in the same manner as *sym*-di-(9-phenanthryl)-ethylene. This change proves that phenanthroin is a stable enediol and not a tautomeric equilibrium mixture and illustrates the powerful "conjugating" influence of the 9-phenanthryl radical.

REHOVOTH, PALESTINE RECEIVED SEPTEMBER 13, 1947

[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

Absorption Spectra and Photo-isomerization of Arylated Dienes

BY YEHUDA HIRSHBERG, ERNST BERGMANN AND FELIX BERGMANN

Zechmeister and co-workers[1,2] have shown that *trans–trans* 1,4-diphenylbutadiene, under the influence of ultraviolet light, isomerizes to the *cis–trans* isomer, and that the same is true for the *cis–cis* compound. They also showed that the *trans–trans* form has the most developed fine-structure and absorbs nearest to the visible spectrum, while the spectra of the (liquid) isomer—considered as *cis–trans*[3]—and of the *cis–cis* form have the maxima in the more remote part of the ultraviolet, and are characterized by absence of fine structure and low extinction coefficients.

Models show that only the *trans–trans* form is free of steric interference between groups on neighboring carbon atoms (no inhibition of resonance); in the isomerides, increasing interference appears between the *o*-hydrogen of the phenyl ring and hydrogen in the chain. In the latter cases, there occurs a marked deviation from that planar arrangement which is the necessary prerequisite of resonance.[4] These effects may well account for the differences in the spectra of the isomers.

The present paper is concerned with the influence substitution of the 1,4-diphenylbutadiene molecule, especially in the phenyl rings, exerts on its ability to resonate and, thereby, on the character of its absorption spectrum. The results are summarized in Table I, columns 2 and 3, and permit the following conclusions: (1) β-naphthyl is more effective than α-naphthyl and phenyl, in shifting the absorption toward the visible and in causing a more elaborate fine-structure to appear. As α- but not β-naphthyl can be considered as an ortho-substituted phenyl, only the former will cause steric interference and will, therefore, restrict resonance. Quantitatively, α-naphthyl is equal to phenyl, in spite of its additional, formally conjugated, double bond, whilst 1,4-di-(β-naphthyl)-butadiene has a spectrum very similar to that of 1,8-diphenyloctatetraene,[5] as the following figures show:

	$\lambda_{\text{Max.}}$	Log E_m	λ_{Max}	Log E_m
1,4-Di-(β-naphthyl)-butadiene	3610	4.84	3810	4.84
1,8-Diphenyloctatetraene	3600	4.79	3770	4.95

It may be recalled that according to Compton and W. Bergmann[6] also the 2-quinolyl group, which is analogous to β-naphthyl, is equivalent to styryl in its influence on the spectrum of the α-phenyl-ω-(2-quinolyl)-polyenes.

(2) The first and only maximum of 1,4-di-(*o*-tolyl)-butadiene lies at 2740 Å. as compared with a wave length of 3450 Å. for the longest of the four maxima of 1,4-diphenylbutadiene. This difference may well be ascribed to resonance inhibition by the *o*-methyl groups. Conversely, 1,4-di-(*p*-methoxyphenyl)-butadiene reflects in the location of the longest of its (three) maxima (3590 Å.) and 1-phenyl-4-(*p*-biphenylyl)-butadiene in the high extinction coefficient (4.9) of the first of its (three) maxima (3480 Å.), the extended resonating system present in the molecules.

(3) The three isomeric 1-phenyl-4-chlorophenyl-butadienes have practically identical absorption spectra, only in the number of absorption bands, not in their location distinguished from the parent compound. All three isomers show the same three bands; only in the para-compound, a fourth one is observed—with relatively low intensity—near the visible end of the ultraviolet spectrum. This unusual indifference to substitution has led to the investigation of 1,4-di-(*o*-chlorophenyl)-butadiene. In the spectrum of this substance, too, there occurs only a slight shift toward the remoter part of the ultraviolet; and the middle band in the spectrum of the monochloro compounds (3160–3200 Å.) disappears.

