Burnett M. Pitt. Oxidation of 10.2 g. (0.07 mole) of *t*-butyl sulfide in 45 ml. of acetic acid solution with 45 ml. (0.45 mole) of 30% hydrogen peroxide was effected by refluxing the solution for one hour. Neutralization of the acetic acid with aqueous sodium hydroxide, and ether extraction gave 9.5 g. (77%) of *t*-**butyl sulfone**, m.p. 129–130°. An analytical sample prepared by crystallization from water melted at 130–130.5°.

Anal. Calcd. for $C_8H_{18}O_2S$: C, 53.89; H, 10.18. Found: C, 53.73; H, 10.25.

2,3-Dihydro-1,4-benzothiapyran 1-dioxide (thiachromane 1-dioxide) was prepared from thiachromanone[18] by a modified Wolff–Kishner reduction,[19] and oxidation of the crude sulfide with 30% hydrogen peroxide in acetic acid. Based on thiachromanone a 76% yield of sulfone, m.p. 87–89°, was obtained. It melted at 88–89° after crystallization from water; von Braun[20] reported 88.5°.

Phenyl vinyl sulfone was prepared from β-chloroethyl phenyl sulfone.[21] A solution of 34.5 g. (0.2 mole) of β-chloroethyl phenyl sulfide[21] in 50 ml. of acetic acid was treated with 100 ml. (1 mole) of 30% hydrogen peroxide. The reaction mixture was refluxed for ten minutes, cooled, diluted with 100 ml. of water and 500 ml. of benzene, and neutralized with sodium bicarbonate. The benzene layer was washed, dried by distilling a portion of the benzene, and treated with 500 ml. of triethylamine. The mixture was filtered and the filtrate evaporated to yield 36 g. of **phenyl vinyl sulfone**, m.p. 65–68° (80% over-all yield from thiophenol). After crystallization from petroleum hexane (b.p. 60–76°) the melting point was 67–68°.

Anal. Calcd. for $C_8H_8O_2S$: C, 57.12; H, 4.79. Found: C, 56.83; H, 4.47.

Reduction of Sulfones to Sulfides with Lithium Aluminum Hydride.—The sulfones were reduced in 2–6 g. quantities at the reflux temperature of ethyl ether or ethyl butyl ether.[22] The reactions in which the molar ratios of lithium aluminum hydride were 9/1 or 10/1 were run by addition of ether solutions or suspensions of the sulfones to ether solutions of the hydride. In later experiments, where the ratio of hydride to sulfone was 3/1 or less, the solid sulfone and hydride were weighed into the reaction flask, and the ether added through the condenser with stirring (a magnetic stirrer was used). At the end of the reaction time the hydride was decomposed by drop-wise addition of water, and the precipitate dissolved in dilute hydrochloric acid. The ether and sulfide were usually separated from the metal salts by steam distillation, separation and drying of the ether layer, and stripping of the ether through a short helix-packed column. The sulfides were distilled from a 5-ml. Claisen flask. Identification was made on the basis of boiling points and also, in most instances, by oxidation to the sulfone (m.p. and mixed m.p.). Thiacyclobutane, thiacyclopentane and 2-methylthiacyclopentane were separated from the ether–sulfide distillate by means of mercuric chloride, the yield of sulfide being calculated on the assumption that a mercuric chloride salt, $R_2S{\cdot}HgCl_2$, was obtained. Phenyl sulfide and dibenzothiophene were isolated from the reaction mixture by ether extraction. Recovery of the sulfones was made by evaporation of the steam distillation residues with the aid of a current of air, extraction with benzene and evaporation.

EVANSTON, ILLINOIS RECEIVED JULY 31, 1950

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[18] Krollpfeiffer and Schultze, *Ber.*, **56B**, 1819 (1923).

[19] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[20] von Braun, *Ber.*, **43B**, 3220 (1910).

[21] Steinkopf, Herold and Stöhr, *ibid.*, **53B**, 1012 (1920).

