Exalted Distortion Polarizations of Some Colored Hydrocarbons

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Several red hydrocarbons possessing centers of symmetry were found to have molar polarizations which are about equal to the molar refractions observed with Na_D light, but considerably larger than those calculated for these molecules from the atomic or bond refractions, or from those of the constituent fragments. The expected zero moment for such hydrocarbons is, therefore, obtained only if the distortion polarization is assumed to be equal to the *observed* molar refraction. Measurements of the molar refraction with light of 1μ, as well as comparison with compounds chemically different, but similar in their absorption spectrum, indicate that the observed exaltations of the distortion polarization are due to an exaltation of the electronic polarization rather than to one of the atomic polarization. A parallelism between the exalted distortion polarization and the peculiar chemical reactivity of these hydrocarbons appears to exist.

The electric dipole moment of a molecule is proportional to the square root of the difference between total and distortion polarization, $P - P_d$, the latter representing the sum of electronic and atomic polarization, $P_d = P_E + P_A$.[1] Compounds, and in particular hydrocarbons, possessing a center of symmetry, should be devoid of any moment, *i.e.*, $P = P_d$.

As it is generally impossible to determine P_A, it is commonly assumed that P_d is given either by the molar refraction R extrapolated to infinite wave length,[2] with 5 to 10% added to allow for P_A, or by the molar refraction R_D observed with the sodium D-line.[3,4]

the refractions observed for the "constituent fragments" of the molecule.

This procedure seems plausible for molecules absorbing in the visible range, since the proximity of absorption bands to the light used in measuring R makes the observed refractions particularly prone to distortion ("anomalous dispersion").

An extreme example is the blue-violet 1,2,7,8-, 1′,2′,7′,8′-tetrabenzodibiphenylene-ethene (I),[5] for which was observed with sodium light in benzene solution a molar refraction of minus 1050 cc., as compared with a total polarization of about 170 cc. Obviously no use can be made of such measurements in order to determine the electronic polarization.
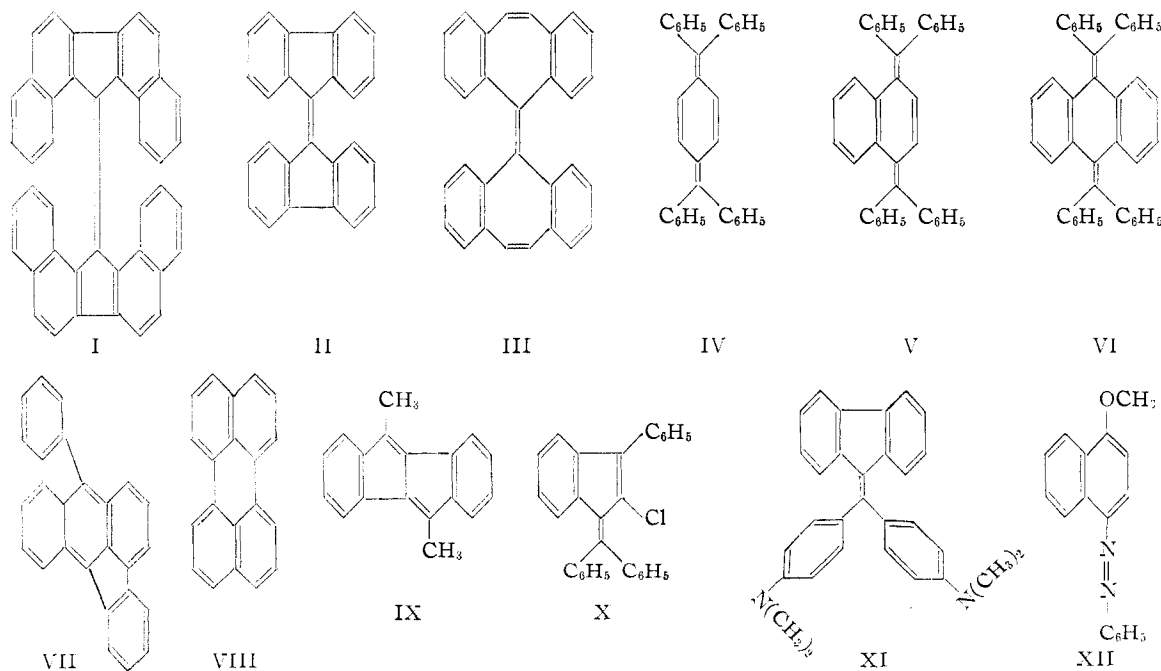
For substances exhibiting unusually large dispersion, both these procedures are difficult or altogether impossible. For such cases, it has been suggested[4] as the best compromise to assume that P_D is equal to the molecular refraction *calculated* from

