volved in bond formation to the four chlorine atoms each bond has $^1/_2$ double bond character. From the vanadium–chlorine single bond distance of 1.20 + 0.99 = 2.19 Å. and the double bond distance of 1.09 + 0.89 = 1.98 Å. together with the resonance curve relating interatomic distance with the amount of double bond character[11] we predict the value 2.04 Å. for the vanadium–chlorine distance; this value is in good agreement with the observed distance 2.03 Å. The unpaired electron in vanadium tetrachloride probably occupies one of the 3d orbitals not involved in bond formation. It is interesting that this electron does not play a significant steric role (similar to that ordinarily played by an unshared electron pair) in the structure of this compound; the observed tetrahedral configuration is that which would be expected if this electron were absent.

In vanadium oxytrichloride, however, five of the six orbitals are required for the three bonds to chlorine atoms and for the double bond to the oxygen atom, thus leaving one orbital to form multiple bonds. If we assume that this extra bond resonates equally among the four atoms surrounding the vanadium atom, we expect a vanadium–chlorine distance of 2.09 Å., corresponding to $^1/_4$ double bond character, and a vanadium–oxygen distance slightly shorter than the double bond distance of 1.09 + 0.55 = 1.64 Å. This shortening can be calculated from the double-bond and triple-bond distances of 1.64 and 1.49 Å., respectively, with the use of the resonance curve and with the assumption of $^1/_4$ triple bond character; thus the vanadium–oxygen distance of 1.64 − 0.08 = 1.56 Å. is expected. These values are in good agreement with the distances observed in vanadium oxytrichloride: V–Cl = 2.12 ± 0.03 Å. and V=O = 1.56. ± 0.04 Å.

Some shortening of the vanadium–sulfur distance in the unusual crystal sulvanite[12] might also be expected from these considerations, inasmuch as the vanadium atom has only four closest sulfur neighbors (along with six copper neighbors, somewhat further away, with which it undoubtedly interacts rather strongly). The observed distance is 2.19 or 0.05 Å. less than the sum of the single bond radii.

In titanium tetrachloride we may expect a value of 2.12 Å. from the sums of the single-bond radii (1.28 + 0.99 = 2.27 Å.) and double-bond radii (1.17 + 0.89 = 2.06 Å.) if we make use of the resonance curve. Similarly, we might expect a value of 2.27 Å. in titanium tetrabromide from the single-bond and double-bond radius sums of 2.42 and 2.21 Å., respectively. The observed values[10] (Ti–Cl = 2.18 ± 0.04 Å. and Ti–Br = 2.31 ± 0.02 Å.) are somewhat larger, suggesting somewhat less double bond character, as if titanium actually had a tendency to employ less than six orbitals in bond formation in these tetrahalides.

Acknowledgment.—We wish to thank Professor Linus Pauling and Dr. Verner Schomaker for helpful discussions.

Summary

An electron diffraction study of vanadium tetrachloride shows it to have the regular tetrahedral structure with the bond distance V–Cl = 2.03 ± 0.02 Å. (Cl–Cl = 3.32 ± 0.03 Å.).

[12] L. Pauling and R. Hultgren, *Z. Krist.*, **84**, 204 (1933).

PASADENA, CALIFORNIA RECEIVED AUGUST 6, 1945

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF QUEEN'S UNIVERSITY]

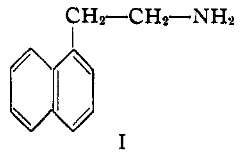
Some Factors Influencing the Ultraviolet Absorption Spectra of Polynuclear Aromatic Compounds. II. The Spectra of Aryl Carbinols and Polybenzfluorenes

BY R. NORMAN JONES

The ultraviolet absorption spectrum of the compound A—(CR$_2$)$_n$—B in which A and B are chromophorically active groups, and R is an alkyl group or a hydrogen atom, should approximate closely to the spectrum calculated for an equimolar mixture of the compounds A—CH$_3$ and B—CH$_3$, since the saturated aliphatic chain can only modify the energy states of the chromophorically active groups through hyperconjugation, or in some other secondary manner, and such effects should not be greatly influenced by the nature of the alkyl group or alkylene chain.

