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

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

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 $A'' = a'' + b_{\text{het}} + B''$.

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[CONTRIBUTION FROM INSTITUTE OF POLYTECHNICS, OSAKA CITY UNIVERSITY]

Absorption Spectra and Chemical Structure. II. Solvent Effect

BY KENZÔ HIRAYAMA

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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).

TABLE I

ABSORPTION MAXIMA OF POLYENE DERIVATIVES IN VARIOUS SOLVENTS (mμ)[a]

No.	Compound	Substituent and structure n	R	A	Ep	rl	N
1	H—(CH=CH)$_3$—H	3	0	0	0	0	3.0
2	Ph—CH$_2$—(CH=CH)$_3$—CH$_2$—Ph	3	2	0	0	0	3.2
3	H—(CH=CH)$_4$—H	4	0	0	0	0	4.0
4	CH$_3$—(CH=CH)$_4$—CH$_2$OH	4	1	1	0	0	4.2
5	{CH$_3$—(CH=CH)$_4$—CHOH}$_2$	4	1	1	0	0	4.2
6	CH$_3$—(CH=CH)$_4$—CHOH—CHOH—CH$_3$	4	1	1	0	0	4.2
7	CH$_3$—(CH=CH)$_5$—CH$_3$	5	2	0	0	0	5.2
8	CH$_3$—(CH=CH)$_6$—CH$_3$	6	2	0	0	0	6.2
9	Dihydrocrocetin	6	4	0	0	0	6.4
10	1,1,20,20-Tetramethyldihydrobixinol	8	6	0	0	0	8.6
11	Dihydronorbixin	8	6	0	0	0	8.6
12	Dihydrobixin	8	6	0	0	0	8.6
13	Dihydromethylbixin	8	6	0	0	0	8.6
14	β-Dihydrocarotene	8	6	0	0	0	8.6
15	Dihydro-β-carotenone	8	6	0	0	0	8.6
16	Dihydro-β-carotenone oxime	8	6	0	0	0	8.6
17	α-Apo-2-carotenol	8	5	1	0	0	8.6
18	CH$_3$—(CH=CH)$_9$—CH$_3$	9	2	0	0	0	9.2
19	5,6-Dihydro-α-carotene	9	6	0	0	0	9.6
20	ϵ_1-Carotene	9	6	0	0	0	9.6
21	Dihydroxy-α-carotene	9	5	1	0	0	9.6
22	Lycopene	11	8	0	0	0	11.8
23	Lycoxanthin	11	8	0	0	0	11.8
24	Lycophyll	11	8	0	0	0	11.8
25	Decapreno-ϵ_1-carotene	13	8	0	0	0	13.8
26	Rhodoviolascin	13	8	0	0	0	13.8
27	Dehydrolycopene	15	10	0	0	0	16.0
28	α-Carotene monoepoxide	9	5	0	1	0	9.7
29	Eloxanthin (xanthophyll epoxide ?)	9	5	0	1	0	9.7
30	Isoantheraxanthin	9	5	0	1	0	9.7
31	Rubixanthin monoepoxide	10	6	0	1	0	10.8
32	β-Carotene diepoxide	9	4	0	2	0	9.8
33	Cryptoxanthin diepoxide	9	4	0	2	0	9.8
34	Violaxanthin (zeaxanthin diepoxide ?)	9	4	0	2	0	9.8
35	Vitamin A$_1$	5	5	1	0	1	4.8
36	β-Apo-2-carotenol	9	7	1	0	1	9.0
37	5,6-Dihydro-β-carotene	10	8	0	0	1	10.0
38	α-Carotene	10	8	0	0	1	10.0
39	Xanthophyll (Lutein)	10	8	0	0	1	10.0
40	Helenien (xanthophyll dipalmitate)	10	8	0	0	1	10.0
41	Capsanthol	10	7	1	0	1	10.0
42	Dihydroxy-β-carotene	10	7	1	0	1	10.0
43	β-Carotene monoepoxide	10	7	0	1	1	10.1
44	Cryptoxanthin monoepoxide	10	7	0	1	1	10.1
45	Antheraxanthin	10	7	0	1	1	10.1
46	Gazaniaxanthin	11	9	0	0	1	11.1
47	Gazaniaxanthin acetate	11	9	0	0	1	11.1
48	γ-Carotene	11	9	0	0	1	11.1
49	Rubixanthin	11	9	0	0	1	11.1
50	Myxoxanthol	11	8	1	0	1	11.1
51	Celaxanthin	13	10	0	0	1	13.2
52	β-Carotene	11	10	0	0	2	10.4
53	Cryptoxanthin	11	10	0	0	2	10.4
54	Zeaxanthin	11	10	0	0	2	10.4
55	Physallien (zeaxanthin dipalmitate)	11	10	0	0	2	10.4
56	Decapreno-β-carotene	15	12	0	0	2	14.6
57	Dodecapreno-β-carotene	19	14	0	0	2	18.8

