U.D.C. 547.677.6 : 544.621/623

10-2

16. Eiji Ochiai, Toshihiko Okamoto, Shin-ichiro Sakai, and Mitsutaka Natsume: Syntheses of Alkylphenanthrenes. IV.[1] On Ultraviolet and Infrared Spectra of Alkylphenanthrenes.

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Previously, we reported that several alkylphenanthrenes were isolated as the dehydrogenation products of anhydroignavinol[2] and hypognavinol,[3] and one of the products from hypognavinol was identified as 1,8-dimethylphenanthrene.[1] The properties of these alkylphenanthrenes are shown in Table I.

TABLE I.

	Alkylphenanthrenes derived from anhydroignavinol			Alkylphenanthrenes derived from hypognavinol	
	m.p. (°C)	Trinitrobenzene complex m.p. (°C)	Picrate m.p. (°C)	m.p. (°C)	Trinitrobenzene complex m.p. (°C)
I	89~90[2,3]	156~158	142~144	89~90.5[3]	—
II	145~147	160~162	135~137	—	—
III	Oil	173~175	155~157	—	173~175
IV	Oil	175~177	—	—	—
V	—	—	—	187~191	—

Fig. 1 shows the infrared spectra (11~15 μ) of these alkylphenanthrenes.

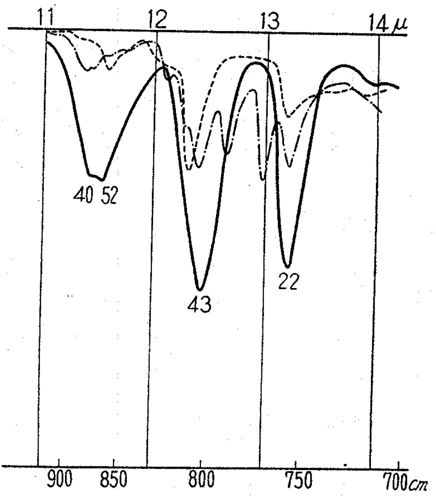

Fig. 1.

————	m.p. 89~90°	10 mg./cc. CS_2
—·—·—	m.p. 145~147°	7 mg./cc. CS_2
------------	Oil (Trinitrobenzene complex, m.p. 173~175°)	5 mg./cc. CS_2

In connection with the structures of these phenanthrenes, we reported the syntheses of alkylphenanthrenes in the previous papers of this series. This paper treats the analyses of the ultraviolet and infrared spectra of these synthesized phenanthrenes as well as those from natural alkamines.[2]

Ultraviolet Spectra

The ultraviolet spectra are summarized in Table II. Askew[4] already pointed out that the size of alkyl group introduced into phenanthrene did not affect the wave length shift and that the shift was affected mostly by the position introduced, while the intro-

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[1] Part III: This Bulletin, **5**, 108(1957).

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[4] J. Chem. Soc., **1935**, 509.