Numerous examples of the "insulation" between two chromophorically active groups provided by a polymethylene chain are recorded in the literature, and a further example is shown in Fig. 1 where the spectra of 2-(1-naphthyl)-ethylamine (I), 1-naphthylamine, and 1-methylnaphthalene are compared. Here the interposed dimethylene chain inhibits interaction between the naphthalene ring system and the potential auxochromic labile electrons of the amino group.

If the chromophorically active groups are separated by one saturated carbon atom only ($n = 1$), the same conditions should hold, although some modification of the spectrum might be caused by



I

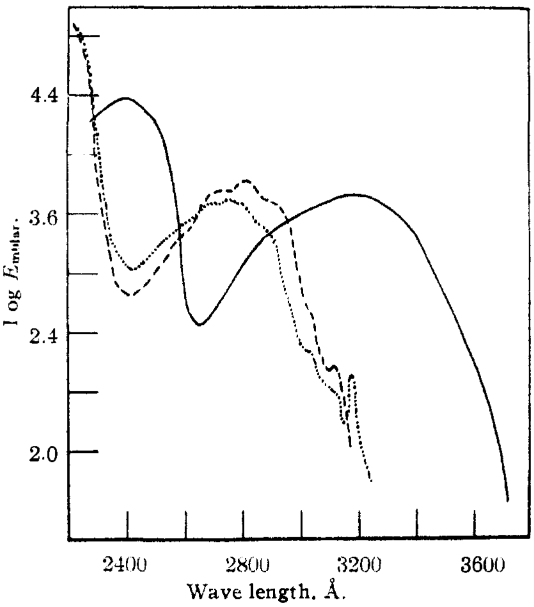
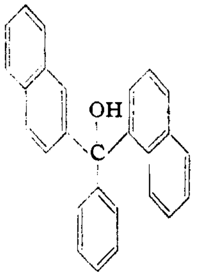


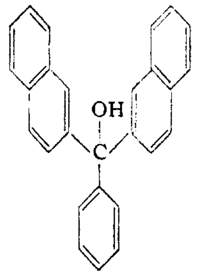
Fig. 1.—Absorption spectra: ———, 1-naphthylamine (solvent ethanol); - - - - -, 2-(1-naphthyl)-ethylamine (solvent *N* NaOH in 50% ethanol); . . . . . . 1-methylnaphthalene (solvent ethanol).

the proximity of the groups to one another, either as a direct result of field effects, or of steric interference with molecular vibration.

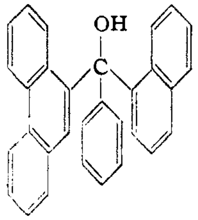
Interesting examples of these effects are provided by the spectra of the three aryl carbinols II-IV recorded in Figs. 2 and 3. For each of these compounds a "calculated curve" has been computed; thus in Fig. 2, the spectrum of phenyl-(1-naphthyl)-(2-naphthyl)-carbinol is compared



II



III



IV

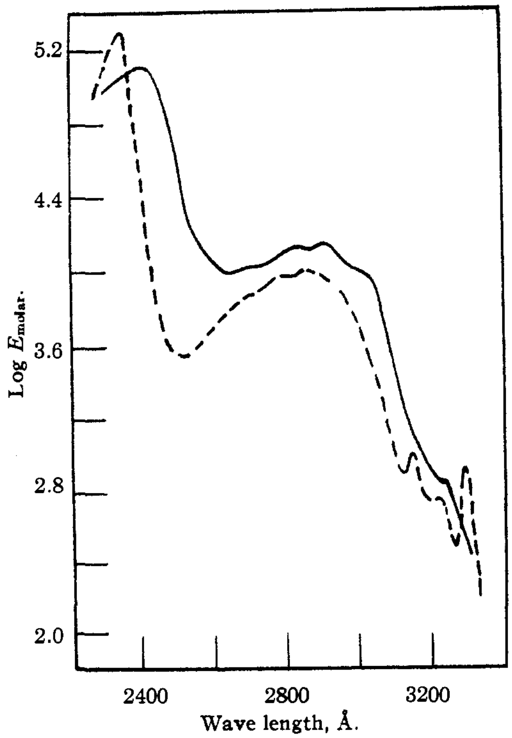


Fig. 2a.—Absorption spectra: ———. phenyl-(1-naphthyl)-(2-naphthyl)-carbinol (solvent dioxane): - - - - -, calcd. summation curve for 1 mole of 1-methylnaphthalene, 1 mole of 2-methylnaphthalene and 1 mole of toluene.

