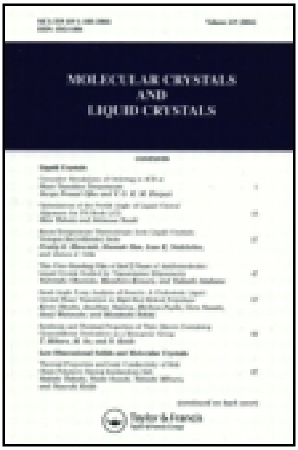

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Liquid Scintillators. XIV. The Synthesis and Evaluation of Some trans-1, 2-Diarylethylenes as Liquid Scintillators. The Steric Effects of a Methyl Group

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Version of record first published: 21 Mar 2007.

To cite this article: Guido H. Daub , F. Newton Hayes , David W. Holty , Lavinel Ionescus & James L. Schornick (1968): Liquid Scintillators. XIV. The Synthesis and Evaluation of Some trans-1, 2-Diarylethylenes as Liquid Scintillators. The Steric Effects of a Methyl Group, Molecular Crystals, 4:1-4, 343-355

To link to this article: http://dx.doi.org/10.1080/15421406808082922

Molecular Crystals, 1968. Vol. 4, pp. 343–355

Printed in Germany

Liquid Scintillators. XIV. The Synthesis and Evaluation of Some trans-1,2-Diarylethylenes as Liquid Scintillators. The Steric Effects of a Methyl Group.[1]

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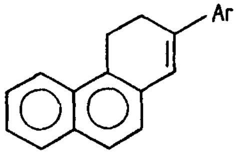
Received August 9, 1966
Revision received September 22, 1966

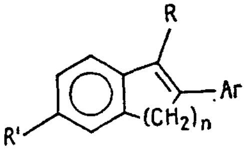
Abstract—2-Arylindenes (*2*), 3-aryl-1,2-dihydronaphthalenes (*3*), 3-aryl-1,2-dihydro-4-methylnaphthalenes (*4*), 2-aryl-6-phenylindenes (*5*), 2-aryl-3-methyl-6-phenylindenes (*6*), 2-aryl-3,4-dihydro-6-phenylnaphthalenes (*7*), 2-aryl-3,4-dihydro-1-methyl-6-phenylnaphthalenes (*8*), 2-aryl-3H-benz[e]indenes (*9*), 3-aryl-1,2-dihydrophenanthrenes (*10*), and 3-aryl-1,2-dihydro-4-methylphenanthrenes (*11*) in which the substituent aryl group was phenyl (*a*), 1-naphthyl (*b*), 2-naphthyl (*c*), or 4-biphenylyl (*d*) were synthesized and tested as liquid scintillator solutes in toluene at various concentrations. Fluorescence spectra in toluene and ultraviolet absorption spectra were also determined. It was found that the compounds having the ethylenic double bond in a five-membered ring were better scintillators at low concentrations than those having the ethylenic double bond in a six-membered ring; however, at increased concentration the six-membered ring systems surpassed the five-membered ring systems in scintillation efficiency. In addition, the presence of a methyl group on the ethylenic carbon adjacent to that holding the substituent aryl group had a profound decreasing effect on the scintillation efficiency in the six-membered ring compounds but no decreasing effect on the five-membered ring compounds.

A few years ago Birkeland[7] found that the 2-aryl-3,4-dihydrophenanthrenes *1a* and *1d* were excellent liquid scintillator solutes in toluene solution. It can be noted that these compounds cannot undergo *cis/trans* isomerism and the activated forms of these may lose energy in the form of light to return to the ground state; however, if *cis/trans* isomerism is possible (as is the case with *trans*-stilbene) an activated *trans* isomer may revert to the higher energy *cis* form without emission of light. Such a process may be responsible for the very poor showing of *trans*-stilbene as a liquid scintillator solute. This work prompted a further study of 1,2-diarylethylenes analogous to *1a* and *1d*.

