[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORY, GENERAL ANILINE AND FILM CORPORATION]

The Ultraviolet Absorption Spectra of Some Polymethylnaphthalenes

BY WILLIAM L. MOSBY[1]

RECEIVED FEBRUARY 5, 1953

The ultraviolet absorption spectra of several polymethylnaphthalenes are given, and features of these spectra are discussed in connection with various properties of the compounds.

The ultraviolet absorption spectra of all of the dimethylnaphthalenes[2] and twelve of the fourteen possible trimethylnaphthalenes[3] have been presented in detail. Of the two trimethylnaphthalenes missing from the Swiss study, the spectrum of 2,3,5-trimethylnaphthalene has been published by Morton and de Gouveia,[4] while that of the 2,3,6-isomer seems unrecorded, although the substance is known.[5] Only one example,[6] apparently, has appeared on the ultraviolet spectra of the higher methylnaphthalenes. The syntheses and infrared spectra of some of these higher methylnaphthalenes were recently presented,[7] but, unfortunately, the infrared spectrograms of these substances, like those of the dimethylnaphthalenes[8] are not amenable to facile interpretation.

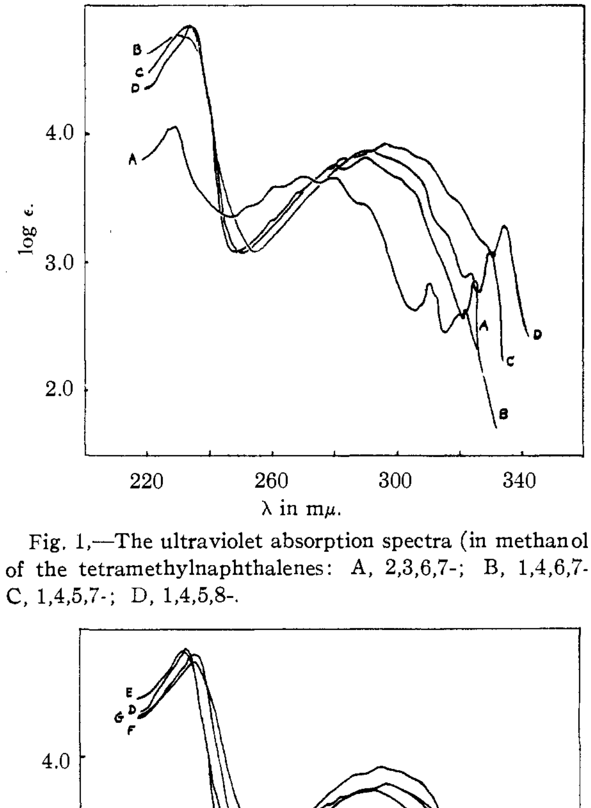

Fig. 1.—The ultraviolet absorption spectra (in methanol) of the tetramethylnaphthalenes: A, 2,3,6,7-; B, 1,4,6,7-; C, 1,4,5,7-; D, 1,4,5,8-.

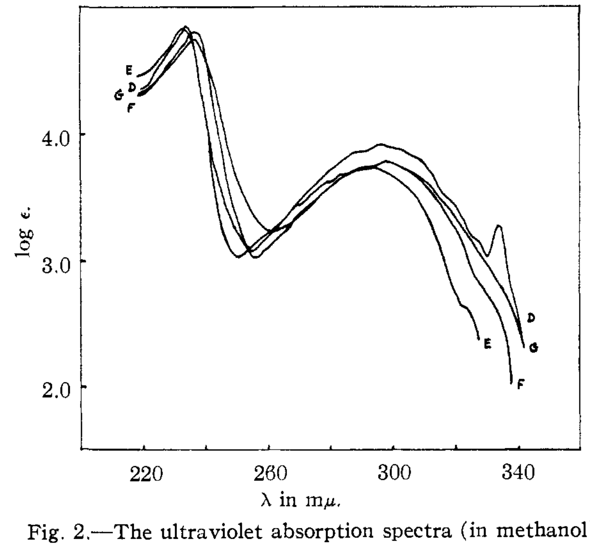

Fig. 2.—The ultraviolet absorption spectra (in methanol) of: D, 1,4,5,8-tetramethylnaphthalene; E, 1,2,3,4-pentamethylnaphthalene; F, 1,2,3,4,5-pentamethylnaphthalene; G, 1,2,3,4,5,8-hexamethylnaphthalene.