(4) Phenyl substitution in the diene system of 1,4-diphenylbutadiene leads to the disappearance of fine-structure and broadening of the absorption bands (Fig. 1). In 1,2,3,4-tetraphenylbutadiene, this is very probably due to interference between phenyl groups on neighboring carbon atoms. For the 1,1,2,4-tetraphenyl compound, an additional reason is that one of the *gem*-phenyl groups is forced out of the plane of the double bond.[7] This feature determines, obviously, the character of the absorption spectrum of 1,1,4,4-tetraphenylbutadiene.

(5) 1-Phenylbutadiene which is the *trans*-compound,[8] when prepared according to Muskat and Herrman[9] from cinnamaldehyde and methylmag-

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[1] Sandoval and Zechmeister, THIS JOURNAL, **69**, 553 (1947).

[2] Pinckard, Wille and Zechmeister, *ibid.*, **70**, 1938 (1948).

[3] Straus, *Ann.*, **342**, 190 (1905); compare Kelber and Schwarz, *Ber.*, **45**, 1946 (1912); Ott and Schroeter, *ibid.*, **60**, 624 (1927).

[4] Zechmeister and Le Rosen, *Science*, **95**, 587 (1942); THIS JOURNAL, **64**, 2755 (1942); Lewis, Magel and Lipkin, *ibid.*, **62**, 2973 (1940).

[5] Hausser, Kuhn and Smakula, *Z. physik. Chem.*, **B29**, 384 (1935).

[6] Compton and W. Bergmann, *J. Org. Chem.*, **12**, 363 (1947).

[7] Coates and Sutton, *J. Chem. Soc.*, 567 (1942); F. Bergmann and Israelashwili, THIS JOURNAL, **68**, 1 (1946).

[8] Grummitt and Christoph, THIS JOURNAL, **71**, 4157 (1949).

[9] Muskat and Herrman, *ibid.*, **53**, 252 (1931).

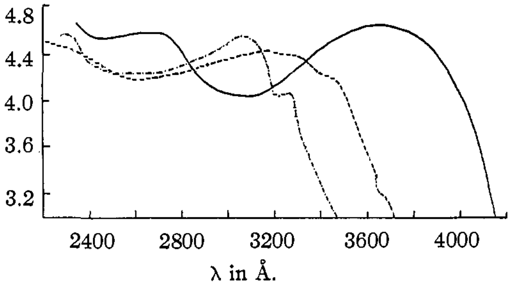

Fig. 1.—Absorption spectra of isomeric tetraphenylbutadienes: 1,2,3,4 - - -; 1,1,4,4 —; 1,1,2,4, -·-·-.

nesium halide, shows less fine-structure than the 1,4-diphenyl derivative. It absorbs at 2833 (log E_m = 4.47) and 3083 Å. (log E_m = 4.53). A similar observation had been made by Jones[10] for the pair styrene–stilbene. Braude[11] observed maxima at 2230 Å. (4.08), 2710 Å. (4.45) and 3050 Å. (3.78), Grummitt and Christoph[8] a maximum at 2800 Å. (4.47). The reason for the deviation in Braude's findings is obscure, it may be due to steric difference between the samples investigated.

Both the existence of fine-structure and the order of magnitude of the extinction coefficients are due to the *trans–trans* configuration of the substituted 1,4-diphenylbutadienes, in analogy to the explanation given for the spectra of the stereoisomeric forms of the parent hydrocarbon. This analogy is further emphasized by the fact that the spectra of all those substances which are capable of formation of geometrical isomers, change upon exposure to light. As an example, Fig. 2 illustrates the changes in the spectrum of 1,4-di-(β-naphthyl)-butadiene; other data are included in Table I. This effect is not due to oxidation, as might be suspected—it also occurs when oxygen is strictly excluded from the system. Only the spectrum of 1,1,4,4-tetraphenylbutadiene which, indeed, is incapable of *cis–trans* isomerization, is unaffected by irradiation. Care has, therefore, to be taken to carry out the measurements of the absorption spectra in reasonably short time.

