[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF OREGON AND INDIANA UNIVERSITY]

ULTRAVIOLET ABSORPTION SPECTRA OF SOME VINYLNAPHTHALENES AND RELATED AROMATIC HYDROCARBONS[1, 2, 3]

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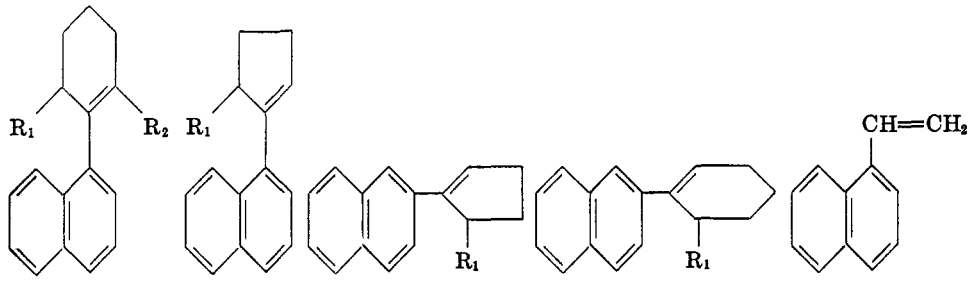
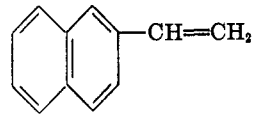
In previous studies on catalytic hydrogenation (1), Diels-Alder condensation (2), polarographic reduction (2), and trinitrofluorenone molecular compound formation (3) it was proposed that inherent differences in coplanarity or steric restriction to the attainment thereof (by the cycloalkenyl double bond and the naphthalene ring) during the processes of (a) complex formation between the olefinic substrate and the absorbing surface or molecule and (b) chemical reaction, were manifested by I–IV. Specifically it was suggested that I was non-



I II III IV V



VI VII VIII IX X

XI

For $R_1 = R_2 = H$: I, II, III, IV
For $R_1 = CH_3, R_2 = H$: VI, VII, VIII, IX
For $R_1 = H, R_2 = CH_3$: XI

coplanar, III and IV were completely coplanar, and II was perhaps non-coplanar but with little energetic restriction to the attainment of coplanarity. To remove the influences which processes (a) and (b) might have on such considerations

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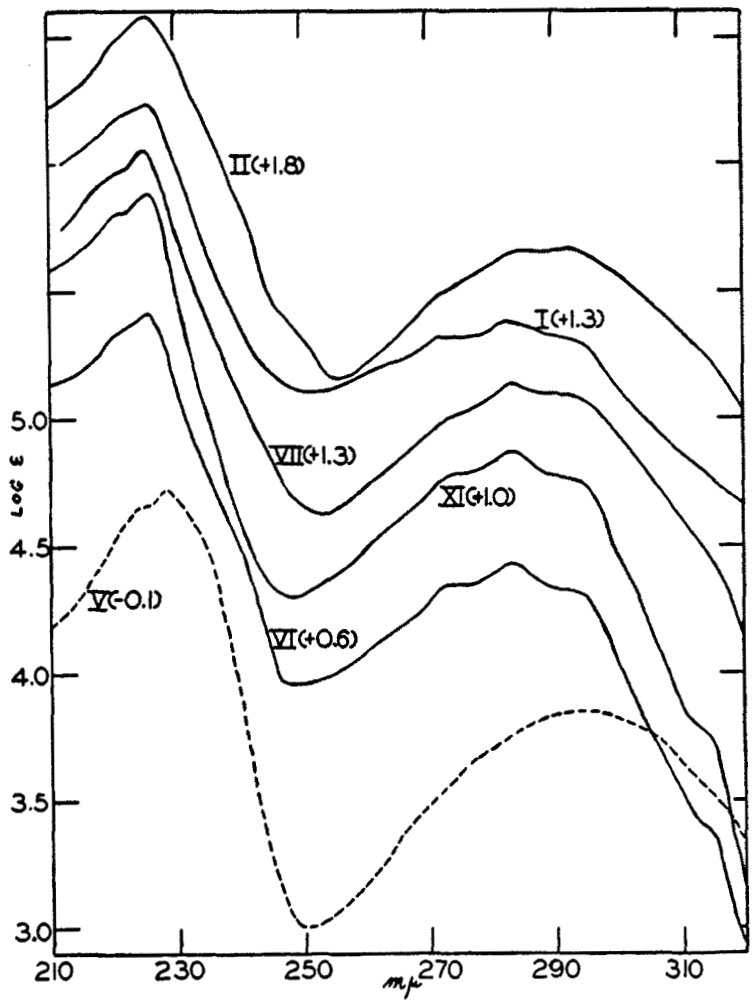


FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA OF SOME 1-ALKENYLNAPHTHALENES. Solvent cyclohexane. Numbers in parentheses represent vertical displacements of the curves. I, 1-(1′-Naphthyl)-1-cyclohexene; II, 1-(1′-Naphthyl)-1-cyclopentene; V, 1-Vinylnaphthalene; VI, 3-Methyl-2-(1′-naphthyl)-1-cyclohexene; VII, 3-Methyl-2-(1′-naphthyl)-1-cyclopentene; XI, 2-Methyl-1-(1′-naphthyl)-1-cyclohexene.

we investigated the absorption of ultraviolet light by I–IV and, for comparison, also by 1-vinylnaphthalene (V), VI–IX, and XI in the non-polar solvent cyclohexane in the range of 210–320 mμ. The absorption curves obtained are shown in Figs. 1 and 2 and data relative to the positions and intensities of absorption are recorded in Table I.[5]

[5] *Added in proof.* We are greatly indebted to Dr. D. P. Stevenson for independent checks on the ultraviolet absorption spectra of I–IV and VI–IX (on samples submitted from our stocks) in the laboratories of the Shell Development Co., Emeryville, California. Their curves corresponded closely to those presented here except for some small differences in

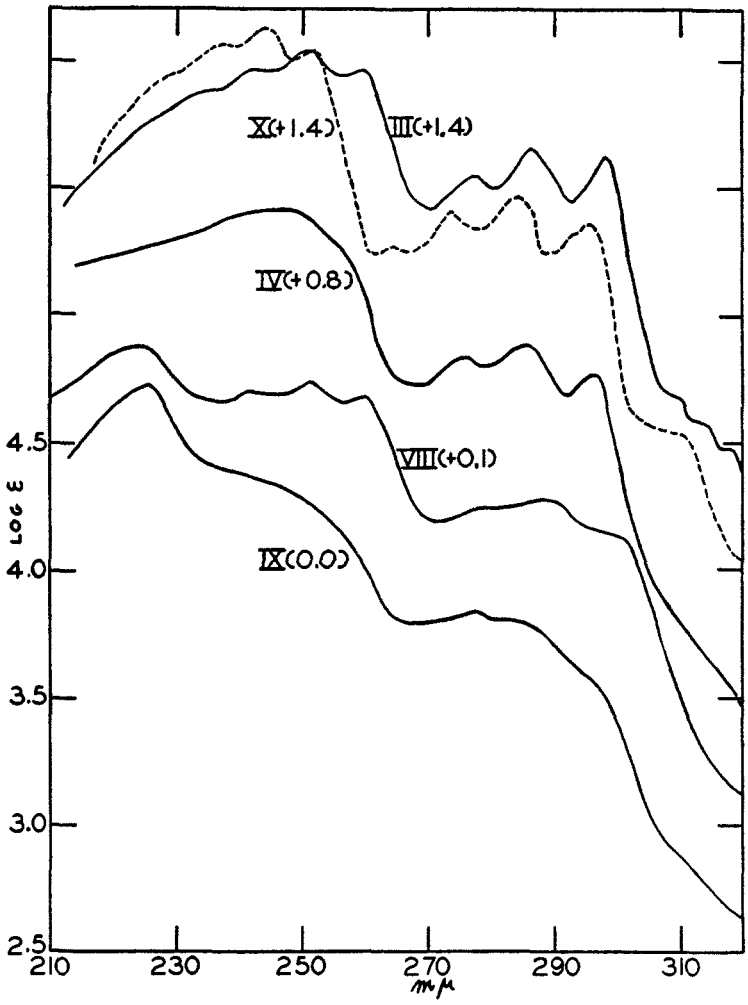


FIG. 2. ULTRAVIOLET ABSORPTION SPECTRA OF SOME 2-ALKENYLNAPHTHALENES. Solvent cyclohexane. Numbers in parentheses represent vertical displacements of the curves. III, 1-(2′-Naphthyl)-1-cyclopentene; IV, 1-(2′-Naphthyl)-1-cyclohexene; VIII, 3-Methyl-2-(2′-naphthyl)-1-cyclopentene; IX, 3-Methyl-2-(2′-naphthyl)-1-cyclohexene; X, 2-Vinylnaphthalene.

Observation of Fig. 1 shows that all of the 1-substituted naphthalenes studied, except V, have remarkably similar spectra with the principal absorption maxima at 225–226 mμ (A-band) and three secondary incompletely resolved maxima of