ABSORPTION MAXIMA

Alcohol

Cpd.	Calcd.	Obsd.
1	256	257[b]
3	299.5	302[b]
4	307	310[c]
7	341	343[d]
12	423	425
13	423	424
16	423	426
17	423	423
19	441	443
22	473	472
23	473	474
24	473	474
25	496	494[g]
26	496	491
29	442	445
33	444	442
34	444	442.5
35	328	328[i]
36	430	426
37	447	448
39	447	446.5
40	447	448
41	447	448
44	449	449
45	449	450
46	463.5	462
49	463.5	463
51	490	488
53	453	452
54	453	451.5
56	504	506[m]
57	537	536[e]

Chloroform

Cpd.	Calcd.	Obsd.
8	378	375[b]
10	432	435
11	432	435
12	432	435
13	432	435
15	432	435
19	451	452
22	483.5	480
25	507	518[g]
26	507	507
27	528	528
28	552	554
32	454	456
33	454	453
34	454	451.5
37	457	457
38	457	454
39	457	456
40	457	456
41	457	456
42	457	456
43	459	459
44	459	456
45	459	460.5
48	474	475
49	474	474
50	474	474
52	464	466
53	464	463
54	464	462
56	515	517[m]

Petroleum ether

Cpd.	Calcd.	Obsd.
15	421.5	424
17	421.5	420
22	471	475.5
23	471	473[f]
25	494	495[g]
29	441	442
31	457	461
36	429	423
37	446	447.5
43	447	447
46	462	462.5
49	462	463
50	462	465
51	488	486.5
56	502	498[m]
57	535	531[e]

Light ligroin

Cpd.	Calcd.	Obsd.
15	423	429
16	423	429
22	473	474
23	473	472
24	473	473
30	443	442
34	444	443
38	447.5	447.5
39	447.5	447.5
40	447.5	447.5[k]
42	447.5	448
44	449	449
48	464	462
52	454	452
53	454	452
54	454	451

Carbon disulfide

Cpd.	Calcd.	Obsd.
10	453	455
11	453	454
12	453	454
13	453	454
14	453	461
15	453	454.5
16	453	454.5
17	453	448
19	471	486.5
20	471	470[e]
21	471	471
22	505	507.5
23	505	506
24	505	506
25	530	532[g]
26	530	534
27	552	557
28	473	471
29	473	472
32	475	472
33	475	473
34	475	470
36	460	456
37	478	476[j]
38	478	477
39	478	475
40	478	477
41	478	477
42	478	475
43	480	479
44	480	479
45	480	478
46	495.5	494.5
47	495.5	494[l]
48	495.5	496
49	495.5	494
50	495.5	494
51	523	521
52	485	485
53	485	483
54	485	482
55	485	484
56	538	544[m]
57	573	577[e]

Benzene

Cpd.	Calcd.	Obsd.
15	436	436
18	447	436[d]
19	454	453.5
22	487	487
23	487	487
24	487	487
25	511	518[g]
26	511	511
27	532	531
28	456	455
29	456	453
32	458	456
33	458	455
37	461	458
39	461	456.5
40	461	462
41	461	462
42	461	457
43	463	460
44	463	461
46	478	476
48	478	477
56	519	522[m]
57	553	555[e]