TABLE

		max.	min.	max.	min.	max.	min.	max.	min.	max.	min.
1	Phenanthrene	345 2.30	341 1.97	337 2.33	333 2.16	329 2.45	326 2.34	322 2.47	318 2.30	314 2.42	310 2.34
2	3-Ethyl	348 2.59	344 2.16	340 2.39	337 2.25	332 2.62	328 2.33	325 2.42	321 2.27	317 2.47	313 2.35
3	3,10-Dimethyl	351 2.78	347 2.56	341~342* 2.65		335 2.84	330.5 2.72	324~327* 2.76		319 2.84	317.5 2.83
4	2-Ethyl-5-methyl	347~348* 2.32				332.5 2.51	329 2.50				
5	1-Ethyl-6-isopropyl	350 2.57	344 2.38			334 2.67	325 2.46			318 2.60	315 2.57
6	1-Isopropyl-6-ethyl	351 2.63	345 2.43			334.5 2.72	325 2.52			318 2.68	316 2.64
7	1,8-Dimethyl	352 2.27	349 2.15	342~344* 2.36		336 2.55	332 2.47	326~328* 2.50			
8	1-Methyl-8-ethyl	352 2.28	348 2.17	343.5 2.35	341 2.34	335 2.51	331 2.43	327~328* 2.48			
9	1,6,9-Trimethyl	354 2.84	349 2.47			337 2.85	330~331* 2.55		327 2.52	321 2.70	318 2.63
10	1-Isopropyl-6,9-dimethyl	354 2.84	348.5 2.50			338 2.85	330~331* 2.58		327 2.57	322 2.71	318 2.65
11	1-Methyl-2,6-dimethyl	352 2.49	348 2.34			336 2.65	332 2.56	329 2.64	325 2.58	321 2.68	318 2.67
12	1,6,7-Trimethyl	352 2.54	348 2.25	343.5 2.34	342 2.32	335 2.69	329~330* 2.46		325 2.42	320 2.60	315 2.51
13	1-Ethyl-6,7-dimethyl	352 2.50	348 2.27	341* 2.34		335 2.63	329 2.46				
14	1-Propyl-6,7-dimethyl	352 2.50	348 2.27	344 2.34	342.5 2.30	335 2.66	326~328* 2.44		325 2.43	319 2.67	316.5 2.66
15	1-Isopropyl-6,7-dimethyl	352 2.55	348 2.39	341~343* 2.48		335 2.73	330 2.59	327 2.60	325.5 2.59	319.5 2.72	316 2.69
16	1-Butyl-6,7-dimethyl	352 2.50	348 2.27	341~342* 2.36		335 2.67	325~330* 2.46			319 2.66	316.5 2.63
17	1,6-Dimethyl-7-isopropyl	353 2.67	348 2.39	343~344* 2.48		335 2.70	325~327* 2.45			319 2.60	317 2.54
18	1,7-Dimethyl-6-isopropyl	352 2.41	347.5 2.32	343* 2.38		336 2.65	326~329* 2.48		319* 2.68		
19	1,7-Dimethyl-6-ethyl	352 2.44	348 2.24	344* 2.31		336 2.63	327.5* 2.40		326 2.39	320 2.57	317 2.54
20	1-Methyl-6,7-diethyl	352.5 2.53	348 2.29	343~344* 2.35		336 2.70	326~331* 2.50			320 2.69	317 2.67
21	1-Methyl-6,7-(2′-methylcyclopenteno)**	353 3.01	347 2.56	343~344* 2.58		336 3.04		330* 2.67	326.5 2.64	321 2.85	316 2.68

* Inflexion.

** 9,10-Dihydro-4,9-dimethyl-8*H*-cyclopenta[*b*]phenanthrene (Ring Index).

II.