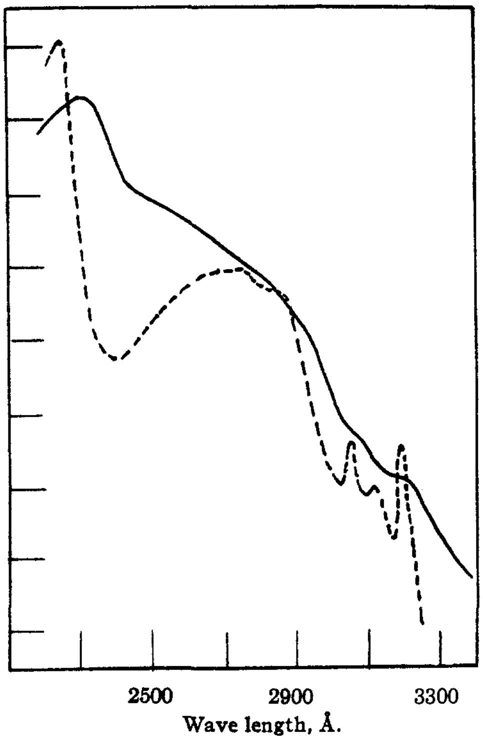


Fig. 2b.—Absorption spectra: ———. phenyl-di-(2-naphthyl)-carbinol (solvent dioxane); - - - - -, calcd. summation curve for 2 moles of 2-methylnaphthalene and 1 mole of toluene.

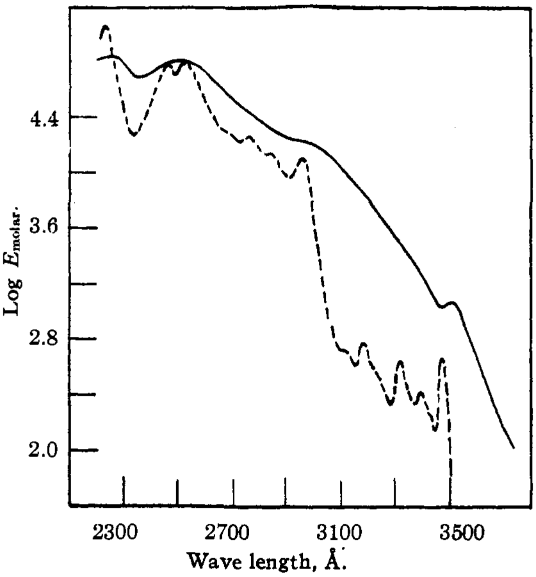
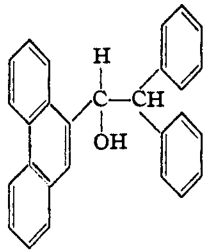


Fig. 3.—Absorption spectra: ———, phenyl-(1-naphthyl)-(9-phenanthryl)-carbinol (solvent *n*-heptane); - - - - -, calcd. summation curve for 1 mole of 9-methylphenanthrene, 1 mole of 1-methylnaphthalene and 1 mole of toluene.

with the curve obtained by adding together at each wave length the molar extinction coefficients of toluene, 1-methylnaphthalene and 2-methylnaphthalene. The spectra of these three carbinols show a reasonably close parallelism with the computed addition curves, although in all cases there is a loss of detail in the resolution of vibrational fine structure, and an over-all increase in the intensity of absorption. The maximum of highest intensity (2240 Å.) in the computed spectra of the carbinols II and III suffers a significant bathochromic shift. While the agreements between the computed and observed curves are by no means perfect, the resemblances are close enough to justify the use of such computed curves in attempts at prediction of the structure of unknown compounds from their ultraviolet absorption spectra. In considering data of this kind, the additive contribution of the benzene chromophore may be neglected, as it is very small in comparison with that of the 1-naphthyl, 2-naphthyl and 9-phenanthryl chromophores. Experimental evidence of this is provided by the comparison of the spectra of benzhydryl-(9-phenanthryl)-carbinol (V) and 9-ethylphenanthrene in Fig. 4.