intensities [$\Delta \log \epsilon$ at $\lambda_{max.} = \pm 0.1$ for II–IV, VI, VII, IX and 0.1 to 0.2 (lower values for theirs) for I and VIII]. Their measurements, extended to 400 mμ, showed the following additional details in the long wavelength region: (a) There is essentially no absorption beyond 350 mμ. (b) Absorption by the four 1-substituted naphthalenes I, II, VI, and VII decreases rapidly and uniformly beyond 320 mμ. (c) III exhibits fine structure somewhat analogous to that of X, even beyond 300 mμ [shoulders at $\lambda = 310$ mμ (log ϵ 3.19), 324 (2.64), 334 (2.28), 339 (2.18)]. (d) VIII has a very broad sloping shoulder extending from 313 to 337 mμ. (e) IV and IX show no definite points of inflection beyond the region of 310 mμ.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA AND PERTINENT SHOULDERS FOR VARIOUS SUBSTITUTED NAPHTHALENES, ETC.[a]

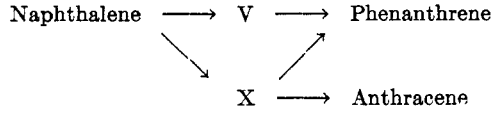
1-Cyclohexylnaphthalene[b,c]		I		II		1-Phenylnaphthalene[b]		VI		VII		XI	
$\lambda_{max.}$[f]	log ϵ	$\lambda_{max.}$	log ϵ	$\lambda_{max.}$	log ϵ	$\lambda_{max.}$	log ϵ	$\lambda_{max.}$	log ϵ	$\lambda_{max.}$	log ϵ	$\lambda_{max.}$	log ϵ
224–226	4.49	225–226	4.93	225–226	4.79	225–226	4.78	225–226	4.81	225–226	4.75	225–226	4.89
274	3.60	(272–274)	4.01	(273)?	3.71	(272)?	3.89	(274)	3.74	(275)?	3.72	(274)	3.78
283	3.68	282	4.07	284–285	3.85	282	4.02	283	3.83	283	3.83	283	3.87
(292)	3.52	(292)	4.01	292–293	3.85	288	4.03	(292)	3.72	(292)	3.79	(292)	3.77
1-Propenylnaphthalene[b,d]		V		III		IV		2-Phenylnaphthalene[b]		VIII		IX	
								213	4.45				
—	—[e]	228.5	4.82					(228)	4.32	225–226	4.78	225–226	4.72
				(242–244)	4.56					242	4.60	(242)	4.37
				251–252	4.64	246–248	4.61	250	4.70	251	4.64		
				259	4.56					260	4.58		
				277	4.15	276	4.03	278	4.02	(282)	4.15	276	3.83
				286	4.25	286	4.08	286	4.04	288	4.18	(284)	3.79
293–296	3.99	292–296	3.95	298	4.23	(296–297)	3.96			(298)	4.05	(295)?	3.57
X[b,c]				Phenanthrene[b]				Anthracene[b]					
		283	4.09	222	4.36	282	4.05	222	4.23				
(230)	4.59	(292)	3.91			(291)	3.88						
237	4.68	296	3.97			293	4.18			(298)	2.65		
243	4.73	(306)	3.15	(246)	4.69	308	2.25	(247)	4.99	310	3.04		
252	4.64			252	4.81	315	2.30	253	5.30				
		323	2.66	(258)	4.48	323	2.35			324	3.42		
265	3.88	331	2.50			330	2.40						
273	4.00	339	2.60	275	4.18	338	2.35			339	3.72		