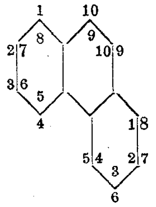
max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.	min.
308 2.35	306 2.32	292.5 4.13	287 3.76	281 4.04	278 3.99	274 4.15	270 4.09			250.5 4.76	245～246* 4.67		226 4.16
		296 4.08	290 3.78	284 3.98	282 3.96	276 4.11	273 4.08			253 4.73			228 4.07
		298 3.99	292 3.81	285 3.97	284 3.96	277.5 4.09	276 4.08	269～272* 4.12		254 4.68			230 4.36
		298 4.01	292.5 3.85	286 3.97	284 3.96	277 4.08	274 4.07			253 4.84			230 4.06
		301 4.13	295 3.90	289.5 4.06	284 3.95	278.5 4.07	275.5 4.05			257 4.72	250* 4.65		232.5 3.99
		301 4.18	295 3.95	289 4.10	285 3.99	279 4.12	276 4.09			257 4.76	250* 4.69		232 4.05
		305 4.25	298 3.87	292.5 4.16	287 3.90	281 4.05	278 3.99			258 4.75	252～254* 4.65		231 3.90
		304 4.22	298 3.93	292 4.16	286 3.97	281 4.07	277 4.02			258 4.77	254 4.68	252 4.69	
		303.5 4.16	297 3.90	291 4.08	287 3.96	281 4.11	278 4.08			259 4.77	251～253* 4.69		233 4.03
		303 4.16	297 3.91	291 4.09	287 3.98	280 4.13	277.5 4.10			259 4.76	251～252* 4.69		233 4.10
		302.5 4.14	297 3.90	291 4.09	287.5 4.05	281 4.19	278 4.16			259.5 4.70	253* 4.62		239.5 4.20
		302 4.09	295.5 3.87	289 4.03	286 4.00	280 4.13	277 4.05			259 4.80	252～253* 4.70		
		302 4.13	296 3.81	290 4.03	286.5 3.99	280.5 4.14	277 4.10			258.5 4.80	250* 4.70		234 4.17
		302 4.13	295 3.78	290 3.99	286.5 3.93	280 4.07	277 4.02			259 4.75	250 4.65		
		302 4.16	296 3.83	290 4.07	286 4.01	281 4.17	277 4.12			259 4.79	252～253* 4.71		
		302 4.05	295 3.58	290 3.78	286 3.62	281 3.82	277 3.67			259 4.63	251～253* 4.52		
		302.5 4.20	297 3.89	290 4.12	286.5 4.07	281 4.22	277.5 4.18			259 4.87	252～253* 4.76		
		303 4.16	296.5 3.89	291 4.08	287 4.01	281 4.21	278.5 4.19			259.5 4.90	252～253* 4.80		
		303 4.17	296.5 3.87	291 4.08	287 4.00	281 4.16	277 4.11			259 4.88	252～253* 4.79		
		303 4.16	297 3.84	291 4.06	287 4.01	281 4.17	278 4.12			260 4.83			
		302 4.27	296.5 4.09	288～289* 4.26		279～281* 4.40		272～274* 4.53		258.5 4.91	252～253* 4.85		

duction of a substituent in the 1-position was the most effective. After Heilbronner,[5] the absorption spectra of phenanthrene and its alkyl derivatives can be classified into three groups; group-I (absorptions between 300~350 mμ), group-II (absorptions between 280~300 mμ), and group-III (absorptions between 240~260 mμ).

The first maximum in the second group (phenanthrene : 291 mμ, log ε 4.17) is most sensitive to wave length shift by introduction of substituents. This absorption maximum was examined with 58 examples and Table III shows the data.

TABLE III.

Position of substituents in phenanthrene	Reverse numbering	Mean value of 1st max. of group-II	Min. and max. values	No. of examples	Reference
0	0	292.2	(291~293)	3	a), b), f)
1	8	300	(300)	1	a)
2	7	294	(294)	1	b)
3	6	296	(296)	1	f)
9	10	297	(297)	2	c)
1,2	7,8	300	(300)	3	a), b), d)
1,3	6,8	303	(303)	1	a)
1,6	3,8	301	(301)	3	b), f)
1,7	2,8	300.4	(300~301)	10	a), b), d)
1,8	1,8	305	(304~306)	3	a), f)
1,9	8,10	303	(303)	1	a)
2,3	6,7	297	(297)	1	a)
2,5	4,7	298	(298)	2	a), f)
3,10	6,9	298	(298)	1	f)
4,5	4,5	313	(313)	1	e)
4,9	5,10	299	(299)	1	a)
9,10	9,10	300	(300)	1	c)
1,2,6	3,7,8	302.3	(302~302.5)	2	b), f)
1,2,7	2,7,8	302	(302)	1	a)
1,2,8	1,7,8	307	(307)	2	a), b)
1,2,9	7,8,10	304	(304)	1	b)
1,3,7	2,6,8	304	(304)	1	a)
1,4,7	2,5,8	307	(307)	1	a)
1,6,7	2,3,8	302.4	(302~303)	10	a), f)
1,6,9	3,8,10	303.3	(303~303.5)	2	f)
1,2,7,8	1,2,7,8	307.5	(307~308)	2	b)