V

Some aryl carbinols readily undergo cyclic de-

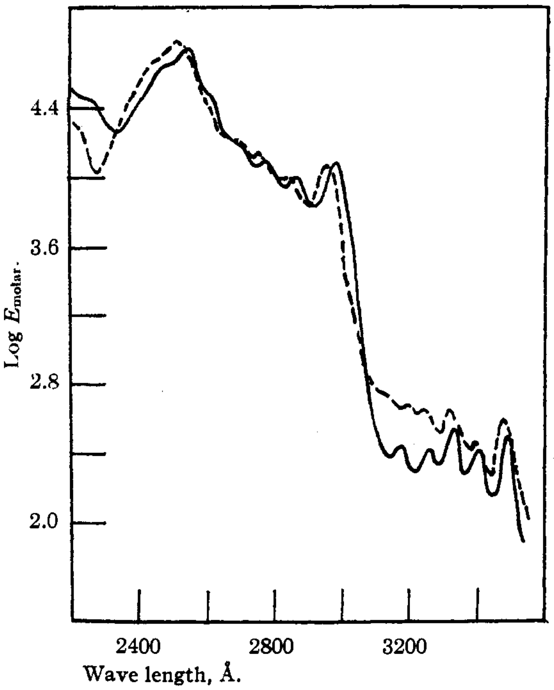
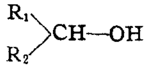


Fig. 4a.—Absorption spectra: ———, benzhydryl-(9-phenanthryl)-carbinol (solvent *n*-heptane); - - - - -, 9-ethylphenanthrene (solvent ethanol).

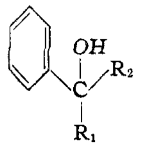
Fig. 4b.—Absorption spectra: - - - - -, fluorene (solvent ethanol); ———, 9-phenylfluorene (solvent ethanol).

hydration to yield polybenzfluorene derivatives.[1] If the diaryl carbinol VI undergoes such a reac-



$R_1R_2CH{-}OH$

VI



VII

tion, the product is a polybenzfluorene unsubstituted at the 9-position, while cyclization of the phenyl-diaryl-carbinol VII yields a 9-phenyl-polybenzfluorene.[2]

The spectra of several unsubstituted polybenzfluorenes have been reported in the literature[3] and, as would be expected on theoretical grounds, the curves differ considerably from those of the related carbinols, the main changes being in the region between 3000 and 4000 Å. where the intensity of absorption is greatly increased. The absorption spectra of many fluorene hydrocarbons show a very steep and unbroken rise at the long wave length end of the curve which is rarely observed in the spectra of other types of polynuclear aromatic hydrocarbons.

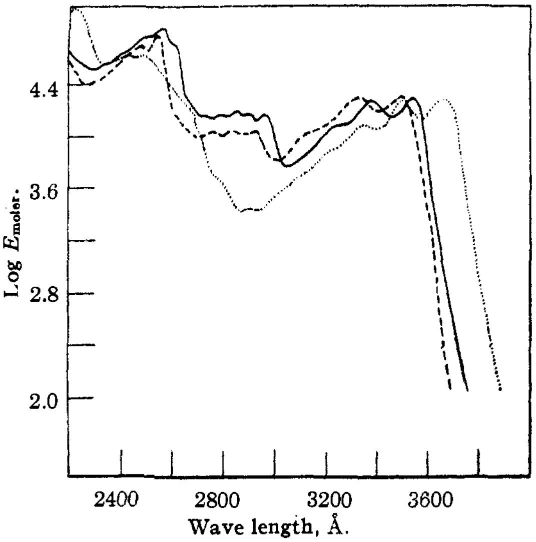
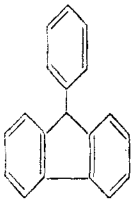
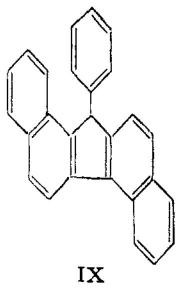


Fig. 5.—Absorption spectra: ————, 9-phenyl-1,2,5,6-dibenzfluorene (solvent dioxane); -----, 1,2,5,6-dibenzfluorene (solvent ethanol); ......, 9-phenyl-3,4,5,6-dibenzfluorene (solvent *n*-heptane).