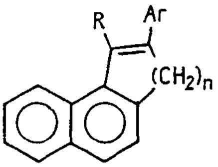
In considering such a study it was felt that the stilbene ethylenic double bond should be part of a five (*2*, *5* and *9*), six (*3*, *7* and *10*), or seven (*12* and *13*) membered ring. A six-membered ring holding double bonds in 1,2- and 3,4-positions would not be planar and therefore the aryl group which is fused to this six-membered ring would not lie coplanar with the ethylenic double bond. This lack of coplanarity should destroy some of the pi orbital overlap across the ethylenic double bond in these six-membered ring systems. Such a system should function less efficiently as a liquid scintillator than a planar system such as that in which the aryl group is fused to a five-membered ring holding the ethylenic double bond. Thus, if the six-membered ring would be replaced with one of five members, it is possible that a better scintillator would result. In the seven-membered ring series one would expect that the aryl group which is fused to the seven-membered ring would be further pushed out of the plane of the ethylenic double bond, and thus the pi bond overlap across the double bond would be further decreased. These compounds would be expected to exhibit lower pulse heights when tested as liquid scintillator solutes. Taber[8] has shown that the angle of twist for sterically hind-



1a, Ar = C_6H_5
1d, Ar = $4\text{-}C_6H_4C_6H_5$



2, $R = R' = H, n = 1$
3, $R = R' = H, n = 2$
4, $R' = H, R = Me, n = 2$
5, $R' = C_6H_5, R = H, n = 1$
6, $R' = C_6H_5, R = Me, n = 1$
7, $R' = C_6H_5, R = H, n = 2$
8, $R' = C_6H_5, R = Me, n = 2$
12, $R' = R = H, n = 3$



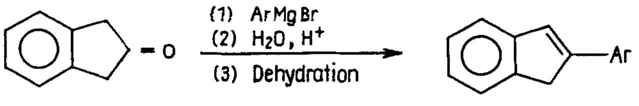
9, $R = H, n = 1$
10, $R = H, n = 2$
11, $R = Me, n = 2$
13, $R = H, n = 3$

ered *p*-quaterphenyls has a decided effect on the relative pulse height, and that such effects are readily distinguishable at low concentrations where self-quenching would be minimized.

We are herewith reporting the progress made thus far in this study, namely the synthesis and properties of the compounds *2* through *11* in which Ar equals phenyl (*2a–11a*), 1-naphthyl (*2b–11b*), 2-naphthyl (*2c–11c*), and 4-biphenylyl (*2d–11d*). We have not succeeded in synthesizing the series of compounds *12* and *13*; however, work on this series is in progress.

The 2-arylindenes (*2*) were prepared as outlined in Scheme I. 2-Indanone was treated with the appropriate aryl magnesium halide and the tertiary carbinol thus formed was readily dehydrated to the desired 2-arylindene (*2*).

