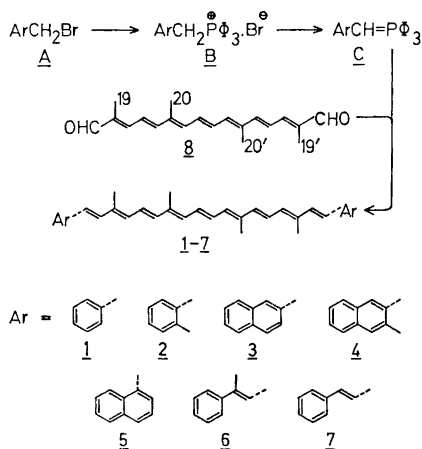


The Synthesis of Some Carotenoid-like Model Compounds

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The aryl polyenes (*1-7*) have been synthesised in connection with a study of carotenoid mass spectra.¹ These compounds resemble carotenoids in that they have the same central C₂₀-unit,⁷ but differ in the nature of the end groups present. Synthesis of the symmetrical polyenes (*1-7*) was accomplished by the well-tried method²⁻³ where a resonance-stabilised phosphorane, generated *in situ*, is condensed with crocetindial (*8*). *1* and *3* have been prepared previously by a different route^{4,5} and *1* alone by the present method.²



Scheme 1. Synthesis and structures of the compounds *1-7*. The numbers on the structure of crocetindial (*8*) are those used in carotenoid nomenclature.

The allylic bromides (*A*) readily yielded the triphenylphosphonium bromides (*B*) on refluxing in benzene with triphenylphosphine for 5 h.⁶ The phosphonium salts were obtained quantitatively by filtration

and washing with boiling benzene. These salts were dried *in vacuo* and used without further purification. To a refluxing dichloromethane solution of crocetindial (*8*) was added, in portions, with stirring and under nitrogen cover, the appropriate phosphorane (*C*) generated by suspending the phosphonium salt in ether and adding a benzene solution of butyl lithium. After about 1 h and the addition of some 50% excess of the phosphorane, reaction was complete. The reaction mixture was washed repeatedly with water and the product precipitated from the organic layer on addition of methanol. The dark red precipitate (40–60% of the theoretically possible yield) was removed by filtration and dried overnight *in vacuo*. The product was recrystallised from dichloromethane-methanol or chloroform-methanol.

The positions of the maxima in the electronic absorption spectra of all-*trans* *1-7* are given in Table 1: all-*trans* pigments were purified by chromatography on aluminium oxide paper (S & S 288) immediately before recording the spectra.⁷ A considerable amount of electronic absorption data is available for natural carotenoids.⁸ The main maxima of δ -carotene (in hexane), lycopene, rhodovibrin, and spirilloxanthin in acetone are at 458, 474, 488, and 497 nm, respectively, while the number of conjugated double bonds increases from 10 to 13 through the series. Comparison thus suggests that a fully conjugated phenyl ring contributes about 0.8 and a naphthyl ring about 1.2 spectroscopically effective double bonds to the chromophore. The single ring-substituents in *2* and *4* make no apparent difference to these effects (*cf.* the effect of several such substituents in Ref. 2). That the main maxima of *6* and *7* are the same is somewhat unexpected since in natural carotenoids the central methyl groups, C-20 and C-20', at least are known to contribute to the chromophore.⁹ A possible explanation is that this contribution is attenuated in the case of methyl groups farther from the centre of the conjugated chain. The extinction coefficients were not determined as a result of solubility problems; similar difficulties have been previously reported.^{4,5}

The infrared spectra of the aromatic polyenes agree well with previous data.^{10,11} The individual frequencies observed in each case are given in the experimental part where the suffixes *s* and *m* are used to indicate those of strong and medium intensity, respectively. Frequencies due to

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Table 1. Spectroscopic and adsorption data for 1-7. R_F -values are for all-*trans* isomers and were determined on Schleicher and Schüll No. 288 paper using 2 % acetone in petroleum ether as developer.