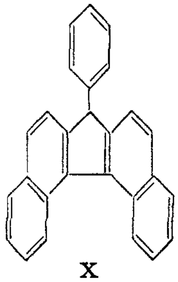
The introduction of a phenyl substituent at the 9-position should not alter the spectrum as the phenyl group in such compounds is not conjugated with the main aromatic system, and, as has been observed above, the additive contribution of the phenyl chromophore under these conditions is negligible. The spectra of 9-phenylfluorene (VIII), and of 9-phenyl-1,2,5,6-dibenzfluorene (IX) which are compared with the relevent unsubstituted polybenzfluorenes in Figs. 4 and 5, provide experimental evidence in support of these considerations. The spectrum of 9-phenyl-3,4,5,6-dibenzfluorene (X) is also included in Fig. 5, although data for the corresponding unsubstituted dibenzfluorene are not available.



VIII



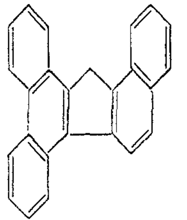
IX



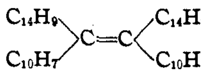
X

Hydrocarbons Produced by the Reaction between Phenanthrene-9-aldehyde and α-Naphthylmagnesium Bromide

Bergmann and Israelashwili[1] isolated as the products of the above reaction two hydrocarbons (melting points 133 and 236°) for which they tentatively suggested the structures XI and XII, respectively.[4]



XI



$(C_{14}H_9)(C_{10}H_7)C{=}C(C_{14}H_9)(C_{10}H_7)$

XII

The spectra of these two hydrocarbons are recorded in Figs. 6 and 7, together with the spectrum of 9-phenyl-1,2,3,4,7,8-tribenzfluorene (XIII) obtained by the cyclic dehydration of the carbinol XIV. A consideration of these curves, together with those of the compounds discussed earlier in this paper, makes it possible to assign probable structures to the two new hydrocarbons.

The spectrum of the compound with structure XI should resemble closely that of XIII, since these differ only in the presence of the 9-phenyl substituent in XIII. A comparison of the two

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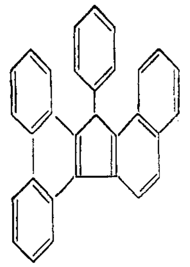
[1] Bergmann and Israelashwili. This Journal, 67, in press (1945); also earlier publication of F. Bergmann, *et al.*

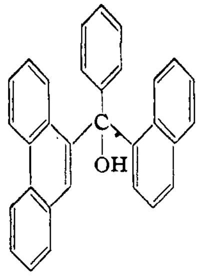
[2] Bergmann and Israelashwili (see ref. 1) have shown that in the cyclic dehydration of aryl carbinols of type VII ring closures involving participation of the phenyl group do not occur.

[3] Jones, *Chem. Rev.*, 32, 1 (1943).

[4] Private communication from Professor Bergmann.



XIII



XIV

curves in Fig. 6 shows that on spectrographic grounds it would seem justifiable to assign structure XI to the hydrocarbon of *higher* melting point (236°).

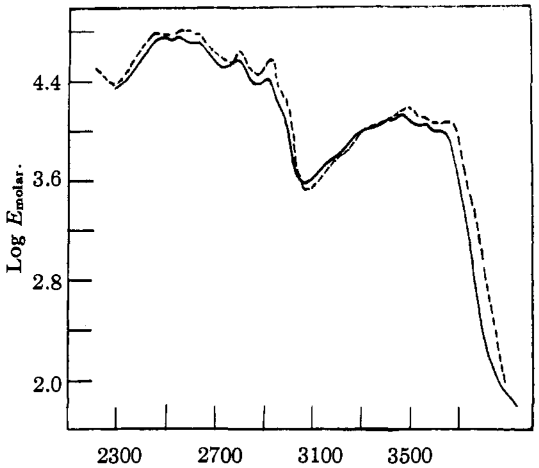
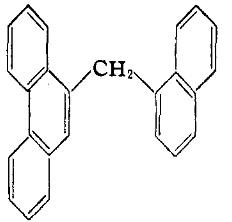