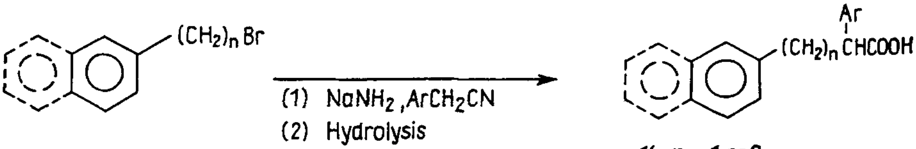
Scheme I



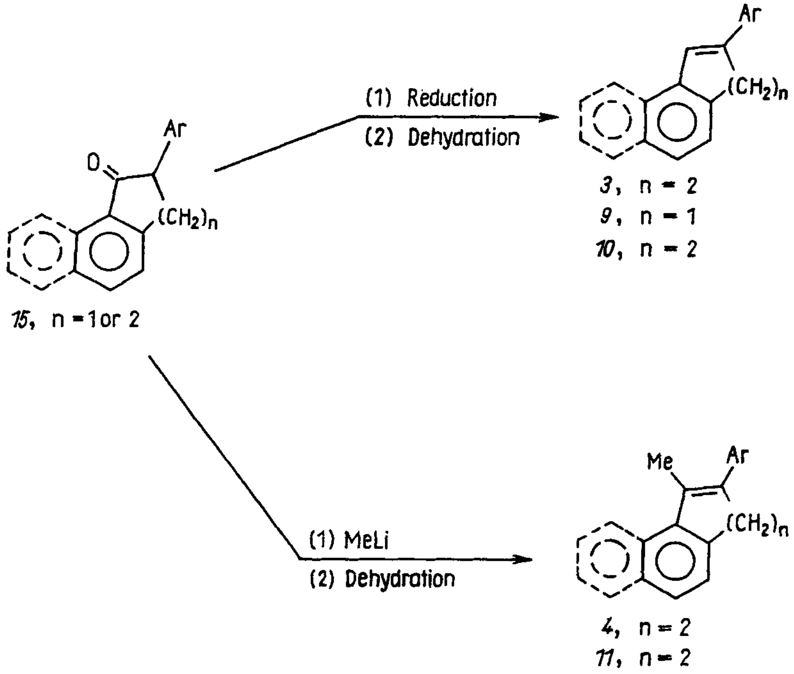
2

The 3-aryl-1,2-dihydronaphthalenes (*3*), 3-aryl-1,2-dihydro-4-methylnaphthalenes (*4*), 2-aryl-3*H*-benz[e]indenes (*9*), 3-aryl-1,2-dihydrophenanthrenes (*10*), and 3-aryl-1,2-dihydro-4-methylphenanthrenes (*11*) were synthesized as outlined in Scheme II. The appropriate arylacetonitrile was alkylated with benzyl bromide, *β*-phenylethyl bromide, 2-bromomethylnaphthalene, or *β*-(2-naphthyl)ethyl bromide in the presence of sodamide. The resulting alkylated nitrile was hydrolyzed to the corresponding substituted propionic acid (*14*, $n = 1$) or butyric acid (*14*, $n = 2$). Cyclization of these acids by the Friedel-Crafts method afforded the cyclic ketones *15* ($n = 1$ or 2). The ketones *15* were converted to

Scheme II



14, n = 1 or 2



15, n = 1 or 2

3, n = 2
9, n = 1
10, n = 2

4, n = 2
11, n = 2

the hydrocarbons *3*, *9* or *10* by reduction with lithium aluminium hydride followed by dehydration of the resulting carbinol. Alternatively, the ketones *15* ($n = 2$) were allowed to react with methyl lithium and the resulting carbinols were dehydrated to the hydrocarbons *4* and *11*.

The indenes *5* and *6* and the dihydronaphthalenes *7* and *8* were also prepared by a series of steps similar to that outlined in Scheme II. In this case the halide used in the initial alkylation step was either 3-(bromomethyl)biphenyl or 3-(2-bromoethyl)biphenyl.

Solutions of the compounds prepared in this study were subjected to conventional scintillation and spectral tests. The scintillation measurements were carried out as described previously[9] with a ten-channel pulse-height analyzer deriving its input signals from an RCA 6903 quartz-face photomultiplier tube having average S-13 spectral characteristics. This particular tube had a POPOP/TP ratio of unity[10]. The ultraviolet-excited fluorescence spectra[11] were obtained by irradiation of toluene solutions (approximately 1 g scintillator/l) contained in a triangular quartz cuvette and analysis of the spectrum with an Aminco-Bowman spectrophotofluorometer. The mean fluorescence wavelengths ($\bar{\lambda}$) were determined as previously described.[11] The ultraviolet absorption spectra of the compounds in cyclohexane solution were determined using a Bausch and Lomb 505 recording spectrophotometer. All measurements were made on solutions which were in equilibrium with air and at room temperature.

All of the compounds were evaluated as primary solutes, and the relative pulse-height values at various concentrations in toluene were plotted to give curves relating relative pulse heights to concentration of solute. In Table 1 are reported the values for RPH_{max} (maximum relative pulse-height), $\text{conc.}_{\text{max}}$ (concentration of solute at RPH_{max}), $\lambda^{\text{fl}}_{\text{max}}$ (maximum fluorescence wavelength), $\bar{\lambda}$ (mean fluorescence wavelength), λ_{max} of the ultraviolet absorption spectrum, and log ε value for each of the compounds. In Table 2 may be punoj data relating the five-membered ring compounds with their corresponding six-membered ring analogs.