Compound	Absorption maxima nm in		Methyl resonances		R_F -values
	Chloroform	Acetone	τ -values (TMS=10.0)		
1	(455), 480, 512	(446), 471, 502	8.01	7.93	0.59
2	(455), 480, 511	(446), 471, 502	8.01	7.94	7.63
3	(470), 492, 519	(462), 481, 510	8.01	7.91	0.27
4	(471), 491, 520	(462), 481, 511	8.01	7.91	7.47
5	(468), 488, 519	(460), 480, 509	8.01	7.85	0.30
6	(475), 501, 536	(465), 491, 522	8.02	8.00	7.79
7	475, 502, 537	465, 491, 525	8.01	8.00	0.47

aromatic C-H out of plane deformation occur in the region 650-900 cm^{-1} , while the corresponding in plane deformations give rise to bands in the 1000-1200 cm^{-1} region. Other indications of aromaticity are seen in the C=C stretching frequencies at *ca.* 1500 and 1600 cm^{-1} . The two bands at *ca.* 1390 and 1440 cm^{-1} may be assigned as symmetric and antisymmetric deformation modes of the C-H bonds of the methyl groups. The bands in the region 2800-3050 cm^{-1} are due to various C-H stretching modes. Finally, the most intense band observed is that at about 970 cm^{-1} and is typical for the C-H out of plane deformations of the *trans*-disubstituted double bonds of the conjugated chain.¹¹

The positions of the methyl resonances in the NMR spectra, determined in CDCl_3 , are given in Table 1. The band at highest field (8.01 τ) is due to the least deshielded methyl groups, *i.e.* those nearest the centre of the conjugated chain¹¹ and numbered C-20 and C-20' in standard carotenoid nomenclature. The band at next highest field can be assigned to the methyl groups at positions closer to the end group (C-19 and C-19'): the deshielding effect of the aromatic end groups^{12,2} is clearly seen and as expected increases in the order phenyl, 2-naphthyl and 1-naphthyl. Similar arguments explain the fact that the final band, due to the methyl group on the aromatic ring in the 2-naphthyl compound 4 is more deshielded than that in the tolyl derivative 2. In the compound 6 the phenyl group deshields only slightly the methyl groups at C-19 and C-19' while as expected increased deshielding is observed for the methyl group closest to the end group. Similar arguments apply to the spectrum of 7.

Like natural carotenoids^{11,13} the compounds 1-7 give mass spectra where ions corresponding to M-78, M-79, M-92, M-106, and M-158 are observed. The intensity ratio of the M-92/M-106 ions has been discussed elsewhere.¹ The molecular ion is in all cases intense and a further indication of stability is seen in the observation of a doubly charged species. Cleavage of in-chain bonds with hydrogen transfer to the lower mass fragments results in series of ions at both low and high masses. These cleavages are more intense where a double bond is broken and the base peak ion in 1-7 is provided by the lower mass fragment resulting from such rupture of the double bond closest to the aromatic residue. These findings are in complete agreement with results previously obtained for natural aromatic carotenoids^{11,13} and some completely conjugated derivatives of carotenoid diosphenols.¹⁴ Ions due to cleavage of the central double bond with hydrogen transfer in each direction and without such transfer are observed.

Experimental. Visible light absorption spectra were recorded on a Coleman Hitachi 124 spectrometer, IR spectra as KBr discs on a Unicam SP 200G instrument and NMR spectra on a Varian A60-A spectrometer. Mass spectra (MS) were obtained on an AEI MS902 instrument using the direct insertion probe with an ion source temperature of 200-250°. Figures given in brackets after mass numbers in the section below are relative intensities in per cent. Melting points were determined in evacuated sealed tubes and are uncorrected. The crocetindial (δ) used in this work was a synthetic sample and originated

from Dr. J. D. Surmatis, Hoffmann-LaRoche Inc., New Jersey, USA.

1,18-Diphenyl-3,7,12,16-tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene (1). M.p. 234–235° (lit.⁴ 209–210° and ² 234–235°). IR: 3025, 2920, ca. 1600, 1490, 1445, 1385m, 1180, 1075, 965s, 835, 755s and 700s cm⁻¹. MS: M=444 (87.5), M-15 (0.5), M-79 (1.1), M-91 (2.5), M-92 (4.2), M-106 (10.6), M-106-15 (0.7), M-131 (1.9), M-144 (2.6), M-157 (4.3), M-197 (6.5), and *m/e* 223 (30.5), 222.5 (10.1), 222 (31.8), 221 (31.8), 145 (18.8), 131 (55.0), 119 (20.5), 115 (14.4), 105 (37.5), 91 (100), 77 (20.0).