a) Askew : J. Chem. Soc., **1935**, 509.
b) Heilbronner : Helv. Chim. Acta, **32**, 1723(1949).
c) J. Chem, Soc., **1952**, 986.
d) J. Org. Chem., **20**, 884(1955).
e) J. Am. Chem. Soc., **71**, 3664(1949).
f) Our data.

From these data the effect of substituents at each position to the wave length shift of the first maximum of group-II was calculated by subtracting the values of absorption maxima of monosubstituted phenanthrenes from those of disubstituted phenanthrenes, disubstituted from trisubstituted, and trisubstituted from tetrasubstituted. The mean values are shown in Table IV.

TABLE IV.

Position of substituent in phenanthrene	Wave length shift(mμ) 292.2+
1 (8)	+6.0
2 (7)	+1.1
3 (6)	+2.7
4 (5)	+4.0
9 (10)	+3.7

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[5] Helv. Chim. Acta, **32**, 1723(1949).

By calculations with these data, the following three cases were observed as exceptions. a) 1,4–Disubstituted alkylphenathrenes show abnormaly strong shift. This fact will be considered as somewhat related to the "diyl" state.⁶⁾ b) The two types, 3,10– and 4,9–disubstituted phenanthrenes show unusually weak shift. In these cases the carbon *para* to the substituents has no hydrogen and this fact may give some explanations to the above phenomenon. Alkylphenanthrenes substituted in 2–position are in smilar situation, so 1.1 mμ of very weak shift by the substituents at this position shown in Table IV can be understood from the above reason. c) 4,5–Disubstituted cases were considered also as an exception (calculated : 300.2 mμ. Found : 313 mμ⁷⁻⁹⁾). This will be considered as an example of the "crowding effect"¹⁰⁾ and understood as a steric hindrance.

Infrared Spectra

The absorptions between 11∼15 μ in benzene derivatives¹¹⁾ are well known to be associated with out–of–plane bending vibrations of the aromatic CH groups. The spectra of methylanthracenes¹²⁾ and cyclopentenophenanthrenes¹³⁾ are also classified from the same point of consideration. The infrared spectra of the present series of compound are shown in Fig. 2.

The spectroscopic data of phenanthrene can be analyzed into six groups of 1,2,3,4,5–pentasubstituted, 1,2,3,4–tetrasubstituted, 1,2,4,5–tetrasubstituted, 1,2,3–trisubstituted, 1,2,4–trisubstituted, and 1,2–disubstituted benzene rings. The band at 11.43∼11.55 μ is of a medium intensity in the spectra and can be assigned to that of 1,2,3,4,5–pentasubstituted benzene ring. The band at 12.17∼12.50 μ (21 examples) are considered to be characteristic of 1,2,3,4–tetrasubstitution. This type of absorption associated with 9,10–CH vibration seems to become weaker or to disappear when A– or C–ring is substituted with one alkyl group at 3– or 6–position.

The absorption at 11.23∼11.58 μ, often doubled, is of medium intensity and observed in 2,3–disubstituted and 1,6,7–trisubstituted phenanthrenes. Also in the latter case, the difference of the group size at 6,7–positions affects the absorption wave length in this region. So this can be characteristic of 1,2,4,5–tetrasubstitution. The region of 12.94∼13.29 μ contains a strong absorption (18 examples) and is taken to be characteristic of 1,2,3–trisubstitution. The band at 11.82∼12.35 μ (10 examples) is a strong absorption and can be characteristic of 1,2,4–trisubstitution. The band at 13.38∼13.58 μ (4 examples) is of strong intensity in the spectra and seems to be characteristic of 1,2–disubstitution. These assignments are compared with those of 1,2–cyclopentenophenanthrenes¹³⁾ and shown in Fig. 3.