As was mentioned earlier it was expected that the compounds having the ethylenic double bond in a five-membered ring (C_5) would be better scintillators than those analogous compounds with the double bond in a six-membered ring (C_6). Indeed, the RPH values (PPO at 3.0 g/l = 1.00) for the five-membered ring (C_5) compounds were in general higher than the corresponding six-membered ring (C_6) compounds *but* only at low concentrations ($\approx$1.4 to 16 mM). As shown in Table 2 at concentrations of solute of 3×10^{-3} M the C_5-ring compound generally shows a higher pulse-height than its C_6-ring homolog. As the concentration of solute is increased the C_5- and C_6-ring pulse-height curves generally cross with the C_5-ring compounds showing their peak pulse-heights at lower concentrations than the corresponding C_6-ring compounds. Examination of the data in Table 2 clearly shows that these generalities hold. In addition, the RPH_{max} for the C_6-ring compounds were generally higher than those for the corresponding C_5-ring compounds although occurring at higher concentrations. Crossover points at which the C_5- and C_6-ring pulse-height curves crossed could readily be determined from the graphs and these values are found in Table 2.

The very poor scintillation efficiency of 3-phenyl-1,2-dihydronaphthalene (*3a*) was unexpected and cannot be explained in terms of structural

TABLE 1 Scintillation, Fluorescence, and Ultraviolet Absorption Spectral Properties of Some *trans*-1,2-Diarylethylenes

Compound	UV-Absorption λ_{max} (logε)	RPH$_{max}$ (conc.†)	λ^{fl}_{max}	$\bar{\lambda}^{fl}$
2a	305 (4.48)	0.89 (11)	362	373
2b	312 (4.43)	0.86 (16)	395	403
2c	329 (4.78)	0.73 (8.0)	395	399
2d	330 (4.60)	0.80 (4.1) (satd.)	390	400
3a	306 (4.37)	0.18 (30)	365	375
3b	298 (4.20)	0.88 (27)	390	400
3c	328 (4.57)	0.84 (15)	380	395
3d	322 (4.59)	1.03 (16)	395	398
4a	282 (4.17)	$<$0.1	375	375
4b	286 (4.16)	0.34 (40)	400	415
4c	280 (4.35)	$<$0.1	400	405
4d	293 (4.33)	$<$0.1	405	403
5a	327 (4.52)	0.98 (11)	385	389
5b	306 (4.05)	0.94 (20)	405	418
5c	332 (4.55)	0.95 (10) (satd.)	402	411
5d	337 (4.62)	0.86 (4.5) (satd.)	408	413
6a	312 (4.51)	1.09 (16)	385	391
6b	302 (4.36)	0.96 (16)	400	408
6c	326 (4.52)	1.04 (20)	402	410
6d	327 (4.61)	1.01 (12)	410	412
7a	327 (4.59)	0.99 (25)	390	401
7b	313 (4.41)	0.95 (16)	410	419
7c	342 (4.63)	1.01 (11) (satd.)	405	413
7d	338 (4.65)	0.88 (4.2) (satd.)	413	422
8a	305 (4.48)	0.13 (58)	395	410
8b	300 (4.44)	0.82 (25)	415	421
8c	312 (4.48)	0.30 (48)	410	425
8d	313 (4.50)	0.52 (11)	415	426
9a	348 (4.58)	0.83 (8.4)	395	408
9b	334 (4.41)	0.90 (15)	425	430
9c	360 (4.65)	0.82 (8.0)	412	425
9d	360 (4.67)	0.92 (15) (satd.)	420	430
10a	351 (4.42)	0.81 (40)	405	414
10b	342 (4.19)	0.93 (25)	420	430
10c	360 (4.47)	0.90 (17)	415	430
10d	360 (4.45)	1.02 (22)	425	432
11a	244 (4.75)	$<$0.1	395	396
11b	225 (4.94)	0.19 (17)	405	415
11c	340 (4.26)	$<$0.1	400	415
11d	298 (4.44)	$<$0.1	410	429

† Approximate concentration of solute in millimoles/liter at middle of peak in pulse height curve.