Figure 1 shows the ultraviolet absorption spectra of four tetramethylnaphthalenes: 2,3,6,7- (A); 1,4,6,7- (B); 1,4,5,7- (C); and 1,4,5,8- (D). Figure 2 gives the corresponding curves for (D), 1,2,3,4-tetramethylnaphthalene (E), 1,2,3,4,5-pentamethylnaphthalene (F) and 1,2,3,4,5,8-hexamethylnaphthalene (G).

All of the curves show, of course, a bathochromic shift relative to the curve of naphthalene, such as is usually characteristic[9] for alkyl substituted aromatic systems. However, a pronounced gradation in the degree of bathochromic displacement is readily apparent as one progresses from compounds A to D. Since, in compound D, all of the methyl groups occupy positions of greater conjugating power, it would be expected, in accordance with Pullman's[10] conclusions,[11] that this compound would show a greater bathochromic shift than other tetramethylnaphthalenes. This is clearly the case among the tetramethylnaphthalenes whose curves are shown in Figs. 1 and 2, and it is almost certainly true for all other tetramethylnaphthalenes. It is apparent,[12] even in the di-[2] and trimethylnaph-

---

[1] Calco Chemical Division, American Cyanamid Company, Bound Brook, New Jersey.

[2] A. S. Bailey, K. C. Bryant, R. A. Hancock, S. H. Morrell and J. C. Smith, *J. Inst. Petroleum*, **33**, 503 (1947).

[3] E. Heilbronner, U. Frölicher and Pl. A. Plattner, *Helv. Chim. Acta*, **32**, 2479 (1949).

[4] R. A. Morton and A. J. A. de Gouveia, *J. Chem. Soc.*, 917 (1934).

[5] L. Ruzicka and L. Ehmann, *Helv. Chim. Acta*, **15**, 140 (1932).

[6] R. Schwyzer, H. Biswas and P. Karrer, *ibid.*, **34**, 669 (1951).

[7] W. L. Mosby, THIS JOURNAL, **74**, 2564 (1952).

[8] E. E. Vago, E. M. Tanner and K. C. Bryant, *J. Inst. Petroleum*, **35**, 293 (1949).

[9] B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson & Cie, Paris, 1952, p. 515.

[10] B. Pullman, *Compt. rend.*, **222**, 1396 (1946); *Bull. soc. chim. France*, **15**, 533 (1948).

[11] Extensive verification of this principle is to be found in the literature, and among the examples cited in R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951. See also, E. Clar and Ch. Marschalk, *Bull. soc. chim. France*, 433 (1950).

[12] *E. g.*, the following data taken from references 2, 3 and 4:

di- or trimethylnapthalene	$\lambda_{max.}$	log ε
1,4-	289	3.88
1,5-	287	3.96
1,8-	285	3.85
2,3-	279	3.71
2,6-	274	3.67
2,7-	275	3.69
1,4,5-	292	3.90
1,3,6-	284	3.70
2,3,5-	283	3.87
1,3,7-	280	3.74

thalenes,[3] that a greater bathochromic shift is associated with α- than with β-methyl substitution. Attention has been drawn by Badger[13] to evidence supporting the contention that substituents in the α-position of naphthalene are conjugated with the rings to a much greater degree than are such substituents in the β-position. Further support for this contention may be adduced from the curves in Fig. 1, and the data in note 12. Both the bathochromic and hyperchromic displacements exhibited are significant, the greater intensity of absorption evidenced, as usual, by the system having a greater degree of conjugation.[14]

Only a slight difference is detectable in the positions of the absorption maxima exhibited by 1,2,3,4,5-pentamethyl- (F) and 1,2,3,4,5,8-hexamethylnaphthalene (G). This is of interest in view of the pronounced trend toward higher values of λ_{max} as one proceeds from the mono- to the tetramethylnaphthalenes. A further characteristic of the absorption spectra of both F and G is the disappearance of fine structure (especially) from the 300–340 mμ range. This latter effect might arise from the presence of intramolecular strain. Everard and Sutton[15] have explained the anomalous dipole moments of the 4,8-dihalo-1,5-dimethoxynaphthalenes on the basis of such distortion. This strain should naturally be at a maximum in the octamethylnaphthalene, the preparation and study of which would be of interest in this connection.[16] This strain might also be expected to produce a hypsochromic displacement[17] which often counteracts the normal bathochromic effect of methyl substitution.