The Ultraviolet and Infrared Spectra of Alkylphenanthrenes obtained as the Dehydrogenation Products of Alkamines

The alkylphenanthrene of m.p. 187∼191°, which was isolated as one of the dehydrogenation products of hypognavinol, was identified as 1,8–dimethylphenanthrene by admixture with the synthesized sample. The observed value of the maximum of ultraviolet spectrum (305 mμ) also agrees well with the calculated value (292.2+6.0+6.0=304.2 mμ). The alkylphenanthrene of m.p. 89∼90.5° shows absorption band at 13.22 μ in the infrared spectrum which is considered to be that of 1,2,3–substitution and the phenanthrene has no absorption in the region of 13.38∼13.58 μ (1,2–substitution), indicating at

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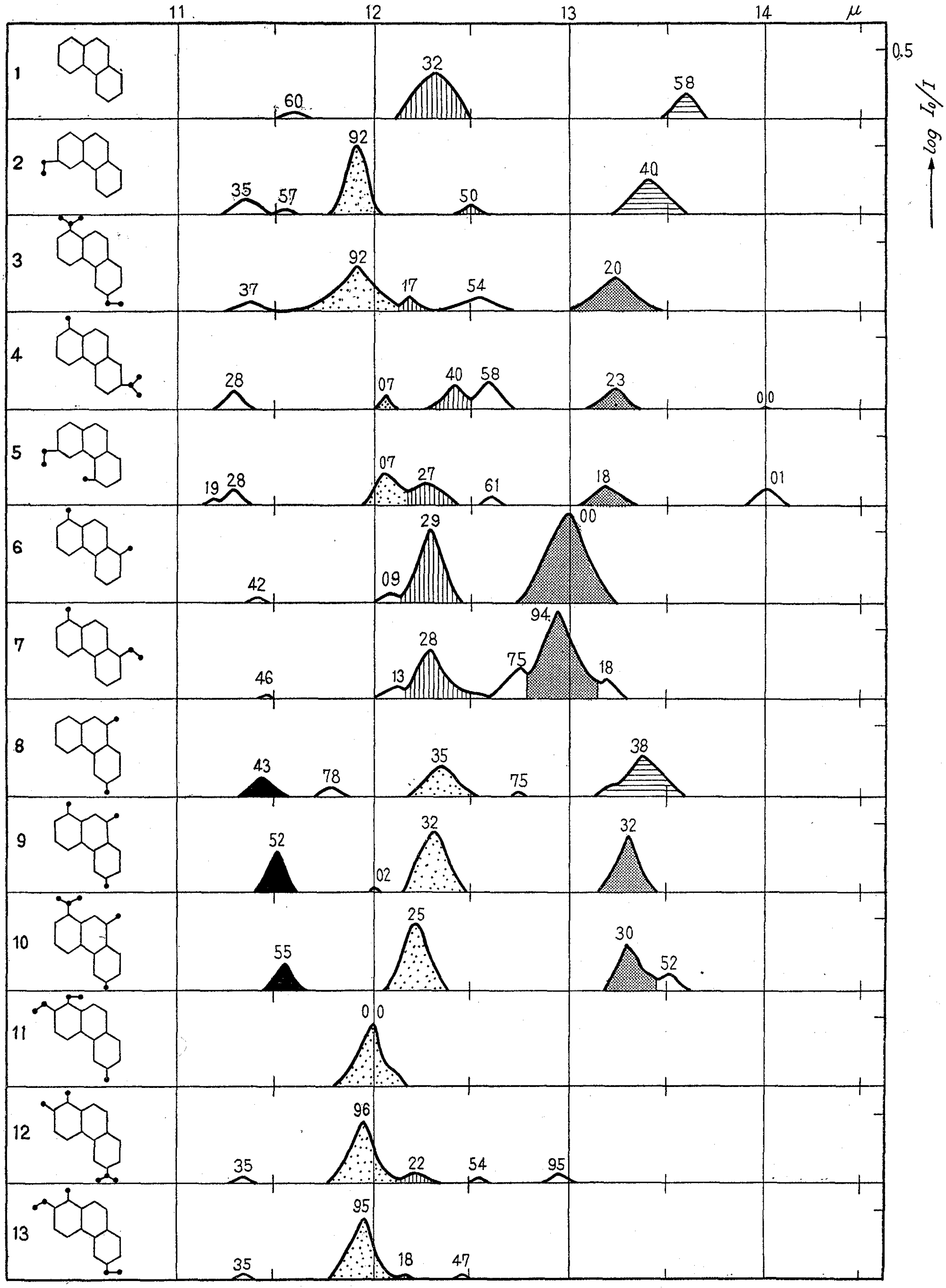
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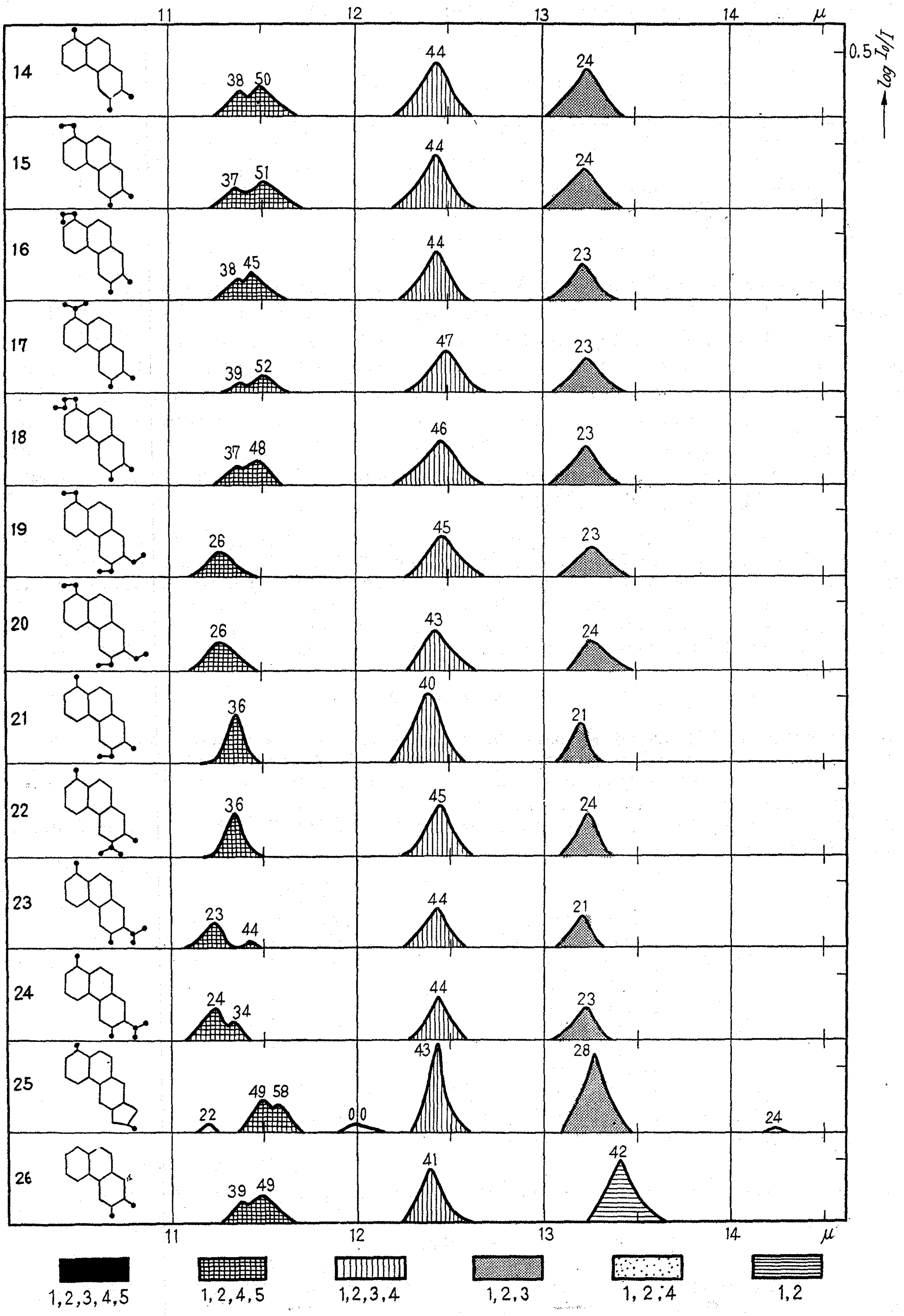
Fig. 2a.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49 58
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28
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Fig. 2b.