Methanol

Cpd.	Calcd.	Obsd.
5	304	304[d]
6	304	299[d]
34	440	440
39	443	444
54	449	449.5

Hexane

Cpd.	Calcd.	Obsd.
2	264	270[c]
9	373	379
14	421	420
15	421	426
19	438	438
20	438	439[e]
22	470.5	472
26	494	491
27	514	504
28	440	442
32	442	443
35	326.5	326[h]
38	445	445
39	445	446
42	445	446
48	461	462
49	461	462
52	451	450
53	451	451
54	451	451

[a] Experimental data from P. Karrer and E. Jucker, "Carotenoids," Elsevier Publishing Co., Inc., Houston, Texas, 1950, unless otherwise indicated. [b] L. N. Ferguson, *Chem. Revs.*, **43**, 385 (1948). [c] K. Dimroth, *Angew. Chem.*, **52**, 545 (1939). [d] F. Bohlman, *Chem. Ber.*, **85**, 386 (1951). [e] P. Karrer and C. H. Eugster, *Helv. Chim. Acta*, **34,** 1805 (1951). [f] L. Zechmeister and L. V. Cholnoky, *Ber.*, **69,** 422 (1936). [g] P. Karrer, C. H. Eugster and M. Faust, *Helv. Chim. Acta*, **34,** 823 (1951). [h] L. F. Fieser, *J. Org. Chem.*, 15, 930 (1950). [i] A. E. Gillam and M. S. El Ridi, *Biochem. J.*, **32**, 820 (1938). [j] P. Karrer and W. Bürgi, *Helv. Chim. Acta*, **34**, 832 (1951). [k] R. Kuhn and H. Brockmann, *Z. physiol. Chem.*, **206,** 41 (1932). [l] K. Schön, *Biochem. J.*, **32,** 1566 (1938). [m] P. Karrer and C. H. Eugster, *Helv. Chim. Acta*, **34,** 28 (1951).

The parameters, (a, B and C) for carbon disulfide solutions of carotenoids were computed from the observed wave lengths; a and C are the same for alcohol and carbon disulfide solutions (-2.12 and 0.920, respectively), and only B is characteristic of the solvent. Formulas for the calculation of λ_{max} in various solvents were determined from the observed values with $a = -2.12$ and $c = 0.920$.

Solvent	(λmax), m$\mu^2 \times 10^{-4}$	
Methanol	$(36.30 - 38.42 \times 0.920^N)$	(5)
Hexane	$(36.62 - 38.72 \times 0.920^N)$	(6)
Petroleum ether	$(36.70 - 38.82 \times 0.920^N)$	(7)
Light ligroin	$(37.05 - 39.17 \times 0.920^N)$	(8)
Chloroform	$(38.60 - 40.72 \times 0.920^N)$	(9)
Benzene	$(39.20 - 41.32 \times 0.920^N)$	(10)
Carbon disulfide	$(42.06 - 44.18 \times 0.920^N)$	(11)

The calculated values of λ_{max} in Table I are based on these formulas, which differ only with respect to B which is characteristic for each solvent; the agreement between the calculated and observed values is good except for compounds 14 in carbon disulfide, 25 in chloroform and in benzene and 27 in hexane. In the case of rhodoviolascin 26, it was assumed that $N_{methoxy} = 0$; the agreement between the observed values and those calculated with $N_{methoxy} = 0$ indicates that this substituent exerts practically no bathochromic effect.