In the course of investigations on the properties of fulvenes and other compounds containing cross-conjugated bonds,[6] it was observed that several red or yellow, mostly centrosymmetric hydrocarbons had molar polarizations about equal to the observed R_D, but considerably larger than the calculated R_D (in the above-defined sense). The rele-

(1) See, *e.g.*, R. J. W. Le Fevre, "Dipole Moments," London, 1948.

(2) This extrapolation usually gives a reduction only by a few per cent; N. A. Soerensen, *Ann.*, **546**, 57 (1941).

(3) K. B. Everard, R. A. W. Hill and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

(4) K. B. Everard, L. Kumar and L. E. Sutton, *J. Chem. Soc.*, 2807 (1951).

(5) E. D. Bergmann, E. Fischer, Y. Hirshberg, D. Lavie, Y. Sprinzak and J. Szmuszkovicz, *Bull. soc. chim. France*, in press (1952).

(6) E. D. Bergmann and E. Fischer, *ibid.*, **17**, 1084 (1950), and later publications in that series.

vant figures are given in the second and third columns of Table I. (For the sake of comparison, the colorless compounds tetraphenylanthraquinodimethane (VI) and tetrabenzoheptafulvalene (III) have been included in this Table). In the fourth column of Table I, the location of the longest absorption maxima of these compounds is recorded.

TABLE I

MOLAR REFRACTION AND VISIBLE ABSORPTION BANDS OF SOME RED OR INTENSELY YELLOW HYDROCARBONS

	$R^D_{calc.,}$[a] cc.	$R^D_{obs.,}$ cc.	Longest absorption bands, Å.
Dibiphenylene-ethene (II)	112[b]	139.5 ± 0.5	4580[f]
2,7,2',7'-Tetramethyl-diphenyl-ene-ethene	128.5[c]	159 ± 2	4620[g]
Tetrabenzoheptafulvalene (III)	125	128 ± 6	2990[h]
Tetraphenyl-p-quinodimethane (IV)	138[d]	182 ± 4	4260[i]
Tetraphenyl-α-naphthoquino-dimethane (V)	154[d]	183 ± 1.5	4040[i]
Tetraphenylanthraquinodi-methane (VI)	170[d]	181 ± 3	3030[i]
Rubicene (VII)[j]	113[d]	131 ± 5	4680; 4960; 5285[k]
Perylene (VIII)	86[e]	99.5 ± 2	4061; 4101; 4287; 4348[l]
Dimethyldiphensuccindadiene (IX)	75.5	86.5 ± 0.8	4120[m]
2,2'-Dibromodibiphenylene-ethene	125	150.0 ± 1.6	4570[g]
4,4'-Dibromodibiphenylene-ethene	125	165.0 ± 1.7	4620[g]