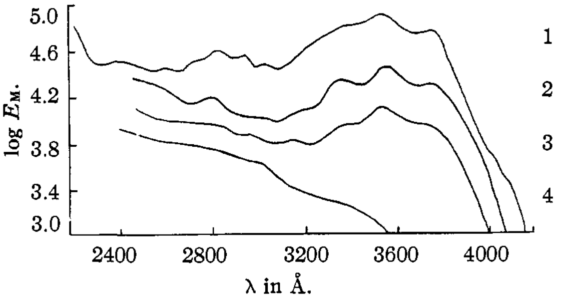

Fig. 2.—Absorption spectrum of 1,4-di-(β-naphthyl)-butadiene in dioxane solution: 1—immediately; 2—after irradiation for 15 min.; 3—after irradiation for 30 min.; 4—after irradiation for 1 hour.

As would be expected, the spectrum of 1,8-diphenyloctatetraene which is the all-*trans* form[12] also changes, upon prolonged irradiation; after three to four hours, the solution becomes almost completely transparent[13] which seems to point to a fundamental molecular change and not only to an alteration in the geometrical structure of the compound (Fig. 3). It is interesting that such far-reaching changes occur also in the case of 1,4-di-(β-naphthyl)-butadiene (Fig. 2), whose analogy with 1,8-diphenyloctatetraene has been emphasized before.

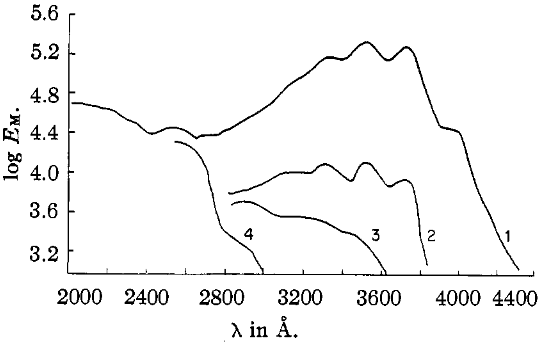

Fig. 3.—Absorption spectrum of 1,8-diphenyloctatetraene in dioxane solution: 1—immediately; 2—after irradiation for 1 hour; 3—after irradiation for 2 hours; 4—after irradiation for 4 hours.

It has been observed by Rotarski[14] and by Fittig and Politis[15] that 1,4-di-(*p*-methoxyphenyl)-butadiene has a double melting point. As the existence of an anisotropic liquid phase of such a substance has only been observed in strictly linear molecules,[16] this observation supports the above assumption that the compound has *trans*-structure.

Experimental

All spectra were measured with the Beckman Spectrophotometer; all boiling and melting points are uncorrected.

trans-**1-Phenylbutadiene** was synthesized by a slight modification of the method of Muskat and Herrman[9] from 20 g. of magnesium, 60 g. of methyl iodide and 60 g. of freshly distilled cinnamaldehyde at 0°. During the distillation of the crude product, dehydration occurred; the distillate was separated from the water formed and redistilled: b. p. 104° (36 mm.); 118–120° (52 mm.); yield, 32 g.

1-Phenyl-4-(*p*-biphenylyl)-butadiene,[17] the three 1-phenyl-4-chlorophenyl-butadienes,[18] 1,1,4,4-tetraphenyl-

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(10) Jones, THIS JOURNAL, **65**, 1818 (1943).

(11) Braude, Jones and Stern, *J. Chem. Soc.*, 1087 (1947); Braude, *Ann. Rep. Progr. Chem.*, 1945, p. 105 ff.