Fig. 6.—Absorption spectra: ———, hydrocarbon of Bergmann and Israelashwili, m. p. 236° (solvent ethanol); - - - - -, 9-phenyl-1,2,3,4,7,8-tribenzfluorene (solvent *n*-heptane).

The structure XI having thus been assigned, on the basis of the spectrographic evidence, to the hydrocarbon of higher melting point, it seemed reasonable to suggest that the other structure (XII) might be attributed to the second hydrocarbon with the lower melting point. A study of the spectrum of this compound (Fig. 7) does not support this view, since a compound with structure XII should show high intensity absorption in the 3000–4000 Å. region of the spectrum.[5] In fact, the spectrum of the lower melting hydrocarbon suggests the presence of a phenanthrene chromophore, and shows a close resemblance to the summation curve calculated for an equimolar mixture of 9-methylphenanthrene and 1-methylnaphthalene. It is therefore proposed that the hydrocarbon of melting point 133° has the structure XV, and results from a reductive Grignard reaction.



XV

The agreement between the calculated summation curve and the observed curve for the compound of structure XV is better than that observed between the aryl carbinols and the computed summation curves recorded in Figs. 2 and 3. It would be reasonable to expect that the presence of the hydroxyl group on the quaternary carbon atom in the carbinols might cause a greater disturbing effect on the adjacent non-conjugated aryl chromophores, both on account of its size and its polar character.

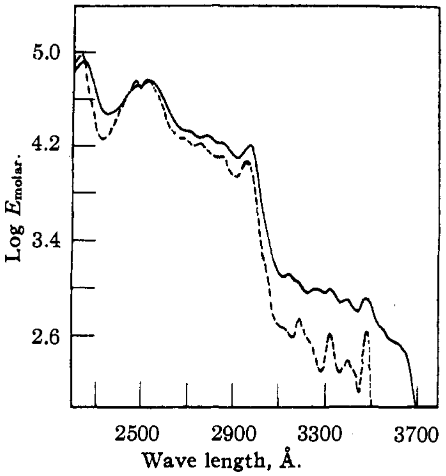
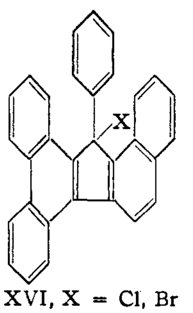


Fig. 7.—Absorption spectra: ———, hydrocarbon of Bergmann and Israelashwili, m. p. 133° (solvent *n*-heptane); - - - - -, calcd. summation curve for 1 mole of 9-methylphenanthrene and 1 mole of 1-methylnaphthalene.

The spectra of the monochloro and monobromo derivatives of 9-phenyl-1,2,5,6,7,8-tribenzfluorene (Fig. 8) to which Bergmann and Israelashwili attribute the structure XVI are of interest in this respect.



XVI, X = Cl, Br

The general shapes of the three curves in Fig. 8 are similar, but the halogen attached to the quaternary carbon atom depresses the intensity

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(5) Compare the spectrum of tetra-(9-phenanthryl)-ethylene, THIS JOURNAL, 65, 1818 (1943).

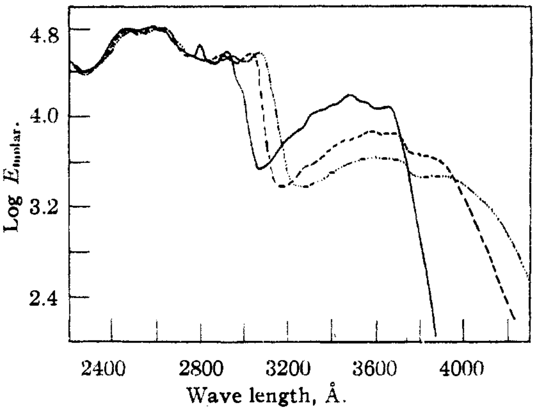

Fig. 8.—Absorption spectra: ————, 9-phenyl-1,2,3,4,7,8-tribenzfluorene (solvent *n*-heptane); - - - - -, monochloro derivative of above hydrocarbon (solvent *n*-heptane); . . . . . ., monobromo derivative of above hydrocarbon (solvent *n*-heptane).