[a] Unless otherwise designated solvent is cyclohexane. [b] Taken from curves in ref. (4). [c] In 95% ethanol. [d] In hexane. [e] Measurements not extended to this region. [f] Numbers in parentheses represent shoulders. Parentheses followed by "?" indicate the shoulder is barely discernible. [g] See footnote 5 in text.

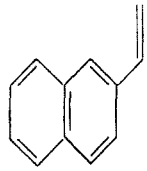
approximately equal intensity (for any one compound) at 272–275, 282–285, and 292–293 mμ (B-band group). But the $\lambda_{max.}$ and general shapes of the curves are essentially identical, except for some small loss of fine structure, with those of typical 1-alkylnaphthalenes [*cf.* 1-methylnaphthalene and 1-cyclohexylnaphthalene (4)] and closely similar to that of 1-phenylnaphthalene (4). Contrariwise, V shows a relatively different spectrum consisting of only two broad smooth absorption bands with the maximum of the more intense one shifted bathochromically by about 3 mμ from the A-band of the others. The spectrum recorded for 1-propenylnaphthalene (4), while not extended through the region of the maximum of the A-band, appears very similar to that of V. According to the interpretations of Jones and Hirshberg (5, 6) and Friedel, Orchin, and Reggel (7) the spectra of V and 1-propenylnaphthalene exhibit the typical conjugation effect for a 1-substituent on naphthalene (*cf.* 1-naphthylamine and 1-naphthoic acid), while those of I, II, VI, VII, and XI show mainly only a bathochromic effect from naphthalene (corresponding $\lambda_{max.}$ at 222, 267, 275, and 286 mμ) with some loss of fine structure, as might result from extensive suppression of conjugation due to steric restriction to coplanarity.

The relationship among the more widely diversified spectra of the 2-substituted naphthalenes (Fig. 2) is relatively complex. Thus the spectra of III, IV, and 2-vinylnaphthalene (X) (4) lack the rather sharp intense A-band (at about 235 mμ) characteristic of 2-naphthylamine and 2-naphthoic acid (6). The most striking of these spectra are the similar ones of III and X, each of which exhibits a wealth of structural detail. This is particularly surprising for X in view of the almost complete absence of fine structure in its isomer V. The bathochromic displacement ($\Delta\lambda_{max.}$ = 2–8 mμ) of III over X is consistent with the fact that the former may be considered a dialkylated X, bearing its substituents attached to the chromophore (8). The curves for IV and III have the same general appearance except that the former is devoid of fine structure in the short wavelength region. The spectra of VIII and IX generally conform to those of their unmethylated parents III and IV, respectively, except that (a) a new principal maximum, of intensity equal to that found in VI or VII for the A-band, appears at 225–226 mμ, and (b) fine structure is less pronounced.