[a] Calculated from bond equivalents (A. J. Vogel, et al., J. Chem. Soc., 514 (1952)). [b] Based on $R^D_{obs.}$ fluorene 56 (E. D. Hughes, et al., ibid., 202 (1937)), and adding 0.65 cc. for each of the four C-C "single" bonds adjacent to the central C=C bond, as suggested by K. G. Denbigh (Trans. Faraday Soc., 36, 936 (1940)) for the C-C "single" bond in butadiene. [c] 158, if calculated from $R^D_{obs.}$ dibiphenylene-ethene (II). [d] Based on bond equivalents, adding 0.65 cc. for each "single" C-C bond (cf. note b). [e] The C-C bond refraction for naphthalene (2.78) has been used in this calculation. [f] E. Bergmann and Y. Hirshberg, Bull. soc. chim. France, 17, 1091 (1950). [g] See ref. 12. [h] See ref. 9. [i] A. Pullman, B. Pullman, E. Bergmann, G. Berthier, E. Fischer, D. Ginsburg and Y. Hirshberg, Bull. soc. chim. France, 18, 707 (1951). [j] Supersaturated solution in methylnaphthalene. [k] The spectrum was measured in dioxan solution, and the following bands were observed: 2310 (4.78); 2460(4.80); 2810(4.52); 2985(4.70); 3590(3.60); 3790(3.96); 4680(4.08); 4960(4.18); 5285(3.86). [l] P. Pogangeanu, Bull. Sect. Sci. Acad. Roumaine, 20, No. 8-10, 24 (1938) (C.A., 34, 3590 (1940)). G. Elsevier, "Encyclopedia of Organic Chemistry," Vol. 14, Amsterdam, 1940, p. 459; Suppl. Vol. 14, Amsterdam, 1951, p. 7340. [m] See ref. 18a.

If the procedure advocated by Sutton, et al., were followed in such cases, comparatively large and, therefore, highly improbable electric moments would result (Table II). It appears, therefore, that for these and related compounds P_d should be taken as equal to $R^D_{obs.}$ rather than $R^D_{calc.}$ which leads to the theoretically expected small dipole moments.

Two explanations of this result seem possible: (1) the electronic polarizations of the compounds concerned are exalted as compared with those calculated for them (in the sense defined above), but their atomic polarizations are normal; (2) the electronic polarizations are more or less equal to those calculated, but the (observed) molecular refractions are considerably exalted over and above the calculated values, because of anomalous dispersion. The atomic polarization must then be as-

sumed to be abnormally high, and fortuitously equal to $R^D_{obs.} - R^D_{calc.}$, thus leading to the equally fortuitous relation $P_d \simeq R^D_{obs.}$.

The second explanation seems a priori rather improbable, since hydrocarbons, as distinct from compounds containing polar groups, are generally characterized by low atomic polarizations.

Additional evidence against the second alternative was obtained as follows. Using the procedure described by Jaffe,[7] the molar refraction of dibiphenylene-ethene (II) was measured with light of about 1μ, i.e., remote from the nearest absorption bands (at about 0.4 and 3μ). The resulting value of 136.5 ± 4.5 ml. is only about 2% smaller than that of 139.5 ± 2 ml. observed with Na_D light. Thus no unusually high dispersion seems to exist in this spectral region.

A further test of explanation (2) is provided by the comparison of the results listed in Table I, with those obtained for a number of compounds which are chemically different from the hydrocarbons in Table I, but have similar absorption spectra (Table III).

TABLE II

MOLAR REFRACTIONS AND APPARENT DIPOLE MOMENTS OF CENTROSYMMETRIC HYDROCARBONS

	$R^D_{calc.,}$ cc.	$R^D_{obs.,}$ cc.	P, cc.	μ^f, D	μ^g, D
Dibiphenylene-ethene (II)[a]	112	139.5	135	1.1	0
2,7,2',7'-Tetramethyl-dibiphenylene-ethene[a]	128	159	156	1.2	0
Tetraphenyl-p-quino-dimethane (IV)[b]	138	182	174	1.3	0
Tetraphenyl-α-naphtho-quinodimethane (V)[b]	154	183	175	1.0	0
Perylene (VIII)[c]	86	99.5	104	0.9	0.45
Dimethyldiphensuc-cindadiene (IX)[d]	75.5	86.5	93.5	0.95	0.6
Fluoranthene[e]	69.5	73.5	73	0.3	0
Tetrabenzonaphtha-lene[e,h]	113	122	120	0.6	0

[a] See ref. 12. [b] A. Pullman, B. Pullman, E. Bergmann, G. Berthier, E. Fischer, D. Ginsburg and Y. Hirshberg, Bull. soc. chim., 18, 707 (1951). [c] See ref. 18. [d] See ref. 18a. [e] A. Pullman, B. Pullman, E. Bergmann, G. Berthier, E. Fischer, Y. Hirschberg and J. Pontis, J. chim. phys., 48, 359 (1951). [f] Moment, calculated using $R^D_{calc.}$ as distortion polarization. [g] Moment, calculated using $R^D_{obsd.}$ as distortion polarization. [h] Ultraviolet spectrum (in alcohol): 2690 (4.36), 2870 (4.22), 3000 (4.26), 3360 (3.88), 3480 (3.86).