TABLE 2 A Comparison of Liquid Scintillation Data for *trans*-1,2-Diarylethylenes Having the Ethylenic Double Bond in a Five-membered Ring with those Having the Double Bond in a Six-membered Ring

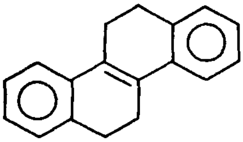
Compound	Ring Size	RPH$_{max}$ (Conc.) (mM)	RPH at 3 × 10^{-3} M	Cross-over† Conc. mM (RPH)
2a	5	0.89 (11)	0.71	
3a	6	0.18 (30)	0.1	—
2b	5	0.86 (16)	0.62	
3b	6	0.88 (27)	0.60	14.0 (0.86)
2c	5	0.73 (8.0)	0.63‡	
3c	6	0.84 (15)	0.64‡	2.0†† (0.55)
2d	5	0.80 (4.1, satd.)	0.70	~1.4†† (0.46)
3d	6	1.03 (16)	0.77††	
5a	5	0.98 (11)	0.79	
7a	6	0.99 (25)	0.50††	16.3 (0.96)
5b	5	0.94 (20)	0.69	4.3 (0.78)
7b	6	0.95 (16)	0.58††	
5c	5	0.95 (10, satd.)	0.80	
7c	6	1.01 (11, stad.)	0.77	3.6 (0.85)
5d	5	0.86 (4.5, satd.)	0.79	3.6 (0.83)
7d	6	0.88 (4.2, satd.)	0.76	
9a	5	0.83 (8.4)	0.70	
10a	6	0.81 (40)	0.45	16.5 (0.77)
9b	5	0.90 (15)	0.67	
10b	6	0.93 (25)	0.61	14.7 (0.89)
9c	5	0.82 (8.0)	0.70	
10c	6	0.90 (17)	0.63	7.0 (0.82)
9d	5	0.92 (14.7, satd.)	0.76	
10d	6	1.02 (22)	0.70	4.9 (0.86)

† Concentration and RPH at which the two curves cross.

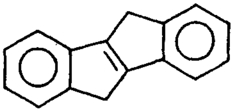
‡ Both compounds have RPH at 2 × 10^{-3} M of 0.55 by extrapolation of 3*c* curve.

†† Estimated by extrapolation of curve.

characteristics since all other members of this series (*3b*, *3c* and *3d*) as well as other analogous compounds we have prepared are good scintillation solutes. For example, 5,6,11,12-tetrahydrochrysene (*16*) has a RPH$_{max}$ of 0.98 while its C$_5$-analog, indeno[2,1-a]-indene (*17*), has a value of only 0.85.[12] The properties of this compound (*3a*) are being studied further.



16



17

The general results of this investigation regarding the C_5-ring system *vs* the C_6-ring system may best be explained by the viewpoint that the more planar and thus more highly conjugated C_5-ring system is basically the more efficient scintillator; however, it is also more susceptible to self-quenching. Thus, at lower concentrations the C_6-ring solute behaves as a better scintillator than the C_6-ring solute, but as the concentration of solute is increased self-quenching effects decrease the scintillation efficiency of the C_5-ring solute at a more rapid rate than the C_6-ring solute. This effect allows the C_6-ring solute to eventually surpass the C_5-ring solute in scintillation efficiency. It would be reasonable to expect the more planar C_5-ring system to fit better into an excimer complex[13] than the puckered C_6-ring system. The completion of our study of the C_7-ring systems should give further information on this subject.

