of unsaturated steroids, the values for the substituent effect should not be rounded-off.

The absorption maxima calculated by this method (Table VII) show good agreement (except for compound 23) especially in the region $2 < N < 3.5$; deviation from the observed values is relatively large when N is greater than 3.6. The values for compounds (Table VII, 3, 4, 27 and 31) calculated with $N_{acetoxy} = 0$ agree well with the observed values.

Acknowledgment.—The author expresses his thanks to Drs. M. Kotake, T. Sakan, R. Tsuchida, M. Kobayashi, H. Kuroya and Y. Saito for their interest and advice and to Dr. N. Fukuwara for his help in preparing the manuscript.

Appendix

In the text, a functional relationship 1 has been established empirically for the wave length of the first absorption maximum of conjugated systems.

$$(\lambda_{max})^2 = A - BC^n \qquad (1)$$

One of the possible justifications for this relationship will be discussed below.

Homoconjugation Series (*p*-Polyphenyls and Non-substituted Polyenes).—Given n vibrating chromophores which absorb light of wave length $\lambda = 2\pi c/\sqrt{k/m}$, in which k is the restoring force constant of each vibrating chromophore, and m is the effective mass of the vibrating electron[7]; when

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[7] (a) If n such chromophores are coupled together so that all vibrating π-electrons of these chromophores oscillate in concert in the molecule, the wave length of the light which this system absorbs is $\lambda_0 = 2\pi c/\sqrt{k/nm}$. By squaring both sides, $\lambda_0^2 = 4\pi^2c^2nm/k$, an equation for a straight line, $\lambda^2 = A + Bn$, where A is the intercept value when $n = 0$, is obtained. This is the model proposed by G. N. Lewis and M. Calvin (*Chem. Revs.*, **25**, 273 (1939)). The modification of this model is outlined as below. (b) L. N. Ferguson (*ibid.*, **43**, 385 (1948)) recognized the possibility of improving the Lewis and Calvin model by using a force constant which depends on the number of conjugated groups, and he stated "this amounts to an increase in the restoring force constant, k, with increasing n; this is contrary to the assumption that k is a constant." (c) W. T. Simpson (*J. Chem. Phys.*, **16**, 1126 (1948)) calculated the wave length of the first absorption maximum of three simple dye-like molecules, solving the Schrödinger equation for the atoms of molecules as oscillators with the assumption that the center of mass of the unsaturation electrons is quantized, rather than that the unsaturation electrons move in concert. (d) The present treatment of the author is also based on a modified Lewis and Calvin model, with the assumption of a quantized oscillation of one of the unsaturation electrons, with the restoring force constant of the conjugated chromophore, K, which is correlated with that of the unit vibrating chromophore, k, by the equation 2.

n such chromophores are coupled together so that the whole conjugated system vibrates as a simple harmonic oscillator with a restoring force constant k, then the wave length of the light which this system absorbs is

$$\lambda_0 = 2\pi c/\sqrt{K/m},\ i.e.,\ \lambda_0{}^2 = 4\pi^2c^2m/K$$

If we assume that when n is an even number

$$\frac{1}{K} = \frac{1}{k}\Big(1 + f + f^2 + \ldots + \underbrace{f^{\frac{n}{2}-1} + f^{\frac{n}{2}-1}}_{\text{center}} + \ldots + f^2 + f + 1\Big) \quad (2)$$

(the factor of the force constant f is always very close to 1 but never larger than 1). Thus, the reciprocal of the force constant of each chromophore contributes to $1/K$ with the weight of

$$1, f, f^2, \ldots, f^{\frac{n}{2}-1}, f^{\frac{n}{2}-1}, \ldots, f^2, f, 1$$

and

$$\lambda_0 = \frac{2\pi c}{\sqrt{K/m}} = \frac{2\pi c}{\sqrt{k/m}}\left(2\sum_{l=0}^{\frac{n}{2}-1} f^l\right)^{1/2} = \frac{2\pi c}{\sqrt{k/m}}\left\{\frac{2\left(1 - f^{\frac{n}{2}}\right)}{1 - f}\right\}^{1/2}$$

If $b = 8\pi^2c^2m/k$, $C = f^{\frac{1}{2}}$, $B = b/(1 - C^2)$, $A = a + B$ and a is the intercept value when $n = 0$

$$(\lambda_{\max})^2 = a + b\,\frac{1 - C^n}{1 - C^2} \quad (3)$$

$$= a + B(1 - C^n) = A - BC^n \quad (4)$$

When n is an odd number, the equation corresponding to 2 is

$$\frac{1}{K} = \frac{1}{k}\Big(1 + f + f^2 + \ldots\ldots + \underbrace{f^{\frac{n-1}{2}}}_{\text{center}} + \ldots\ldots + f^2 + f + 1\Big) \quad (2')$$

so

$$(\lambda_{\max})^2 = A - B\,\frac{C^{n-1} + C^{n+1}}{2} \quad (4')$$

As the value of f (*i.e.*, C^2) is almost 1, C should still be close to 1; it is possible to substitute equation 4 for 4′ with negligible error.