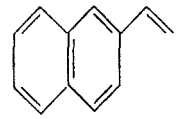
Constitutional configurations giving rise to fine structural features in ultraviolet spectra have been considered by Jones (5) and Merkel and Wiegand (9, 10) and modified by Beaven, *et al.* (11). In application of these proposals to X, for example, a molecule in which molecular models indicate no steric restriction to rotation around the pivotal bond (joining the substituent to the naphthalene nucleus), one considers the possible existence of a relatively rigid coplanar pseudoaromatic configuration inherent in its structure. In this regard the writings of Platt (12) are valuable in pointing out that V and X lie on the variconjugate sequences



built up by the hypothetical successive additions of π-electrons. In such a series the spectrum of an intermediate member should lie on a smooth sequence connecting (possibly between) the two spectra of its predecessor and successor provided the molecule in question is coplanar. The lack of close resemblance between the spectra of V and its congeners conforms with non-coplanarity (as shown by models, Table II) in V, while the remarkable similarity of the spectrum of X to that of phenanthrene (but not particularly to those of naphthalene or anthracene) (Table I) signifies analogous geometrical conformations in these molecules. In accordance with this observation we propose that X exists predominantly in the coplanar (region 0° to α, *vide infra*) *phene*-orientation (XII), as contrasted to the *acene*-orientation (XIII). Possibly lending some credence to this orientation is the facile Diels-Alder reaction of X to an adduct having the carbon skeleton of phenanthrene.[6] It might be noted in this regard that Price and Halpern (13) reported only one absorption maximum for 9-vinylphenanthrene (steric restriction to coplanarity as for V) while 2- and 3-vinylphenanthrenes (no steric restriction) showed several maxima each. Introduction into styrene of substituents which sterically hinder attainment of coplanarity in the molecule have similar effects in elimination of fine structure (14).



XII



XIII

For an interpretation of conjugation effects in some of our spectra, let us first consider the case of the extensively investigated biphenyl (and its derivatives). In a critical survey of the situation Beaven, *et al.* (11) offer convincing arguments that (a) coplanarity of the two benzene rings is not prerequisite to the appearance of conjugation in the spectrum and (b) the degree of conjugation observed is dependent on the natures of any substituents present even when they are not directly involved in steric restrictions to coplanarity (as, for example, when they occupy *para* positions). Guy (15) has calculated that the resonance interaction between the benzene rings will decrease sigmoidally from a maximum value (100%) for coplanarity (θ, the interplanar angle, = 0°) through the values of 90% for θ = 12°; 19% for 45°; and 10% for 61°; to 0% for perpendicularity [*cf.* calculations by others on different compounds (16, 17)]. By electron diffraction Bastiansen (18) has found $\theta_{ave.} = 45 \pm 10°$ (11) for biphenyl vapor. Spectra indicate the same configurations for biphenyl in the gaseous state and in solution in a non-polar inert solvent (10). Let us assume, therefore, that at any instant there is a distribution of molecules over the range of orientations from $\theta = \theta_1$ to $\theta = \theta_2$ and that the entire population of molecules can absorb energy involving

[6] The structure was established by dehydrogenation to the known phenanthrene-3,4-dicarboxylic anhydride (26).

electronic transitions effectively along the direction of the pivotal bond (5, 19). In accordance with the Franck-Condon principle (16, 20) the relative positions of the atomic nuclei, including the value of θ for the particular molecule, should not change during the process of absorption. If then, as we here propose, the energy of transition is dependent on θ (*i.e.* increases with θ up to 90°), one should find a smooth, presumably broad, absorption band resulting from the summation of transitions by the population of molecules in orientations from θ_1 to θ_2. The position of the absorption maximum (*e.g.* $\lambda_{max.}$ 247 mμ for biphenyl) would not necessarily correspond to $\theta_{ave.}$ but would be dependent on the population distribution and the transition probability as functions of θ. The hypsochromic shift of this maximum to 238 mμ in 2-methylbiphenyl (4) seems to conform with this idea.