[22] Kindly furnished by Dr. R. W. McNamee, Carbide and Carbon Chemicals, Charleston, W. Va.

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Ultraviolet Absorptions of Some 2,5-Diphenylfurans and Related Compounds[1]

BY SPENCER M. KING,[2a] CARL R. BAUER[2b] AND ROBERT E. LUTZ

The ultraviolet absorptions of 2,5-diphenylfuran and twenty-five derivatives and analogs, including 2,5-diphenylthiophene and three 2,5-diphenylpyrroles, have been measured and found to resemble those of the 1,4-diphenylbutadienes. Absorption at the longer wave length is suppressed by substitution of mesityl groups for the 2,5-phenyls, and increased by substitution of *p*-xenyl groups.

Furan does not absorb in the near ultraviolet above 220 mμ but does so when the conjugation is increased by even one α-ethylene linkage[3] or a phenyl group.[3b] Diphenylfuran (Ia) and a number of its derivatives (Ib-q) have now been studied and have been found to possess two distinctive bands, one in the range 226–235 mμ and the other (and stronger) in the range 312–340 mμ. Illustrations are given in Figs. 1–3 and the data are tabulated. These absorptions are similar to those of the 1,4-diphenylbutadienes,[4] $C_6H_5CH{=}CHCH{=}CHC_6H_5$. The λ_{max} (324 mμ) of the longer-wave length band of 2,5-diphenylfuran itself is intermediate between the maxima of the main long wave length bands of the all-*cis* and all-*trans* diphenylbutadienes but it is closer to that of the all-*trans* isomer; and the extinction coefficient (29.2×10^3) is not far below that of the all-*cis* isomer but it is about half that of the strongly-absorbing all-*trans* isomer. On the whole it may be said that the absorption of 2,5-diphenylfuran more closely resembles that of the all-*cis* diphenylbutadiene than that of the all-*trans* isomer. It should be noted, however, that, configurationally, 2,5-diphenylfuran is not strictly comparable with either the all-*cis* or the all-*trans* diphenylbutadiene system because, although it corresponds to all-*trans* with respect to the double bonds, it has a *cis* arrangement of the molecule as a whole with respect to the 3,4-furan bond, a condition which does not exist in either of the diphenylbutadienes.

In the case of the mono and disubstituted diphenylfurans Ib-m there is no doubt as to structures; in certain of the others, In-q, the comparability of the ultraviolet absorptions supports the furan structures given[5] and excludes the conceivable though most unlikely 2-substituted-3-methylene-2,5-diphenyl-2,3-dihydrofuran formulations.

2,4-Diphenylfuran (II, Fig. 1) which does not contain the 1,4-diphenylbutadiene system, has a quite different ultraviolet absorption from that of the 2,5-diphenyl compounds; the two peaks ob-

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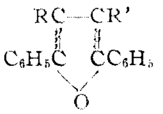
[1] Taken from Doctorate Dissertations of the first two authors, University of Virginia, July, 1950.

[2] (a) Experiment, Inc., Richmond, Va.; (b) du Pont Co. Fellow, 1949–1950, now at University of Virginia Medical School.

[3] (a) Hughes and Johnson, THIS JOURNAL, **53**, 737 (1931); (b) Johnson, *J. Chem. Soc.*, 895 (1946).

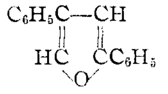
[4] Sandoval and Zechmeister, THIS JOURNAL, **69**, 553 (1947).

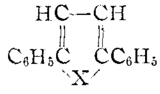
[5] Lutz and Bailey, *ibid.*, **67**, 2229 (1945).