1,18-Di-(o-tolyl)-3,7,12,16-tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene (2). M.p. 192–193°. IR: 3030, 2930, ca. 1600, 1490, 1465, 1395m, 1170, 1020, 970s, 840 and 760s cm⁻¹. MS: M=472 (62.5), M-15 (1.2), M-78 (1.1), M-79 (1.4), M-91 (2.4), M-92 (3.3), M-105 (6.0), M-106 (14.5), M-145 (1.8), M-158 (1.8), M-171 (2.5), and *m/e* 237 (9.4), 236.5 (4.5), 236 (14.0), 145 (42.5), 119 (22.0), 115 (21.5), 105 (100), 91 (57.5), 77 (25.5).

1,18-Di-2-naphthyl-3,7,12,16-tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene (3). M.p. 258–261° (lit.⁵ ca. 250°). IR: 3060, 2930, 2860, ca. 1600, 1500, 1440, 1390m, 1370, 1130, 970s, 900, 870, 835s and 750s cm⁻¹. MS: M=544 (36.4), M-15 (0.5), M-78 (0.5), M-79 (0.5), M-92 (0.8), M-106 (10.7), M-141 (1.5), M-158 (0.7), M-181 (1.1), M-194 (1.6), M-106-92 (1.5), M-207 (1.9), M-106-106 (1.7), and *m/e* 273 (11.8), 272.5 (2.8), 272 (10.2), 271 (15.2), 141 (100), 119 (11.4), 115 (12.7), 105 (16.8), 91 (27.2), 77 (16.9).

1,18-Di-2-(3-methyl)naphthyl-3,7,12,16-tetramethyloctadeca-1,3,5,7,9,11,13,15,17-nonaene (4). M.p. 211–212°. IR: 3040, 2930, 2870, ca. 1600, 1500, 1440, 1390m, 1130, 1010, 970s, 890, 750m and 680m cm⁻¹. MS: M=572 (60.5), M-15 (0.2), M-78 (0.5), M-79 (0.6), M-92 (4.5), M-106 (62.9), M-155 (4.8), M-158 (4.0), and *m/e* 287 (7.1), 286.5 (1.9), 286 (8.8), 285 (12.4), 155 (100), 119 (3.2), 115 (37.8), 105 (37.8), 91 (86.4), 77 (26.0).

1,18-Di-1-naphthyl-3,7,12,16-tetramethylnonadeca-1,3,5,7,9,11,13,15,17-nonaene (5). M.p. 224–226°. IR: 3030, 2890, ca. 1600, 1500, 1435m, 1395, 1195, 1120m, 970s, 795m, 775m, 750, 720s and 695m cm⁻¹. MS: M=544 (59.0), M-15 (0.6), M-92 (2.6), M-106 (35.9), M-141 (2.8), M-158 (1.4), M-194 (2.2), M-106-92 (2.4), M-207 (3.1), M-106-106 (2.8), and *m/e* 273 (9.0), 272.5 (2.7), 272 (10.6), 271 (15.1), 141 (100), 119 (12.3), 115 (15.4), 105 (28.2), 91 (61.6), 77 (26.1).

2,23-Diphenyl-6,10,15,19-tetramethyltetracos-2,4,6,8,10,12,14,16,18,20,22-undecaene (6). M.p. 235–236°. IR: 3050, 2940, 2870, ca. 1600,

1495, 1445, 1385m, 1170, 1080, 970s, 760s and 700s cm⁻¹. MS: M=624 (24.4), M-15 (0.7), M-78 (0.5), M-79 (0.5), M-92 (2.0), M-105 (2.3), M-106 (5.3), M-131 (0.8), M-158 (2.8), M-171 (0.9), M-185 (1.6) and *m/e* 263 (2.8), 262.5 (1.2), 262 (4.6), 261 (4.0), 131 (46.8), 119 (12.4), 115 (16.7), 105 (100), 91 (60.0), 77 (16.7).

1,22-Diphenyl-5,9,14,18-tetramethyldocos-1,3,5,7,9,11,13,15,17,19,21-undecaene (7). M.p. 255–257°. IR: 3030, 2940, 2870, ca. 1600, 1495, 1450m, 1400, 1170, 1080, 970s, 850, 760s and 700s cm⁻¹. MS: M=496 (39.0), M-15 (0.2), M-91 (2.2), M-92 (5.0), M-105 (1.1), M-106 (2.1), M-117 (0.5), M-157 (1.0), M-158 (1.8), M-183 (1.8), and *m/e* 249 (5.0), 248.5 (2.7), 248 (10.1), 247 (7.0), 117 (27.3), 115 (13.9), 105 (20.1), 91 (100), 77 (8.9).

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