If the exaltations observed for the hydrocarbons of Table I are due to anomalous dispersion, the compounds in Table III should exhibit similar exaltations. The results presented in Table III show that this is not the case.

The general inference thus seems to be that explanation (2) is not correct, and that, in accordance with explanation (1), the observed exaltations of the molecular refraction for the substances in Table I are largely due to enhanced electronic polarizations. The exaltations of the molecular refractions in certain fulvenes and fulvene-type com-

(7) J. H. Jaffe, J. Optical Soc. Am., 41, 166 (1951).

TABLE III

MOLAR REFRACTIONS AND VISIBLE ABSORPTION BANDS OF SOME RED AND INTENSELY YELLOW COMPOUNDS

	$R^D_{calcd.,}$[a] cc.	$R^D_{obsd.,}$ cc.	$R^D_{obsd.} - R^D_{calc.,}$ ($\%$ of $R^D_{calcd.}$)	Visible abs. bands, Å.
2,3-Diphenylindone	88.5	87.5 ± 0.5	0	4400[g]
Chrysoquinone	82.0	81.5 ± 0.8	0	4000[h]
Fluorenone-ketazine	118[b]	128.0 ± 1	8	3610[i]
Isatin[c]	38	41 ± 0.4	8	4200[j]
1-Methylamino-anthraquinone	78[d]	79.5 ± 2.5	0	5100[k]
2-Chloro-3-phenyl-1-benzhydrylidene-indene (X)	133[e]	137 ± 3	0	3660[l]
Bis-(4-dimethylamino-phenyl)-dibenzoful-vene (XI)	145[f]	170 ± 0.8	17	4160-4300[m]
Azobenzene	58.5	62.5 ± 0.5	7	4430[n]
4-Methoxyazobenzene	63.0	72.0 ± 0.8	14	4320[o]
4-Benzeneazo-1-meth-oxynaphthalene (XII)	81.0	94.0 ± 1.2	16	3920[p]

[a] Calculated from bond equivalents, unless otherwise stated. [b] Based on $R^D_{obs.}$ fluorene. [c] Solution in ethyl alcohol. [d] Based on $R^D_{obs.}$ anthracene. [e] Based on $R^D_{obs.}$ benzhydrylideneindene. [f] Based on $R^D_{obs.}$ diphenylbenzofulvene (benzhydrylidenefluorene). [g] In alcoholic solution, the following bands were observed: 2600 Å. (4.50) and 4400 Å. (3.24). [h] In alcoholic solution, bands were observed at 2340 Å. (4.40); 2560 Å. (4.56); 4000 Å. (3.78). [i] In alcoholic solution, the following bands were measured: 2240 Å. (4.66); 2600 Å. (4.84); 3260 Å. (4.27); 3610 Å. (4.26). [j] Absorption bands (in alcoholic solution): 2440 Å. (4.34); 2980 Å. (3.50); 4200 Å. (2.88). [k] In alcoholic solution, the following bands were observed: 2440 Å. (4.56); 2760 Å. (4.00); 3160 Å. (3.80); 5100 Å. (3.80). [l] In alcoholic solution, the following bands were observed: 2260 Å. (4.41); 2540 Å. (4.39); 3040 Å. (4.07); 3660 Å. (4.18). [m] E. Bergmann, E. Fischer, Y. Hirschberg and D. Lavie, Bull. soc. chim., 19, 709 (1952). [n] The alcoholic solution showed three bands: 2280 Å. (4.08); 3180 Å. (4.24); 4430 Å. (2.92). [o] In alcoholic solution, the following bands were observed: 2340 Å. (4.06); 3460 Å. (4.40); 4320 Å. (3.18). Cf. F. Kehrmann and S. Hempel, Ber. 50, 856 (1917); cf. C. R. Crymble, A. W. Stewart and R. Wright, ibid., 43, 1188 (1910). [p] In alcoholic solution, the following bands were observed: 2400 Å. (4.34); 2720 Å. (4.14); 3920 Å. (4.22). The spectrum of 4-hydroxyazobenzene has been measured by W. R. Brode, Ber., 61, 1722 (1928).

pounds have recently been calculated by Berthier and Pullman,[8] who found their values in good agreement with the experimental figures.