I

R	R'	R	R'	R	R'
a, H	H	g, C_6H_5	C_6H_5	m, H	$N(CH_2CH_2)_2O$
b, H	CH_3	h, H	mesityl	n, H	CH_2Cl
c, CH_3	CH_3	i, H	*p*-tolyl	o, H	CH_2OH
d, H	Br	j, H	OCH_3	p, H	$CH_2N(CH_2CH_2)_2O$
e, Br	Br	k, H	OC_6H_5	q, CH_3	$OCOCH_3$
f, H	C_6H_5	l, H	$OCOCH_3$	r, H	xenyl

served (242 and 277 mμ) correspond in wave length to the characteristic absorptions of styrene and 1-phenylbutadiene (*cf.* ref. 3b).


II


III

a, X = NH
b, X = S
c, X = NCH_3
d, X = NC_6H_5

2,5-Diphenylpyrrole (IIIa) and 2,5-diphenylthiophene (IIIb) show absorption curves very similar to those of the 2,5-diphenylfurans, with peaks occurring at approximately the same wave lengths (Fig. 1). These results are consistent with the similarities of the ultraviolet absorption characteristics within the analogous series, 2-phenylcoumarin, 2-phenylindole, 2-phenylindene and *trans*-stilbene.[6] The fact that the wave length of absorption of the 2,5-diphenylfuran system is not significantly increased by substitution of sulfur or nitrogen for oxygen is perhaps consistent with the current view that the positive-heteroelement forms are of secondary importance. The substitution of a methyl or phenyl at the nitrogen of 2,5-diphenylpyrrole (IIIc, d; Fig. 1) causes a distinct drop in the extinction coefficient of the main band and a pronounced shift toward the shorter wave length, which is doubtless related to an appreciable steric interference with the planarity of the trinuclear system. Calculations on the basis of van der Waals radii indicate that the N-substituents would interfere significantly with coplanarity, especially if these substituents also were in the plane of the pyrrole nucleus as would be required in order for the positive-nitrogen structures to make significant contributions.

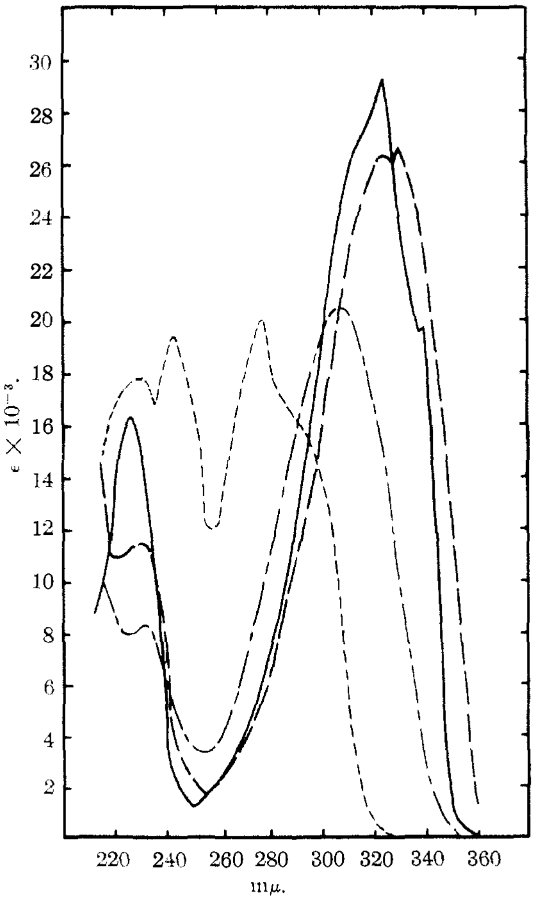


Fig. 1.———, 2,5-diphenylfuran (Ia); — — — — —, 2,5-diphenylpyrrole (IIa); ———————, 2,5-diphenyl-1-methylpyrrole (IIIc); - - - - - - - - - -, 2,4-diphenylfuran (II).

The substitutions in 2,5-diphenylfuran of methyl or bromine at the 3- and/or 4-positions (Ia-e) have little effect on the absorption; however, some of the long-wave length peaks of these derivatives are bifurcated or serrated.