Further, though less precise, evidence of intramolecular strain might be inferred from the melting points of, for example, 1,4,5,6-tetramethylnaphthalene (D) which melts at 132°, and the strain-free 2,3,6,7-analog, which melts at 191°.

Experimental[18]

The ultraviolet spectrograms were obtained from methanol solutions of the compounds, using a Cary recording spectrophotometer. Thanks are due to Dr. C. E. Larrabee for a sample of 1,2,3,4-tetramethylnaphthalene which he prepared by a modification of Hewett's method.[19] The synthesis and properties of 2,3,6,7-tetramethylnaphthalene[20] and the other polymethylnaphthalenes[7] discussed have been described. When the spectrum of 1,4,5,8-tetramethylnaphthalene was measured in isoöctane instead of methanol, a very slight hyperchromic displacement of the longer wave length maxima was the only observable effect. The values of λ_{max} for the different compounds together with the corresponding values of the intensity are tabularized below. The parenthesized figures represent "shoulders" or inflections.

	λ_{max}	log ε
2,3,6,7-Tetramethylnaphthalene (A)	(227)	(4.04)
	229	4.06
	255	3.46
	260	3.58
	270	3.68
	280	3.67
	290	3.46
	310	2.83
	(313)	(2.67)
	325	2.86
1,4,6,7-Tetramethylnaphthalene (B)	230	4.77
	(260)	(3.33)
	(271)	(3.59)
	280	3.76
	290	3.82
	(300)	(3.67)
	322	2.62
1,4,5,7-Tetramethylnaphthalene (C)	233	485
	(284)	(3.80)
	392	3.87
	(313)	(3.32)
	324	2.92
	330	3.09
1,4,5,8-Tetramethylnaphthalene (D)	233	4.83
	(290)	(3.87)
	296	3.92
	(307)	(3.83)
	(318)	(3.50)
	(326)	(3.18)
	334	3.28
1,2,3,4-Tetramethylnaphthalene (E)	233	4.84
	(285)	(3.70)
	293	3.75
	(323)	(2.65)
1,2,3,4,5-Pentamethylnaphthalene (F)	236	4.80
	(291)	(3.74)
	298	3.78
	(327)	(2.87)
1,2,3,4,5,8-Hexamethylnaphthalene (G)	236	4.73
	(285)	(3.68)
	297	3.78

EASTON, PA.

---

[13] G. M. Badger, *J. Chem. Soc.*, 2500 (1949); G. M. Badger, R. S. Pearce and R. Pettit, *ibid.*, 1112 (1952).

[14] The author is indebted to the referee for stressing the importance of the position of substitution upon the vertical and horizontal polarizations possible within the molecule. The high intensities of the peaks at 310 and 325 mμ in (A) may find explanation on such a basis, as suggested for other β-substituted naphthalene derivatives by Y. Hirshberg and R. N. Jones [*Can. J. Research*, **B27**, 437 (1949)].

[15] K. B. Everard and L. E. Sutton, *J. Chem. Soc.*, 2312 (1949).

[16] While this manuscript was in press, the synthesis of, *inter alia*, octamethylnaphthalene was described by B. J. Abadir, J. W. Cook and D. T. Gibson [*ibid.*, 8 (1953)], and the non-planar configuration as a result of intramolecular strain was confirmed through X-ray analysis by D. M. Donaldson and J. M. Robertson [*ibid.*, 17 (1953)].

[17] See for example: A. van Dormael, *Ind. chim. belge*, **15**, 138 (1950); R. N. Jones, *Chem. Revs.*, **32**, 1 (1943); G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 858 (1952); H. Brockmann and R. Randebrock, *Chem. Ber.*, **84**, 533 (1951); M. S. Newman and M. Wolf, THIS JOURNAL, **74**, 3225 (1952); M. S. Newman and H. Whitehouse, *ibid.*, **71**, 3664 (1949); G. M. Badger, J. E. Campbell and J. W. Cook, *J. Chem. Soc.*, 2326 (1950); R. N. Jones, THIS JOURNAL, **63**, 313 (1941); E. Clar and D. G. Stewart, *ibid.*, **74**, 6235 (1952), and ref. 9, p. 467.

[18] The author is indebted to Dr. Henry Hemmendinger and Mrs. Janet Schwar for the ultraviolet measurements.

[19] C. L. Hewett, *J. Chem. Soc.*, 293 (1940).

[20] W. L. Mosby, THIS JOURNAL, **75**, July 20, (1953).