Since the C_7-ring systems (*12* and *13*) were unavailable to us, the effect of a suitably placed methyl group on the scintillation efficiency was investigated. It was felt that the methyl group would present a steric factor which would cause the substitutent aryl group to be twisted out of the plane of the ethylene double bond. This sterically caused twisting should make itself manifest in the scintillation efficiency of the compounds, and we expected to find a resultant decrease in pulse height for the methyl substituted compounds. These expected results were only partially realized as can be seen in the relative pulse-height data for these methylated derivatives (Table 1). In the C_5-ring series the presence of the methyl group had no decreasing effect on the scintillation efficiency of the solute; if anything, it had an increasing effect. In the C_6-ring series a profound decreasing effect on scintillator efficiency is brought on by the presence of the methyl group. The methyl group can apparently disrupt the conjugation in the C_6-ring compounds but is essentially without effect in the C_5-ring systems. Evidence that the methyl group does interfere with the conjugation across the diarylethylene system is obtained from the examination of ultraviolet absorption data for the compounds. In all cases there was a hypsochromic shift of the main absorption band when hydrogen was replaced by methyl, and this hypsochromic shift was larger in the case of the C_6-rings. These ultraviolet absorption bands may be found in Table I and several representative plots are shown in Fig. 1–4.

Molecular models of the Stuart type clearly show that the methyl substituent can effectively twist the adjacent aryl substituent out of the plane of the rest of the molecule in the compounds of the C_6-ring series; however, in the C_5-ring series there is less crowding around the methyl group and the substituent aryl group can essentially assume a position which is coplanar with the rest of the molecule. The hydrogen atom in the 5-position of the 3-aryl-1,2-dihydro-4-methylnaphthalenes appears to provide a buttressing effect[14] on the steric requirements of the 4-methyl group in these compounds. In the 3-aryl-1,2-dihydro-4-methylphenanthrene system the 5-hydrogen atom appears to provide an even stronger buttressing effect on the 4-methyl group. These effects are illustrated with line drawings in Fig. 5 along with the C_5-ring analogs. As can be seen in the drawings the crowding in the C_5-ring is less severe than in the C_6-ring series.

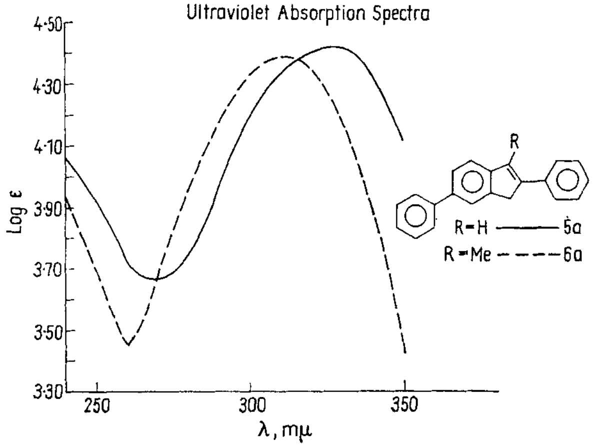
We are presently engaged in the synthesis of the 2-aryl-1-methyl-3*H*-benz[e]indenes and expect these compounds to show decreased scintillation efficiencies compared to the corresponding 2-aryl-3*H*-benz[e]indenes (*9*).