(12) (a) Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928); (b) Zechmeister and Le Rosen, *Science*, **95**, 587 (1942); THIS JOURNAL, **64**, 2755 (1942); (c) Zechmeister and Polgar, *ibid.*, **65**, 1522 (1943).

(13) Compare Kuhn and Winterstein, ref. 12a; Stoermer, *Ber.*, **42**, 4865 (1909).

(14) Rotarski, *Ber.*, **41**, 1994 (1908).

(15) Fittig and Politis, *Ann.*, **255**, 293, 307 (1889).

(16) Vorlaender, "Kristallinisch-fluessige Substanzen," Stuttgart, 1908; Voigt, *Physik. Z.*, **17**, 76, 128, 752 (1916); THIS JOURNAL, **72**, 1200 (1950).

(17) F. Bergmann and J. Weizmann, *J. Org. Chem.*, **9**, 415 (1944).

(18) F. Bergmann, J. Weizmann and Shapiro, *ibid.*, **9**, 408 (1944).

TABLE I

THE ABSORPTION SPECTRA OF SUBSTITUTED 1,4-DIPHENYLBUTADIENES AND THEIR CHANGE UPON IRRADIATION

Maxima in Å. ($\lambda_{\text{max.}}$) and log of extinction coefficients (log E_{m}) at the maxima)

1,4-( )-butadiene	$\lambda_{\text{Max.}}$	log E_{m}	Spectrum after irradiation for					
			Time, hours	$\lambda_{\text{Max.}}$	log E_{m}	Time, hours	$\lambda_{\text{Max.}}$	log E_{m}
Diphenyl[a]	3450	4.40						
	3280	4.66						
	3140	4.62						
	2320	4.08						
Phenyl-(α-naphthyl)[a]	3640	4.67	1	3505	3.12			
	3380	4.70		2970	3.85			
	2920	4.69		2845	3.85			
				2720	3.85			
Phenyl-(β-naphthyl)[a]	3580	4.66	2	3120	3.32			
	3400	4.80		2900	4.14			
	3260	4.70		2800	4.25			
	2920	4.46		2625	4.40			
	2860	4.37						
	2420	4.44						
Di-(α-naphthyl)[b]	3620	4.33	1	3410	4.05	3	2910	3.75
	2920	3.70		3230	4.03		2725	3.85
	2840	3.66		2620	4.04		2475	4.35
	2400	4.38						
(α-Naphthyl)-(β-naphthyl)[b]	3640	4.64	2	3410	4.15	3	3190	3.52
	2760	4.40		3130	4.34		2830	4.15
	2380	4.55		2740	4.42			
Di-(β-naphthyl)[b]	3760	4.74	0.25	3740	4.27	0.5	3530	4.10
	3560	4.90		3530	4.44		3110	3.86
	3380	4.77		3360	4.30			
	3020	4.46		2790	4.18			
	2940	4.53						
	2820	4.60						
	2580	4.43						
	2400	4.50						
Di-(*o*-tolyl)[a]	2740	4.42	0.5	2620	4.22			
Di-(*p*-methoxyphenyl)[a]	3590	4.48	2	3150	3.10			
	3440	4.68		2910	3.65			
	2480	4.02		2640	3.95			
Phenyl-(*p*-biphenylyl)[a]	3480	4.85	0.5	3430	4.59	4	3330	3.56
	2640	3.90		2530	3.78			
	2580	3.86						
Phenyl-(*o*-chlorophenyl)[b]	3300	4.61						
	3180	4.61						
	2380	4.08						
Phenyl-(*m*-chlorophenyl)[b]	3320	4.68						
	3160	4.64						
	2390	4.16						
Phenyl-(*p*-chlorophenyl)[b]	3500	4.46						
	3320	4.68						
	3200	4.63						
	2360	4.20						
Di-(*o*-chlorophenyl)[b]	3240	4.64						
	2440	4.27						
1,1,4,4-Tetraphenyl[b]	3440	4.56						
1,2,3,4-Tetraphenyl[b]	3560	4.62	1	3300	4.22	3	3150	3.66
1,1,2,4-Tetraphenyl[b]	3580	4.42	1	3280	3.75	3	3050	3.48
	3380	4.60						
1-Phenyl[a]	3083	4.50	3	3083	4.05			
	3833	4.50		2833	3.90			
1,8-Diphenyloctatetraene[b]	4180[c]	4.29	1	3920	3.87	2[d]	3620	3.26
	3940	5.17		3720	3.99		3400	3.44