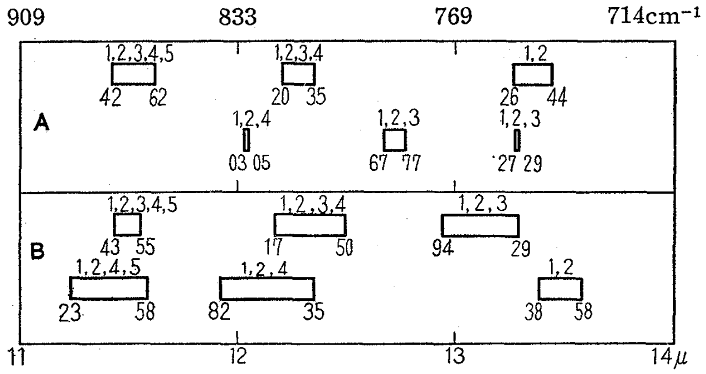

Fig. 3.

A. Cyclopentenophenanthrene

B. Alkylphenanthrene

least one substitution in both rings A and C. The band at 12.43 μ is in the region of 1,2,3,4-substitution, which might be attributed to the absorption of 9,10-CH vibration. The bands at 11.40 and 11.52 μ can be that of 1,2,4,5- or 1,2,3,4,5-substitution. From these considerations, one of the possible type is the 1,6,7-trisubstituted compound and the synthesized samples showed the same absorption type. This agrees also with the calculation of ultraviolet spectra, where the observed value (302.0 mμ) is equal to the calculated value (292.2+6.0+2.7+1.1=302.0 mμ). Although several 1,6,7-trisubstituted alkylphenanthrenes of $C_{19}H_{20}$ type were synthesized, these samples were not indentical with the phenanthrene of m.p. 89~90.5°.

We are grateful to Prof. T. Reichstein and Dr. P. Zoller, Organisch-Chemische Anstalt der Universität Basel, and also to Dr. W. Nagata, Shionogi & Co. Ltd., for kind suggestions to the analyses of the spectroscopic data. The authors are indebted to Mr. S. Tanaka, Engineering Research Institute, University of Tokyo, for many helpful discussions and determinations of infrared spectra, and also for spectral determinations by Dr. K. Kuratani, Institute of Science and Technology, University of Tokyo, and Mr. H. Shindo, Sankyo Co. Ltd., to all of whom the authors' thanks are due.

Experimental

Determination of Ultraviolet Spectra—Beckman Model DU spectrophotometer and Unicam Sp 500 were used and the wave lengths were corrected by Hg-296.7 mμ band. The two bands of phenanthrene (292.5 mμ) and retene (300 mμ) were determined at the same time with each sample. The spectra were measured in 95% EtOH solution.