In extending these proposals to our olefins, the lower symmetry of these molecules requires consideration of changes in resonance interaction during rotation over the span from $\theta = 0°$ to $\theta = 180°$ (where 0° is taken as the *phene*-orientation as in I and III). In this span the following spectral regions should be discernible:

θ-Distribution	Spectral characteristics
0° to α	phenanthrene-type, fine structure
α to 90° $-\beta$	"conjugation"—or diffuse-type
90° $-\beta$ to 90° $+\beta$	alkylnaphthalene-type, fine structure
90° $+\beta$ to 180° $-\gamma$	diffuse-type
180° $-\gamma$ to 180°	anthracene-type for 2-substituents only (fine structure), ?-type for 1-substituents

The variation tolerated in α, β, and γ without noticeable alteration of spectral type should depend on the inherent conjugative effect, C_t, of the substituent in such a fashion that as C_t increases β will decrease and α will increase, and *vice versa* as C_t decreases.[7] It might be noted that, either due to an appropriate θ-distribution or to broad or ill-defined boundaries between regions, intermediate and/or composite spectra could result.

For cycloalkenyl groups C_t has been identified as a measure of the facility of the transformation cycloalkenyl → cycloalkylidene. Chemical evidence for the order cyclopentenyl > cyclohexenyl in C_t has been reviewed.[8] The same order is derivable from ultraviolet absorption spectra of the 1-acetylcycloalkenes and 1-aldehydocycloalkenes where $\lambda_{max.}$ [corresponding to the cycloalkenyl → cycloalkylidene transition of the type $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O \rightarrow -\overset{|}{\underset{+}{C}}-\overset{|}{C}=\overset{|}{C}-\underset{-}{O}$ (21)] is higher for the 5-ring than for the 6-ring (22). Extension of measurements of Diels-Alder reactivity of V and X toward maleic anhydride[8] indicates C_t for vinyl is greater than it is for cyclopentenyl.

[7] In general it is to be expected that α can be identified with that part of the sigmoid curve of resonance interaction *versus* θ where asymptotic approach to the maximum resonance interaction commences. The angle 90° $-\beta$ would correspond to a similar position approaching the minimum value of interaction.

[8] *Cf.* (2) and references given therein.

TABLE II

θ′-DISTRIBUTIONS FOR SOME SUBSTITUTED NAPHTHALENES

Compound	θ′-Distribution[a]	Compound	θ′-Distribution[a]
I	80–128°	IX	0°, (53)87–133°[e, f]
II	44–136°[b]		4°, 43–92(105)°[e, g, h]
III	0–180°[c]	X	0–180°[i]
IV	0–3°, 43–133°, 177–180°[d]	XI	80–122(149)°[e]
V	36–138°	1-Phenylnaphthalene	57–123°
VI	(80)94–102(128)°[e, f]	1-*o*-Tolylnaphthalene	(57)70–123°[e]
	(75)86–95(128)°[e, g]	2-Phenylnaphthalene	18–162°
		2-*o*-Tolylnaphthalene	(34)55–125(146)°[e]

[a] Unless otherwise designated, data were obtained from visual estimation of Fisher-Hirschfelder-Taylor molecular models using a transparent protractor and a ruler. The θ′-distribution is defined as the range of interplanar angles (between the plane of naphthalene and the plane of the double bond(s) of the substituent) allowed in the molecule without distortion or overlapping. [b] Based on numerical calculations assuming a planar cyclopentene ring. [c] Based on mental extrapolation of models for I and IV and calculations for II. [d] Very little steric interference in the intervals 3–43° and 133–177°. [e] Numbers in parentheses represent extreme orientations available, usually by appropriate rotation of the methyl group. Numbers not in parentheses represent orientations available for all conformations. [f] For methyl group in the polar position. [g] For methyl group in the equatorial position. [h] Rather small steric interference in the intervals 0–4° and 4–43°. [i] Hydrogen contact only at the two extreme values.