TABLE I (*Continued*)

1,4-( )-butadiene	$\lambda_{Max.}$	log E_m	Spectrum after irradiation for					
			Time, hours	$\lambda_{Max.}$	log E_m	Time, hours	$\lambda_{Max.}$	log E_m
	3740	5.23		3510	3.97		3100	3.62
	3540	5.08		3320	3.91			
	3080	4.40						
	2920	4.31						
	2700	4.39						

[a] In alcoholic solution. [b] In dioxane solution. [c] Inflection. [d] After three hours, no maximum was observed any longer, but two inflections at 3050 (log E_m 3.22) and 2820 Å. (log E_m 4.16).

butadiene,[19] the 1,2,3,4-[20] and the 1,1,2,4-isomer,[21] and 1,8-diphenyloctatetraene[12a] were prepared according to literature data.

For the preparation of **1-phenyl-4-(α-naphthyl)-butadiene**, described before by Friedmann and van Heyningen,[22] the following method was adopted: a mixture of 11 g. of α-naphthylacetic acid (purified by distillation *in vacuo;* b. p. 195° (25 mm.)), 8 g. of cinnamaldehyde, 7 g. of yellow lead oxide and 9 g. of acetic anhydride was refluxed for five hours. After cooling, the crystalline magma was diluted with 10 cc. of glacial acetic and the solid product filtered. After recrystallization from butyl alcohol, it melted at 109°; yield, 7 g. (46.4%).

The synthesis of the other naphthyl-substituted dienes will be published shortly.[23]

For the synthesis of 1,4-di-(*o*-tolyl)- and 1,4-di-(*p*-methoxyphenyl)-butadiene, the condensation of succinic anhydride with *o*-tolylaldehyde and anisaldehyde, respectively, appeared to be the method of choice. While the condensation of succinic anhydride with 2 moles of ω-phenyldienic aldehydes in presence of lead oxide and acetic anhydride has been studied, no attention seems to have been paid to the analogous reaction of benzaldehydes.[24] The yields of 1,4-diarylbutadienes, so obtained, are not satisfactory, but the substances are accessible by this method with great ease.

1,4-Di-(*p*-methoxyphenyl)-butadiene.—A mixture of 52 g. of anisaldehyde, 22 g. of succinic anhydride, 46 g. of yellow lead oxide and 60 g. of acetic anhydride was refluxed for eight hours. After cooling, the product was diluted with 30 cc. of glacial acetic acid and the diene filtered with suction. It was triturated with methyl alcohol and recrystallized from dibutyl ether or toluene and formed colorless leaflets, which in solid state exhibited a strong violet fluorescence. It has a double melting point (226° and 242°), as already stated by Rotarski[14] and by Fittig and Politis[15] who obtained the substance as a by-product in the condensation of anisaldehyde and sodium succinate in presence of acetic anhydride; yield, 17 g. (33.4%). *Anal.* Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8. Found: C, 81.3; H, 6.6.

1,4-Di-(*o*-tolyl)-butadiene.—The necessary *o*-tolylaldehyde was prepared from *o*-tolylmagnesium bromide (16.3 g. of magnesium and 115 g. of *o*-bromotoluene), and ethyl orthoformate (135 g.). The mixture was refluxed for eight hours and then decomposed with ice and ammonium chloride. The diethyl acetal of *o*-tolylaldehyde boiled at 126–128° (38 mm.); yield, 104 g. (80%). *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3. Found: C, 73.9; H, 9.2. The acetal was converted into the aldehyde (b. p. 105° (40 mm.)) with boiling 20% sulfuric acid (150 cc.) for three hours; yield, 58 g. (90%).