The 2,3,5-tri- and 2,3,4,5-tetraphenylfurans (If, g) (Fig. 2) and 2,5-diphenyl-3-*p*-tolylfuran (Ii)

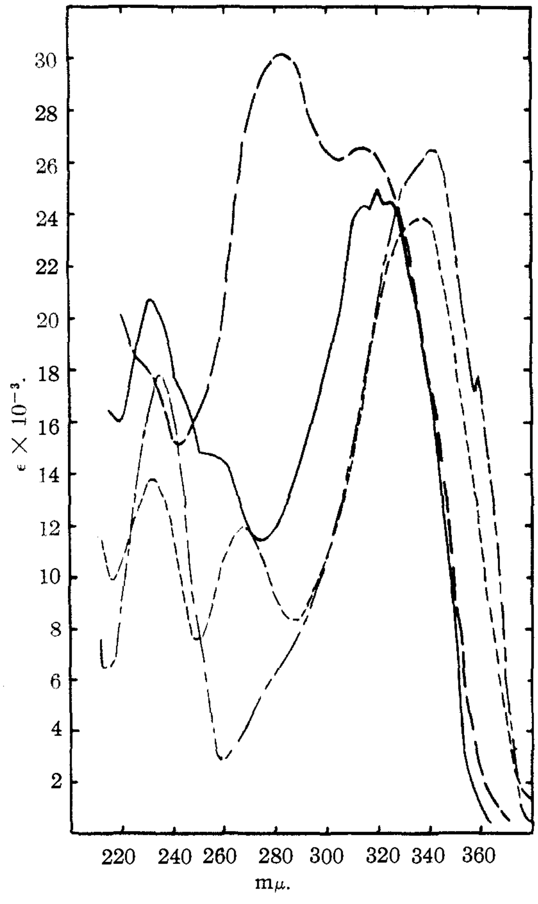


Fig. 2.———, 2,3,5-triphenylfuran (If); — — — —, 2,5-diphenyl-3-xenylfuran (Ir); ———————, 2,5-diphenyl-3-methoxyfuran (Ij); - - - - - - - - - - - - -, 2,5-diphenyl-3-morpholinylfuran (Im).

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(6) Wiegand and Merkel, *Med. u. Chem.*, **4**, 585 (1942).

show the same type of absorption as the 2,5-diphenyl compound (Ia). The 3 and 4 aryl groups seem to have little effect although there is in each of these three cases an extra and smaller absorption peak in the range 253 to 260 mμ. The 3,4-diphenyl compound (Ig) has the lowest extinction coefficient at its long-wave length band, of the whole series of 2,5-diphenylfurans, namely, 21.9 × 10^3. This may be of some significance in connection with the likelihood on steric grounds that there would be appreciable interference by the 3 and/or 4 aryl groups with the planarity of the diphenylbutadiene system, and that the 3,4-aryl groups by virtue of interference each from two sides, would involve greater interference with coplanarity than would the terminal 2,5-phenyls each of which are hindered from only one side. The substitution of a 3-xenyl (biphenyl) group (Ir) for the 3-phenyl causes a new high-extinction peak to appear at 282 mμ, but does not significantly diminish the long-wave length absorption (312 mμ) which corresponds to that of an all-*cis* diphenylbutadiene system. Possibly the 3-xenyl group, as a super-resonator, plays a much more significant role than a phenyl in this position, and it is suggested that the steric interference with planarity between the 2-phenyl and the 3-aryl group is not enough in the case of the 3-xenyl compound to prevent both the 2- and 3-aryl groups from making major contributions to the resonance.

TABLE I

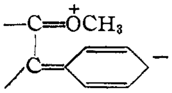
ULTRAVIOLET ABSORPTION MAXIMA

Serrations of main peaks are indicated by bracketing the figures involved.