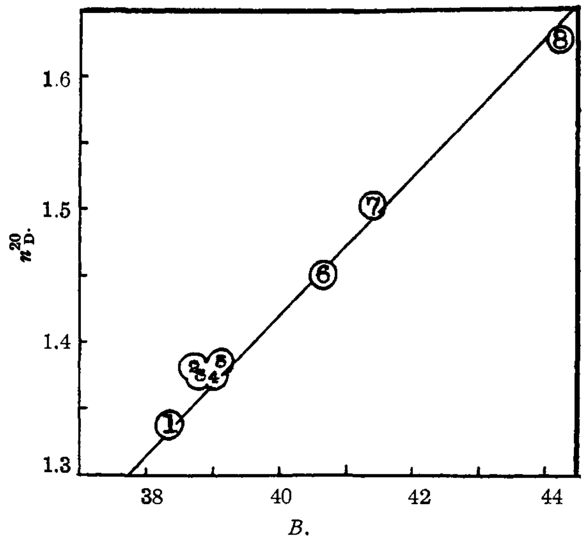

Fig. 1.—1, methanol; 2, hexane; 3, petroleum ether; 4, alcohol; 5, light ligroin; 6, chloroform; 7, benzene; 8, carbon disulfide.

Figure 1 shows that there is an approximately linear relationship between B^{solv} and the refractive index of the solvent.[2] The values for B^{solv} in formulas 5–11 agree well with the values calculated by the equation (see Table II)

$$B^{solv}_{calcd} = 12.976 + 19.019 \times n^{20}D \qquad (12)$$

TABLE II

B^{solv}/IN VARIOUS SOLVENTS

Solvent	$n^{20}D$	B^{solv}	B^{solv}_{calcd}
Methanol	1.3288	38.42	38.25
Hexane	1.3751	38.74	39.13
Petroleum ether	1.37	38.82	39.03
Ether	1.3556	...	38.76
Alcohol	1.3633	39.10	38.91
Light ligroin	1.38	39.17	39.22
Cyclohexane	1.4264	...	40.10
Chloroform	1.4486	40.72	40.53
Benzene	1.5017	41.32	41.54
Pyridine	1.5085	...	41.67
Carbon disulfide	1.6319	44.18	44.01

Because the number of observations made in ether, cyclohexane and pyridine was insufficient for the determination of B^{solv}, B^{solv}_{calcd} computed from equation 12 was used in the calculation of λ_{max} in these solvents (Table III); the good agreement between the calculated and experimental values indicates the reliability of relation 12.

TABLE III

ABSORPTION MAXIMA IN ETHER, CYCLOHEXANE AND PYRIDINE

No.[a]	Compound	N	λmax (in mμ)	Ether	Cyclohexane	Pyridine
25	Decapreno-ϵ_1-carotene	13.8	Obsd.	497[b]	504[b]	...
			Calcd.	494	503	
27	Dehydrolycopene	16.0	Obsd.	..	..	535[c]
			Calcd.			534.5
40	Helenien (xanthophyll dipalmitate)	10.0	Obsd.	..	..	463[c]
			Calcd.			463
41	Capsanthol	10.0	Obsd.	..	..	463[c]
			Calcd.			463
56	Decapreno-β-carotene	14.6	Obsd.	..	509[d]	...
			Calcd.		511	
57	Dodecapreno-β-carotene	18.8	Obsd.	536[e]	541[e]	...
			Calcd.	534	544	

[a] The numbers of compounds are the same as in Table I. [b] P. Karrer, C. H. Eugster and M. Faust, *Helv. Chim. Acta.*, **34**, 823 (1951). [c] P. Karrer and E. Jucker, "Carotenoids," Elsevier Publ. Co., Inc., Houston, Texas, 1950. [d] P. Karrer and C. H. Eugster, *Helv. Chim. Acta*, **34**, 28 (1951). [e] *Ibid.*, p. 1805.

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(2) Regarding the solvent as a continuous dielectric medium, N. S. Bayliss (*J. Chem. Phys.*, **18**, 292 (1950)) shows that the solvent effect on the absorption of light by solute molecules must be expressed in terms of the electronic polarization part of its dielectric constant, $K = n^2$ (n is the refractive index of the solvent); and using methods based both on quantum theory and on classical dispersion theory, he shows that the red shift of absorption in solution depends directly on f, the oscillator strength, and inversely either on a^3 (a is the radius of the spherical solute molecule) or the polarizability α. The expression is $\Delta\nu = \text{const.}\ (f/\nu a^3)[(n^2 - 1)/(2n^2 + 1)]$ alternatively with the substitution of α for a^3.