For assistance in evaluating plausible θ-distributions for these molecules ranges of θ, designated here as θ′-distributions (where the θ- and θ′-distributions may or may not be identical),[9] over which no steric interference in the molecules would occur were approximately determined (Table II). In general such steric data were obtained by visual measurement made on Fisher-Hirschfelder-Taylor molecular models. Since it is impossible to construct the cyclopentene ring with these models data for II and III are based on mental and mathematical considerations involving a planar cyclopentene ring. No data are given for the more complex molecules VII and VIII, but it is apparent that the θ′-distributions for them should be more extensive (at both ends of the scale) than those for VI and IX, respectively (*cf.* II and III with I and IV, respectively).

In accordance with the similarities in C_t values, θ′-distributions, and spectra[10] of III and X, we believe III is also predominantly coplanar within the θ-distribution 0° to α. The intermediate spectrum of IV [between that of III or X and that of 2-phenylnaphthalene, *cf.* also styrene, 1-phenylcyclohexene (23), and biphenyl] may be interpreted as resulting from the smaller C_t value of the cyclohexenyl group and a decreased population of molecules within the preferred θ-distribution 0° to α due to the existence of the slight steric barrier to rotation imposed in the range 3–43° (Table II). In chemical processes, especially those involving flatwise adsorption or complex formation, such deviation from coplanarity in IV would not be readily apparent (3). The lack of steric interference

[9] The θ-distribution refers to spectroscopy, while the θ′-distribution refers only to geometry.

[10] As well as the structures of the maleic anhydride adducts [*Cf.* (29) and footnote 6].

for at least part of the range 0° to α contrasts with the case of 2-phenylnaphthalene (smoother spectrum), for which there is little reason to expect a θ-distribution appreciably different from that of biphenyl, particularly if, as proposed by Bastiansen (18), non-coplanarity in biphenyl ($\theta' = 18$–$162°$) results from repulsion of *ortho* hydrogens.

The spectra of VIII and IX appear to be composite ones, which can be considered to result from significant θ-distributions in each of three regions. Thus VIII retains the fine structure of III (0° to α orientation) but considerably smoothed out (α to 90° $-\beta$ orientation) and, in addition, shows a "2-alkyl" band at 225 mμ (90° $-\beta$ to 90° $+\beta$ orientation). Like considerations can be applied to IX, as compared to IV [*cf.* also 2-(*o*-tolyl)naphthalene (4), $\lambda_{max.}$ at 227 mμ, with 2-phenylnaphthalene].

Interpreted in terms of θ-distributions VI, VII, and XI show spectral types largely of the 90° $-\beta$ to 90° $+\beta$ region with some lesser contribution from the α to 90° $-\beta$ region. The order I, II, V [*cf.* the order 9-cyclohexenyl-, 9-cyclopentenyl- (24), 9-vinylphenanthrene (13), for which analogous spectra apparently occur] represents a transition in spectral type attendant to a combined gradual increase in C_t and a conversion from a θ-distribution largely in the 90° $-\beta$ to 90° $+\beta$ region (with lesser contribution from the α to 90° $-\beta$ region) to a θ-distribution largely in the α to 90° $-\beta$ region (with lesser contribution from the 90° $-\beta$ to 90° $+\beta$ one) [*cf.* Bachmann and Deno (25)].

EXPERIMENTAL

Compounds I–XI were prepared and purified as indicated elsewhere (1, 27, 28). Spectra were determined with a Beckman spectrophotometer, model DU.