of the long wave length group of absorption bands, and broadens them considerably, the effect increasing progressively in changing from chlorine to bromine. While the spectra of these two halogen derivatives are reconcilable with the proposed structures, not sufficient is known regarding the effects of similarly placed halogens in other compounds to justify stronger support of the proposed structures on the basis of the spectrographic data.

Experimental

The absorption spectra were determined on a Beckman ultraviolet spectrophotometer, using a constant band width of 10 Å. The positions and intensities of the absorption maxima are listed in Table I.

TABLE I

WAVE LENGTHS (Å.) AND INTENSITIES (LOG E_{molar}) OF ABSORPTION MAXIMA

Compound	Solvent	Absorption maxima	
		Wave length	Intensity
2-(1-Naphthyl)-ethylamine (I)[a]	*N* NaOH in 50% ethanol	(2520)[e]	3.30
		(2620)	3.58
		2720	3.77
		2830	3.84
		(2920)	3.68
		3135	2.60
Phenyl-(1-naphthyl)-(2-naphthyl)-carbinol (II)[b]	Dioxane	2300	5.10
		2730	4.12
		2810	4.14
		(2940)	3.93
		3130	2.85
Phenyl-di-(2-naphthyl)-carbinol (III)[b]	Dioxane	2320	4.95
		(2820)	3.94
		(2940)	3.60
		(3080)	3.04
		(3200)	2.82
Phenyl-(1-naphthyl)-(9-phenanthryl)-carbinol (IV)[c]	*n*-Heptane	2270	4.86
		2520	4.81
		(3000)	4.20
		3530	3.06
Benzhydryl-(9-phenanthryl)-carbinol (V)[c]	*n*-Heptane	(2250)	4.48
		(2470)	4.72
		2540	4.76
		(2620)	4.48
		(2700)	4.23
		2770	4.12
		2860	4.02
		2980	4.08
		3180	2.43
		3260	2.42
		3330	2.52
		3410	2.41
		3480	2.49
9-Ethylphenanthrene[c]	Ethanol	(2480)	4.72
		2520	4.79
		(2700)	4.21
		2760	4.14
		2840	4.00
		2960	4.06
		3200	2.68
		3240	2.66
		3320	2.66
		3400	2.46
		3480	2.60
9-Phenylfluorene (VIII)	Ethanol	(2580)	4.18
		2650	4.24
		(2750)	4.08
		2920	3.73
		3030	3.92
9-Phenyl-1,2,5,6-dibenzfluorene[b] (IX)	Dioxane	(2500)	4.78
		2570	4.84
		(2620)	4.72
		2720	4.17
		2780	4.17
		2850	4.21
		(2900)	4.17
		2960	4.18
		(3240)	4.08
		3380	4.29
		3550	4.32
1,2,5,6-Dibenzfluorene	Ethanol	*d*	*d*
9-Phenyl-3,4,5,6-dibenzfluorene[b] (X)	Dioxane	2220	4.98
		2440	4.62
		2490	4.63
		(2680)	4.20
		(2780)	3.68
		2920	3.44
		(3210)	3.88
		3360	4.09
		3500	4.29
		3660	4.30
Hydrocarbon of Bergmann and Israelashwili (m. p. 236°)[c] (XI)	Ethanol	2490	4.87
		2550	4.87
		2620	4.83
		2770	4.69
		2910	4.56
		(3300)	4.13
		3470	4.26
		3560	4.18
		3630	4.12

TABLE I (*Concluded*)