The mixture of 23 g. of *o*-tolylaldehyde, 11 g. of succinic anhydride, 23 g. of yellow lead oxide and 30 g. of acetic anhydride was refluxed for ten hours, the reaction product poured into water and the oily layer extracted with chloroform. The diene was isolated from the chloroform residue by high vacuum distillation; it crystallized spontaneously and was recrystallized from isopropyl alcohol; m. p. 128°; yield, 4.6 g. (20%). *Anal.* Calcd. for $C_{18}H_{18}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 7.6.

1,4-Di-(*o*-chlorophenyl)-butadiene.—When a mixture of 84 g. of *o*-chlorobenzaldehyde, 36 g. of succinic acid, 30 g. of lead oxide and 96 g. of acetic anhydride was refluxed for ten hours, a viscous mass was obtained which separated slowly some crystals. They were collected, washed with glacial acetic acid and recrystallized successively from glacial acetic acid and butyl acetate. The substance formed soft needles of m. p. 209°, yield, 7.3 g.; however, it contained oxygen, and, therefore, the following method of preparation for the derived diene was adopted:

A mixture of 6 g. of *o*-chlorophenylacetic acid, 6 g. of *o*-chlorocinnamic aldehyde, 5 cc. of acetic anhydride and 4 g. of lead oxide was refluxed for five hours with stirring. The reaction mixture was diluted with water, extracted with ether, and the ether solution washed with sodium carbonate, dried and concentrated. The oily residue was triturated with methanol and the product recrystallized from an alcohol–acetone mixture. It melted at 149.5°. *Anal.* Calcd. for $C_{16}H_{12}Cl_2$: C, 69.8; H, 4.3; Cl, 25.9. Found: C, 69.8; H, 4.7; Cl, 25.8.

Summary

Spectrographic investigation of a number of substituted 1,4-diphenylbutadienes led to the following conclusions:

1. Substitution in the molecule of 1,4-diphenylbutadiene which leads to steric interference around the double bonds can cause a shift of the longest absorption maximum of 1,4-diphenylbutadiene to the ultraviolet, a disappearance of fine-structure and a lowering of the extinction coefficient. Substitution in the phenyl groups which extends the resonating system (4-methoxy, 4-phenyl; replacement of phenyl by β-naphthyl) has the opposite effect. Introduction of chlorine into the phenyl rings has no influence on the spectrum.

2. In accordance with the observations of Zechmeister and co-workers,[1,2] all *trans–trans* compounds are stereoisomerized by ultraviolet light.

3. This isomerization shows effects on the absorption spectrum, which are to be expected from an increased steric interference around the dienic double bonds.

The syntheses of 1,4-di-(*p*-anisyl)-, 1,4-di-(*o*-tolyl)- and 1,4-di-(*o*-chlorophenyl)-butadiene and a new synthesis of 1-phenyl-4-(α-naphthyl)-butadiene, are described.

REHOVOTH, ISRAEL RECEIVED AUGUST 19, 1949

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(19) Valeur, *Bull. Soc. Chim. France*, [3] **29**, 683 (1903); Schlenk and E. Bergmann, *Ann.*, **463**, 101 (1918).

(20) E. Bergmann, Winter and Schreiber, *ibid.*, **500**, 122 (1933).

(21) E. Bergmann and Ukai, *Ber.*, **66**, 54 (1933).

(22) Friedmann and van Heyningen, *J. prakt. Chem.*, [2] **146**, 163 (1936).

(23) F. Bergmann and Israelashwili, unpublished results.

(24) The reaction of succinic anhydride with fluorenone has been studied by Kuhn and Winterstein, *Helv. Chim. Acta*, 11, 116 (1928).