SUMMARY

Ultraviolet absorption spectra are reported for vinylnaphthalenes, cyclopentenylnaphthalenes, and cyclohexenylnaphthalenes and are interpreted in terms of conjugative tendencies of the substituents and distributions of the size of angle, θ, between the planes of the naphthalene ring and the double bond of the substituent. Regions are defined for θ = 0° to α, α to 90° $-\beta$, and 90°$-\beta$ to 90°$+\beta$ which are characterized in the spectrum by extensive phenanthrene-like fine structure (as shown by 2-vinyl- and 2-cyclopentenylnaphthalenes), broad diffuse bands (*e.g.* 1-vinylnaphthalene), and alkylnaphthalene-like fine structure (*e.g.* 1-cyclohexenylnaphthalene), respectively. Some compounds (*e.g.* 2-cyclohexenylnaphthalene) are considered to show intermediate types of spectra; and others [*e.g.* a methylated 2-cyclopentenylnaphthalene (VIII)], composite types of spectra.

EUGENE, OREGON

REFERENCES

(1) KLEMM AND HODES, *J. Am. Chem. Soc.*, **73**, 5181 (1951).
(2) KLEMM, HODES, AND SCHAAP, *J. Org. Chem.*, **19**, 451 (1954).
(3) KLEMM AND SPRAGUE, *J. Org. Chem.*, **19**, 1464 (1954).

(4) FRIEDEL AND ORCHIN, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, Inc., New York, 1951.
(5) JONES, *J. Am. Chem. Soc.*, **67**, 2127 (1945).
(6) HIRSHBERG AND JONES, *Can. J. Research*, **27B**, 437 (1949).
(7) FRIEDEL, ORCHIN, AND REGGEL, *J. Am. Chem. Soc.*, **70**, 199 (1948).
(8) WOODWARD, *J. Am. Chem. Soc.*, **64**, 72 (1942).
(9) MERKEL AND WIEGAND, *Naturwissenschaften*, **34**, 122 (1947).
(10) MERKEL AND WIEGAND, *Z. Naturforschung*, **3B**, 93 (1948).
(11) BEAVEN, HALL, LESSLIE, AND TURNER, *J. Chem. Soc.*, 854 (1952).
(12) PLATT, *J. Chem. Phys.*, **19**, 101 (1951).
(13) PRICE AND HALPERN, *J. Am. Chem. Soc.*, **73**, 818 (1951).
(14) HIRSCHBERG, *J. Am. Chem. Soc.*, **71**, 3241 (1949); ALLARD, *Helv. Chim. Acta*, **19**, 1270 (1936).
(15) GUY, *J. chim. Phys.*, **46**, 469 (1949).
(16) BRAUDE, SONDHEIMER, AND FORBES, *Nature*, **173**, 117 (1954).
(17) KLEVENS AND PLATT, *J. Am. Chem. Soc.*, **71**, 1714 (1949).
(18) BASTIANSEN, *Acta Chem. Scand.*, **3**, 408 (1949).
(19) LEWIS AND CALVIN, *Chem. Revs.*, **25**, 273 (1939); CRAIG, *Proc. Roy. Soc. N. S. Wales*, **79**, 160 (1945).
(20) SPONER AND TELLER, *Revs. Mod. Phys.*, **13**, 75 (1941).
(21) FERGUSON, *Electron Structures of Organic Molecules*, Prentice-Hall, Inc., New York, 1952, p. 283.
(22) HEILBRON, JONES, TOOGOOD, AND WEEDON, *J. Chem. Soc.*, 1827 (1949).
(23) CARLIN AND LANDERL, *J. Am. Chem. Soc.*, **75**, 3969 (1953).
(24) HENRI AND BERGMANN, *Nature*, **143**, 278 (1939).
(25) BACHMANN AND DENO, *J. Am. Chem. Soc.*, **71**, 3062 (1949).
(26) COHEN AND WARREN, *J. Chem. Soc.*, 1315 (1937).
(27) KLEMM AND ZIFFER, *J. Org. Chem.*, **20**, 182 (1955).
(28) KLEMM, SPRAGUE, AND ZIFFER, *J. Org. Chem.*, **20**, 200 (1955).
(29) BACHMANN AND KLOETZEL, *J. Am. Chem. Soc.*, **60**, 2204 (1938).