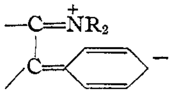
Compound			λmax. in mμ	$\epsilon \times 10^{-3}$
1,4-Diphenylbutadienes[5]				
		all-*cis*[5]	229	17.2
			313	30.4
		all-*trans*[5]	230.4	12.6
			314.5	46.5
			328	56.1
			344	35.3
2,5-Diphenylfurans				
(I)	R	R'		
a	H	H	226	16.2
			324	29.2
b	H	CH_3	229	17.1
			313	26.1
			319	26.0
c	CH_3	CH_3	232	16.4
			318	24.9
d	H	Br	228	21.9
			319	29.1
e	Br	Br	230	19.5
			314	24.2
f	H	C_6H_5	231	20.7
			255	14.8
			315	24.3
			320	25.0
			325	24.5
g	C_6H_5	C_6H_5	232	23.9
			260	16.8
			314	21.6
			320	22.3
			325	21.9
h	H	C_9H_{11}	228	24.4
		(mesityl)	261	7.7
			327	27.9
i	H	*p*-Tolyl	230	19.6
			260	16.7
			325	24.0
j	H	OCH_3	235	17.9
			340	26.5
k	H	OC_6H_5	230	20.6
			270	7.8
			276	8.6
			326	27.7
l	H	$OCOCH_3$	227	19.1
			322	27.9
m	H	NC_4H_8O	232	13.8
		(morpholinyl)	267	12.0
			337	23.9
n	H	CH_2Cl	228	17.4
			314	26.3
o	H	CH_2OH	228	16.2
			316	24.8
p	H	$CH_2NC_4H_1O$	228	15.6
		(morpholinyl)	312	24.1
q	CH_3	$OCOCH_3$	230	19.5
			322	26.8
r	H	$C_{12}H_9$	282	30.2
		(*p*-xenyl)	313	26.7
2,4-Diphenylfuran (II)			230	17.8
			242	19.4
			277	20.0
2,5-Diphenylpyrrole (IIIa)			230	11.9
			325	26.4
			330	26.7
2,5-Diphenylthiophene (IIIb)			230	11.5
			323	25.8
1-Methyl-2,5-diphenylpyrrole (IIIc)			231	8.4
			307	20.5
1,2,5-Triphenylpyrrole			301	19.5
2,5-Dimesitylfuran (VIa)			218	24.0
			265	13.0
2,5-Dimesityl-3-phenylfuran (VIb)			266	16.8
2-Phenyl-5-xenylfuran (VIIa)			258	8.3
			330	30.9
			338	30.8
2,4-Diphenyl-5-xenylfuran (VIIb)			253	20.4
			343	30.6
2,3-Diphenyl-5-xenylfuran (VIIc)			270	17.7
			338	30.9

The substitution of phenoxyl and acetoxyl at position 3 of 2,5-diphenylfuran (Ik,l,q) has little effect on the absorption but a methoxyl (Ij) increases the wave length of the absorption peaks slightly (Fig. 2) as would be expected if an appreciable positive-oxygen contribution of this substituent (IV) were involved.

IV



V



A tertiary-amine nitrogen in the 3-position (V), should involve greater donor effectiveness by the 3-heteroelement but undoubtedly at the same time a much greater steric interference with the planarity required for its full effectiveness[7]; actually the 3-morpholinyl group (Im) causes little change in the long-wave length band (*cf.* Fig. 2) but a new low-extinction peak appears at 267 mμ.