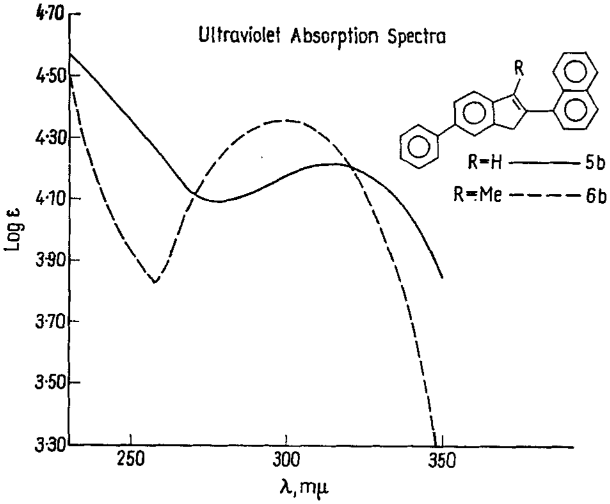
Acknowledgements

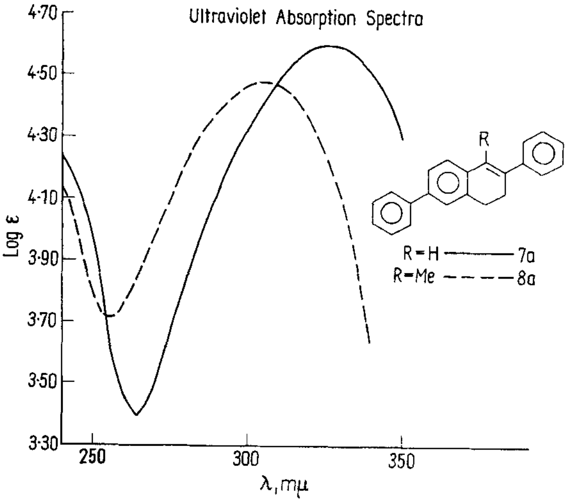
The authors are grateful to Dr. Wright H. Langham, Biomedical Research Group Leader, and to Dr. Thomas L. Shipman, Health Division Leader, of the Los Alamos Scientific Laboratory for the loan of the scintillation pulse-height analyzer used in this study.

Financial aid provided by the Division of Biology and Medicine of the U.S. Atomic Energy Commission (Contract No. AT(29–2)–915) is gratefully acknowledged.

Figures 1, 2, 3, 4 Typical Ultraviolet Absorption Spectral Curves Showing Hypsochromic Shift in Methylated Compounds.



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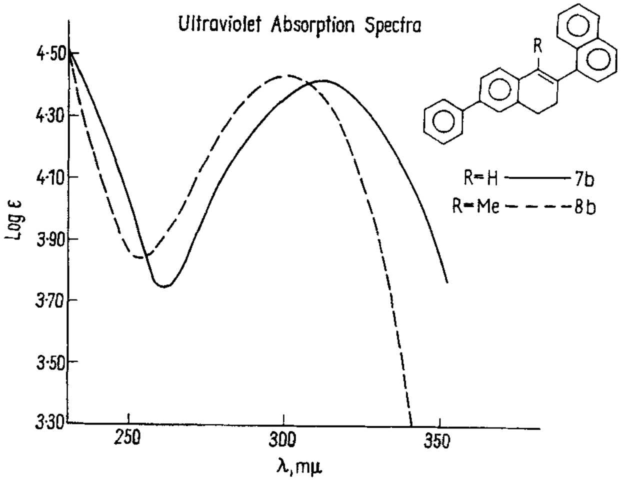
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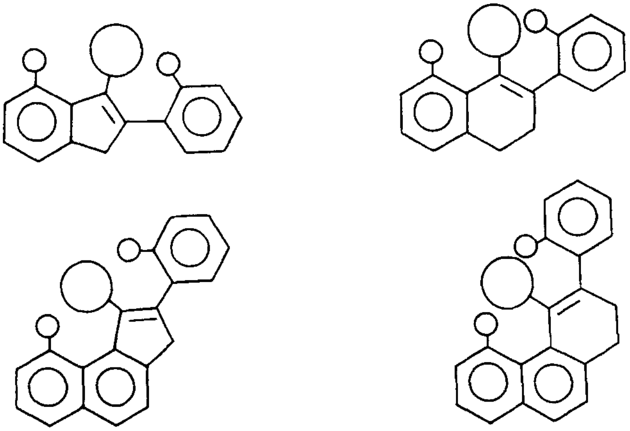

Figure 5. Line Drawings Showing Relative Steric Effect of Methyl Group in Five- and Six-membered Ring Systems.

Upper Left:	2-Aryl-3-methylindene System
Upper Right:	3-Aryl-1,3-dihydro-4-methylnaphthalene System
Lower Left:	2-Aryl-1-methyl-3*H*-benz[e]indene System
Lower Right:	3-Aryl-1,2-dihydro-4-methylphenanthrene System

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3. Work performed under the auspices of the U.S. Atomic Energy Commission.
4. National Aeronautics and Space Administration predoctoral trainee, September, 1963 to August, 1965, on Grant NsG(T)-62. Taken in part from the dissertation presented by David W. Holty to the graduate faculty of the University of New Mexico in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
5. Taken in part from the thesis presented by Lavinel Ionescu to the graduate faculty of the University of New Mexico in partial fulfillment of the requirements for the M.S. degree in Chemistry.
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