An Example of the Calculation of the Substituent Effect to the First Band of Group-II in Ultraviolet Spectra

Position of substitution		Wave length shift to phenanthrene max.(292.2 mμ)	
1~0	: 300 ~292.2=	+7.8 mμ	avg. +6.0
1,2~2	: 300 ~294 =	+6.0	
1,3~3	: 303 ~296 =	+7.0	
1,6~6	: 301 ~296 =	+5.0	
1,7~7	: 300.4~294 =	+6.4	
1,8~8	: 305 ~300 =	+5.0	
1,9~9	: 303 ~297 =	+6.0	
1,2,8~2,8	: 307 ~300.4=	+6.6	
1,6,8~6,7	: 302.4~297 =	+5.4	
1,6,9~6,9	: 303.3~298 =	+5.3	
1,2,7,8~2,7,8	: 307.5~302 =	+5.5	
1,4,7~4,7	: 307 ~298 =	+9.0	exception

Infrared Spectra—Baird Infrared spectrophotometer was used and determined in CS_2 solution.

Summary

Ultraviolet and infrared spectra of alkylphenanthrenes were analyzed. In ultraviolet spectra, the absorption maxima were classified into three groups and the first maximum of the group-II (phenanthrene : 291 mμ, log ε 4.17) was the most sensitive to

the wave length shift by introduction of substituents. In infrared spectra the bands between 11∼15 μ were analyzed as out-of-plane bending vibrations of the aromatic CH groups.

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15

17. **Tyunoshin Ukita, Kinzo Nagasawa, and Masachika Irie**: Organic Phosphates. I. Synthesis of 1,2-Diol Cyclic Phosphates.

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Isolation and identification of cyclic 2′,3′-nucleotides as intermediates in the mild alkaline hydrolysis of ribonucleic acid were reported by Markham and Smith.[1] Baer and Kates[2] proposed glycerol 1,2-cyclic phosphate (GCP) (I) as an intermediate in the acid hydrolysis of lecithin to glycerol-L-1, -DL-1 and -2 phosphates.

Recently, Ukita, Bates, and Carter,[3] assuming that GCP should also be an intermediate of the alkaline breakdown of lecithin analogs, tried to isolate this compound. Lecithin (II), L-α-glycerylphosphorylcholine (III), and benzyl-GP[4] (IV) were hydrolysed in various solvents under alkaline conditions. In no case, however, was GCP isolated from the hydrolysis product, although its presence in minor amount was qualitatively detected by paper chromatographic identification with synthetic GCP only in the case of the hydrolysis of (III) and (IV).

The instability of the synthetic GCP in alkaline solutions made it appear unlikely that the cyclic ester can be isolated from alkaline hydrolysates of lecithin.

Several researches on the chemical[5] and enzymatic[6] hydrolysis of cyclic nucleotides as well as on their properties as substrates for enzymatic synthesis of polynucleotides have been reported.[7] However, no investigations have been made on synthesis and properties of cyclic phosphates of simple aliphatic 1,2-diols other than that of glycerol, ones which are also important in biochemical respects.

This paper deals with the synthesis of 1,2-propanediol cyclic phosphate (PCP) (V), ethyleneglycol cyclic phosphate (ECP) (VI), and 2,3-butanediol cyclic phosphate (BCP) (VII), in order to have some evidence on the relationship between chemical or enzymatic properties of these products and their structural differences, which will be reported in subsequent papers.

Two methods have been developed for synthesizing 1,2-diol cyclic phosphates. In

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4) Following abbreviations are used: GCP=glycerol 1,2-cyclic phosphate, PCP=1,2-propanediol cyclic phosphate, ECP=ethyleneglycol cyclic phosphate, BCP=2,3-butanediol cyclic phosphate, EP=ethyleneglycol phosphate, BP=2,3-butanediol phosphate, GP=glycerol phosphate, PP=1,2-propanediol phosphate (preceded by alkyl or cation substituted or number of the position of hydroxyl group concerned with phosphoryl ester where necessary), and TFA=trifluoroacetic acid.

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