The increased mobility of the electrons, which is indicated by this phenomenon, is probably related to the high degree of conjugation in these and related substances.[9] Regarding dibiphenylene-ethene (II), it appears that its high distortion polarization is also reflected in its peculiar chemical reactivity; it is capable of adding metal-organic compounds and ammonia, of reacting with lithium

(8) G. Berthier and A. Pullman, Compt. rend., 234, 332 (1952).

(9) Exaltations (in the above sense) of $R^D_{obs.}$ of 5–10% have been reported for polycyclic aromatic hydrocarbons (Y. K. Syrkin and M. E. Dyatkina, "Structures of Molecules and the Chemical Bond," London, 1950) and for fulvene derivatives. Diphenylfulvene, e.g., has a calculated molecular refraction of 77 cm. while the observed value is 84 ± 0.5 (E. D. Bergmann and E. Fischer, ref. 6). Even higher exaltations are exhibited by compounds of the p-nitroaniline type, in which electrons are shifted from electron releasing to electron withdrawing groups (C. Curran and F. M. Palermiti, THIS JOURNAL, 73, 3733 (1951)). For exaltations in the styrene and stilbene series and their relationship to conjugation effects, see L. E. Sutton, et al., ref. 4.

aluminum hydride and of undergoing the Michael condensation—all reactions typical of highly polar substances, e.g., of the ketone type.[10] Some implications of this parallelism between exaltation of the distortion polarization and unusual reactivity are now being investigated.

Experimental

(a) **Materials.**—Tetrabenzoheptafulvalene (III),[11] from toluene, m.p. 281°.

Dibiphenylene-ethene (II)[12] from chloroform, m.p. 194°.

2,2'-Dibromodibiphenylene-ethene,[12,13] from butyl acetate, m.p. 268–269°.

4,4'-Dibromodibiphenylene-ethene,[13] from butyl alcohol, m.p. 190–193°.

2,7,2',7'-Tetramethyldibiphenylene-ethene,[13] from butanol–toluene, m.p. 274–275°.

Tetraphenyl-p-quinodimethane (IV),[14,15] from xylene, m.p. 268°.

Tetraphenyl-α-naphthoquinodimethane (V),[15] from toluene, m.p. 263°.

Tetraphenylanthraquinodimethane (VI),[14,15] from xylene, m.p. 305°.

Rubicene (VII),[16] from xylene, m.p. 308°.

Perylene (VIII),[17] from butyl acetate, m.p. 264°.

Tetrabenzonaphthalene,[18] from toluene, m.p. 218°.

Dimethyldiphensuccindadiene (IX),[18a] from butyl acetate m.p. 212°.

Fluorenone-ketazine,[19] recrystallized from xylene, m.p. 265°.

2,3-Diphenylindone,[20] from butyl alcohol, m.p. 151°.

2-Chloro-3-phenyl-1-benzhydrylideneindene (X),[21,22] from propyl alcohol, m.p. 159–160°.

Chrysoquinone,[23] from benzene, m.p. 240°.

1-Methylaminoanthraquinone commercial product, recrystallized from butanol, m.p. 160°.

Bis-(p-dimethylaminophenyl)-dibenzofulvene (XI),[24] from amyl alcohol, m.p. 238°.

Azobenzene, commercial product, recrystallized from alcohol, m.p. 68°.

Isatin, commercial product, recrystallized from amyl alcohol, m.p. 200°.