Compound	Solvent	Absorption maxima	
		Wave length	Intensity
9-Phenyl-1,2,3,4,7,8-tribenzfluorene[c] (XIII)	*n*-Heptane	2460	4.80
		2560	4.81
		(2610)	4.80
		2800	4.68
		2930	4.61
		(3000)	4.20
		(3310)	4.02
		(3410)	4.10
		3490	4.20
		(3550)	4.12
		3660	4.09
Hydrocarbon of Bergmann and Israelashwili (m. p. 133°)[c] (XV)	*n*-Heptane	2240	4.91
		2480	4.75
		2530	4.80
		2700	4.35
		2770	4.33
		2840	4.27
		2970	4.24
		3140	3.14
		3250	3.03
		3320	3.03
		3400	2.95
		3480	2.98
		(3550)	2.70
		(3630)	2.58
Monochloro derivative of 9-phenyl-1,2,3,4,7,-8-tribenzfluorene[c] (XVI, X = Cl)	*n*-Heptane	(2420)	4.73
		2470	4.80
		2580	4.82
		2640	4.82
		(2860)	4.55
		2900	4.57
		3015	4.59
		(3280)	3.56
		(3420)	3.74
		3580	3.87
		3660	3.86
		(3820)	3.66
Monobromo derivative of 9-phenyl-1,2,3,4,7,-8-tribenzfluorene[c] (XVI, X = Br)	*n*-Heptane	2480	4.82
		2600	4.80
		(2650)	4.77
		2930	4.58
		3060	4.60
		(3450)	3.56
		3610	3.65
		3860	3.48

[a] Compound supplied by Dr. R. C. Clapp. [b] Compound supplied by Dr. E. Berliner. [c] Compound supplied by Dr. F. Bergmann. [d] See Maynoerd and Roe, *Proc. Roy. Soc.* (London), **A158**, 634 (1937). [e] Wave lengths in parentheses refer to points of inflexion.

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Summary

The ultraviolet absorption spectra of three aryl carbinols are compared with the computed summation spectra which would be predicted for compounds of this type on the assumption that each aryl group contributes to the spectrum as an independent chromophore. The effects on the spectra of the cyclic dehydration of these carbinols to polybenzfluorenes are noted, and on the basis of these observations structures are assigned to two hydrocarbons which have been isolated by Bergmann and Israelashwili from the products of the reaction between phenanthrene-9-aldehyde and α-naphthylmagnesium bromide.

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The Continuous Thermal Isomerization of α-Pinene in the Liquid Phase

BY T. R. SAVICH AND L. A. GOLDBLATT

The thermal isomerization reaction of α-pinene at atmospheric pressure in the vapor phase at temperatures from 300–400° has been extensively studied by Arbuzov,[1] Charlton and Day,[2] Dupont and Dulou,[3] and Goldblatt and Palkin.[4] The results of the vapor phase reaction at 375° indicate that roughly equal proportions of dipentene and *allo*-ocimene each in approximately 40% yield[4] could be obtained with substantially complete conversion of α-pinene. The remainder of the product included about 12% α- and β-pyronenes. It has been further shown by Goldblatt and Palkin[5] that α- and β-pyronenes result from *allo*-ocimene cyclization.

Previous study of the reaction in the liquid phase by Wallach,[6] Smith,[7] Thurber and Johnson,[8] Conant and Carlson,[9] and Fuguitt and Hawkins[10] has been limited to batch reactions in

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[1] Arbuzov, *J. Gen. Chem.* (U.S.S.R.), **3**, 21 (1933); *Ber.*, **67B**, 563 (1934).

[2] Charlton and Day, *Ind. Eng. Chem.*, **29**, 92 (1937).

[3] Dupont and Dulou, *Compt. rend.*, **201**, 219 (1935); *Atti X° Congr. Intern. Chim.*, **3**, 127 (1939).

[4] Goldblatt and Palkin, THIS JOURNAL, **63**, 3517 (1941).

[5] Goldblatt and Palkin, *ibid.*, **66**, 655 (1944).

[6] Wallach, *Ann.*, **227**, 282 (1885).

[7] Smith, THIS JOURNAL, **49**, 43 (1927).

[8] Thurber and Johnson, *ibid.*, **52**, 786 (1930).

[9] Conant and Carlson, *ibid.*, **51**, 3464 (1929).

[10] Fuguitt and Hawkins, *ibid.*, **67**, 242 (1945).