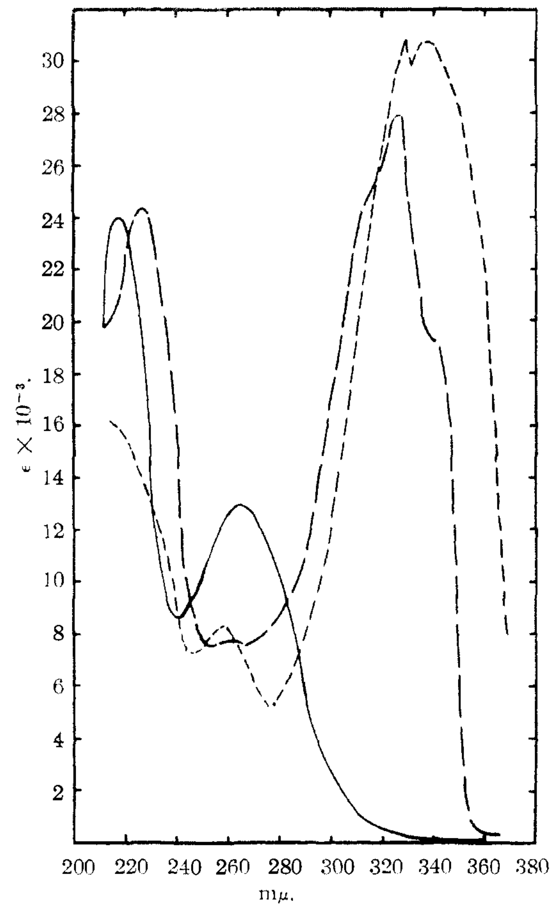
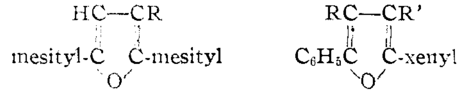


Fig. 3.————, 2,5-dimesitylfuran (VIa); — — — —, 2,5-diphenyl-3-mesitylfuran (Ih); - - - - - - - -, 2-phenyl-5-xenylfuran (VIIa).

The substitution of mesityl groups for the 2,5-phenyls should give rise to a non-planar arrangement in the main. The entirely different ultraviolet absorption curves in two cases (VIa,b), and the suppression of the long-wave length band, are in accordance with this view (Fig. 3). It is of interest incidentally to note that the butadiene system which in the 2,5-diphenylfurans is particularly vulnerable to oxidation, is effectively protected by the steric hindrance offered by the two presumably non-coplanar mesityl groups.[8]



VIa, R = H; b, R = C_6H_5 VIIa, R,R' = H; b, R = H, R' = C_6H_5; c, R = C_6H_5, R' = H

The absorption curve for 2,5-diphenyl-3-mesitylfuran (Ih) (Fig. 3), as would be expected assuming the phenyls to be coplanar with the furan ring and the mesityl group to be non-coplanar, is closely similar to that of 2,5-diphenylfuran.

The substitution of xenyl for one of the 2,5-phenyls should increase the wave length of absorption of the diphenylbutadiene system present, and does so in the three cases studied (VIIa, b, c; see Fig. 3).

Experimental

The ultraviolet absorptions were determined using a Beckman DU quartz spectrophotometer, in absolute ethanol at concentrations of 0.00005 molar. Four of the compounds measured, those involving the xenyl group, are new, and were made by standard procedures (Ir, m.p. 124°; VIIa, m.p. 164°; VIIb, m.p. 135–136°; VIIc, m.p. 158°); the 2,5-diphenyl-3-*p*-tolylfuran (new, m.p. 133–134°) was kindly furnished by Dr. Philip S. Bailey (University of Texas); the experimental data on these compounds will be included in other papers.

All of the 2,5-diphenylfurans studied in this work and in others to be reported shortly, and also 2,5-diphenylthiophene and pyrrole, like the 1,4-diphenylbutadienes,[9] show strong fluorescence under ultraviolet light. In a limited way we have been using this property as a test to distinguish these compounds from 1,4-diketones and other related compounds in the field.

CHARLOTTESVILLE, VIRGINIA RECEIVED AUGUST 29, 1950

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(7) *Cf.* Discussion by Braude, *et al.*, *J. Chem. Soc.*, 1893 (1949).

(8) (a) Lutz and Kibler, THIS JOURNAL, **62**, 1520 (1940); (b) Lutz and Boyer, *ibid.*, **63**, 3189 (1941).

(9) *Cf.* Y. Hirshberg, E. Bergmann and F. Bergmann, *ibid.*, **72** 5117 (1950).