2-Benzeneazo-1-methoxynaphthalene (XII): the hydroxy compound[25] was methylated by means of an excess of diazomethane: from methanol, m.p. 82°.[26]

4-Methoxyazobenzene, from the hydroxy compound[27] with diazomethane; from methanol, yellow leaflets, m.p. 56.[26]

(10) (a) E. Bergmann, G. Berthier, A. Pullman and B. Pullman, Bull. soc. chim. France, 17, 1079 (1950); (b) D. Lavie and E. Bergmann, ibid., 18, 250 (1951); (c) E. Bergmann, G. Berthier, E. Fischer, Y. Hirschberg, D. Lavie, E. Loewenthal and B. Pullman, ibid., 19, 78 (1952).

(11) E. D. Bergmann, D. Ginsburg, Y. Hirschberg, M. Mayot, A. Pullman and B. Pullman, ibid., 18, 697 (1951).

(12) H. Wagner and J. Schmidt, Ber., 43, 1796 (1910).

(13) E. D. Bergmann, G. Berthier, E. Fischer, Y. Hirschberg, D. Lavie, E. Loewenthal and B. Pullman, Bull. soc. chim. France, 19, 78 (1952).

(14) H. Staudinger, Ber., 41, 1355 (1908).

(15) H. Staudinger and St. Bereza, Ann., 380, 276 (1911).

(16) W. Schlenk and M. Karplus, Ber., 61, 1675 (1928).

(17) R. Scholl, C. Seer and R. Weitzenboeck, ibid., 43, 2202 (1910).

(18) E. D. Bergmann, E. Fischer and B. Pullman, J. chim. phys., 48 356 (1951).

(18a) B. Pullman, A. Pullman, E. Bergmann, G. Berthier, E. Fischer, Y. Hirschberg and J. Pontis, ibid., 49, 24 (1952).

(19) H. Wieland and A. Roseeu, Ann., 381, 229 (1911); H. Staudinger and O. Kupfer, Ber., 44, 2197 (1911); T. Curtius and K. Kof, J. prakt. Chem., [2] 86, 113 (1912).

(20) A. Loewenbein and G. Ulich, Ber., 58, 2662 (1925); R. Weiss and R. Sauermann, ibid., 58, 2736 (1925).

(21) H. Wieland and H. Kloss, Ann., 470, 201 (1929).

(22) E. Bergmann and A. v. Christani, Ber., 63, 2559 (1930).

(23) C. Graebe and F. Koenigsberger, Ann., 311, 257 (1900).

(24) E. Bergmann and J. Hervey, Ber., 62, 893 (1929).

(25) O. N. Witt and T. Dedichen, ibid., 30, 2655 (1897).

(26) C. Smith, J. Chem. Soc., 93, 845 (1908).

(27) G. Oddo and E. Puxeddu, Ber., 38, 2752 (1905).

(b) **Measurement and Computation.**—Refractive indices, n, were measured on benzene solutions of the substances in an Abbe precision refractometer. The measurement of dielectric constants ϵ and densities d, as well as the computation of the molar refractions and polarizations from the slopes of the lines depicting ϵ, n, and d versus weight fraction have been described before.[28] The variations in the

approximate error in $R^D_{obs.}$ given in each case are due mainly to differences in the range of the solute concentrations.

(28) E. D. Bergmann, A. Weizmann and E. Fischer, This Journal, **72**, 5009 (1950); E. Fischer, J. Chem. Phys., **19**, 395 (1951).

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Dicyclic Hydrocarbons. VI. 1,2,3,4-Tetrahydronaphthalene and 1-Alkyl-1,2,3,4-tetrahydronaphthalenes

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Methods of synthesis and purification as well as physical properties are presented for four 1-alkyl-1,2,3,4-tetrahydronaphthalenes along with the physical properties of 1,2,3,4-tetrahydronaphthalene. The boiling point, refractive index, density, net heat of combustion and kinematic viscosities at four different temperatures are given for each compound. Two compounds, 1-butyl-1,2,3,4-tetrahydronaphthalene and 1-pentyl-1,2,3,4-tetrahydronapthalene, are described for the first time.