Conjugation Series with Heterochromophores at α- and ω-Positions (α,ω-Diphenylpolyenes).—Two heterochromophores are conjugated at the α- and ω-position in the case of α,ω-diphenylpolyenes. Therefore, the following equation pertains to these compounds instead of 2

$$\frac{1}{K} = \frac{1}{k_{\text{het}}} + \frac{f_{\text{het}}}{k}\Big(1 + f + f^2 + \ldots + \underbrace{f^{\frac{n}{2}-1} + f^{\frac{n}{2}-1}}_{\text{center}} + \ldots + f^2 + f + 1\Big) + \frac{1}{k_{\text{het}}} \quad (5)$$

where k_{het} is the restoring force constant of the unit vibrating phenyl chromophore, and f_{het} is the factor of the restoring force constant exerted on the ethylene chromophore by the phenyl chromophore.

If equation 5 is rewritten as

$$\frac{1}{K} = \frac{1}{k}\left\{\frac{k}{k_{\text{het}}} + f_{\text{het}}\Big(1 + f + f^2 + \ldots + f^{\frac{n}{2}-1} + f^{\frac{n}{2}-1} + \ldots + f^2 + f + 1\Big) + \frac{k}{k_{\text{het}}}\right\}$$

we obtain the expression for 3

$$(\lambda_{\max})^2 = a'' + b\,\frac{k}{k_{\text{het}}} + bf_{\text{het}}\,\frac{1 - C^n}{1 - C^2}$$

where b and C have the same values, respectively, as in 3 and a'' is the intercept value when $n = 0$.

If $b_{\text{het}} = 8\pi^2c^2m/k_{\text{het}}$, and $C_{\text{het}} = f_{\text{het}}{}^{1/2}$

$$(\lambda_{\max})^2 = a'' + b_{\text{het}} + bC_{\text{het}}{}^2\,\frac{1 - C^n}{1 - C^2}$$

This equation can be expressed in a functional form similar to that for the homoconjugation series.

$$(\lambda_{\max})^2 = A'' - B''C^n \quad (6)$$

where $B'' = bC_{\text{het}}{}^2/(1 - C^2)$ and $A'' = a'' + b_{\text{het}} + B''$.

OSAKA, JAPAN

[CONTRIBUTION FROM INSTITUTE OF POLYTECHNICS, OSAKA CITY UNIVERSITY]

Absorption Spectra and Chemical Structure. II. Solvent Effect

BY KENZÔ HIRAYAMA

RECEIVED JULY 16, 1953

Previously it was stated that the $\lambda_{\max}$ of polyenes is given by $(\lambda_{\max})^2 = a + B(1 - C^N)$. In the present paper, it is shown that the solvent modifies B, and that there is a linear relationship between B and the refractive index $n^{20}\text{D}$ of the solvent.

It was pointed out in part I[1] that the $\lambda_{\max}$ of polyenes containing conjugated homochromophoric groups and auxochromic substituents may be expressed by

$$(\lambda_{\max})^2 = A - BC^N \quad (1)$$

$$= a + B(1 - C^N) \quad (2)$$

where N is the homoconjugation index, which is determined by substituent and structural effects as well as by the number of conjugated chromophoric groups.

Thus, the following equation was given for alcholic solutions of polyene derivatives with auxochromic substituents

$$(\lambda^{\text{alc}}_{\max})^2 = (36.98 - 39.10 \times 0.920^N) \times 10^4\ \text{m}\mu^2 \quad (3)$$

$$= \{-2.12 + 39.10 \times (1 - 0.920^N)\} \times 10^4\ \text{m}\mu^2 \quad (4)$$

We shall discuss the influence of the solvent on $\lambda_{\max}$, *i.e.*, which parameters are effected by a change in solvent.

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[1] K. Hirayama, THIS JOURNAL, 77, 373 (1955).