In connection with an investigation of aviation fuel components carried out at this Laboratory, several series of dicyclic hydrocarbons have been synthesized and purified. Among the compounds previously described, for example, have been the diphenyl- and dicyclohexylbutanes.[1] For the purpose of correlating the physical properties with molecular structure, it was deemed desirable to extend this study to the fused dicyclic system. The preparation of 1-alkylnaphthalenes has been reported upon earlier.[2] In this paper 1,2,3,4-tetrahydronaphthalene and four of its homologs are described. The latter hydrocarbons are 1-methyl-, 1-ethyl-, 1-butyl- and 1-pentyl-1,2,3,4-tetrahydronaphthalene. Of these, the 1-butyl- and 1-pentyl- compounds are reported for the first time. The other compounds in this series were synthesized in order to obtain a consistent set of precise physical constants on highly purified samples of these structurally related hydrocarbons. Although all of the 1-alkyl-1,2,3,4-tetrahydronaphthalenes are capable of optical activity, no attempt was made to resolve racemic mixtures.

Among the reported syntheses of 1-methyl- and 1-ethyl-1,2,3,4-tetrahydronaphthalene in which the alkyl substitutents are unequivocally attached to the indicated position in the saturated ring portion of the molecule have been those of Darzens[3] and of Bogert, Davidson and Roblin.[4] These procedures involve the formation of the aliphatic ring by the cyclization of a variety of alkyl benzene derivatives of appropriate chain length.

Since it was the object of the present research to prepare the desired hydrocarbons on such a scale that approximately 500-ml. quantities would be available after the final distillation, the ring closure method was not considered a suitable procedure because low over-all yields were anticipated. A synthesis was sought which did not involve the initial

preparation of a relatively complex alkyl benzene derivative for each desired hydrocarbon but which instead permitted the use of a single starting material with a preformed fused ring system. An effective synthetic route was found in the method of Hock and Lang[5] modified by substitution of catalytic hydrogenation for the sodium–pentanol reduction used by these authors. Thus, it was possible to prepare the desired homologs of 1,2,3,4-tetrahydronaphthalene conveniently.

The preparation of 1-methyl-, 1-ethyl-, 1-butyl- and 1-pentyl-1,2,3,4-tetrahydronaphthalene involved the reactions of methyl-, ethyl-, butyl- and pentylmagnesium bromide, respectively, with 1-tetralone. The resultant Grignard complexes were decomposed to yield tertiary alcohols, the 1-alkyl-2,3,4-trihydronaphthalene-1-ols. These carbinols were dehydrated to the corresponding olefins. Selective high pressure hydrogenation of the olefinic bond afforded the desired hydrocarbon.

The final purification of the 1-alkyl-1,2,3,4-tetrahydronaphthalenes consisted of fractional distillation of each product in six-foot Podbielniak columns.[6] The individual fractions were percolated through columns of activated silica gel prior to the determination of all physical constants. Only those fractions exhibiting constancy of both refractive index and density were combined for analyses and for the determination of precise physical constants. The physical constants, particularly those which, like the density, exhibit large variation with slight traces of impurities, were measured on samples of the products immediately after final passage through silica gel to obviate the effects of possible air-oxidation.

The parent hydrocarbon of this series, 1,2,3,4-tetrahydronaphthalene, was obtained from commercial sources. This material was fractionally distilled in a 30-foot column two inches in diameter,

(1) K. T. Serijan and P. H. Wise, This Journal, **74**, 365 (1952).

(2) H. F. Hipsher and P. H. Wise, National Advisory Committee for Aeronautics, Technical Note 2430, Cleveland (1951).

(3) G. Darzens, Compt. rend., **183**, 748 (1926).

(4) (a) M. T. Bogert, D. Davidson and R. O. Roblin, Jr., This Journal, **56**, 248 (1934); (b) R. O. Roblin, Jr., D. Davidson and M. T. Bogert, ibid., **57**, 151 (1935).

(5) H. Hock and Shon Lang, Ber., **75B**, 300 (1942).

(6) (a) G. H. Sugimura and T. W. Reynolds, paper presented before the Division of Physical and Inorganic Chemistry of the New York Meeting of the XIIth International Congress of Pure and Applied Chemistry, Abstracts, 607 (1951); (b) T. W. Reynolds and G. H. Sugimura, National Advisory Committee for Aeronautics, Technical Note 2342 Cleveland (1951).