

956. *Syntheses and Properties of Derivatives of Dibenzofuran and Dibenzothiophen. Part I. Monophenyl Derivatives.*

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Syntheses of all the isomeric monophenyl derivatives of dibenzofuran and dibenzothiophen are described. Melting points, complex formation, and absorption spectra are discussed in terms of steric hindrance to the coplanarity of the phenyl substituents and the parent rings.

CURRENT interest in thermally stable materials of wide liquid range formed the basis for this study of the properties of derivatives of dibenzofuran (I; X = O) and dibenzothiophen (I; X = S). Previous work has shown that the 3-phenyl derivatives of benzofuran¹ (II; X = O), benzothiophen² (II; X = S), and indole³ (II; X = NH), and 1-phenylnaphthalene⁴ have much lower melting points than the corresponding 2-phenyl derivatives. Planar-projection diagrams^{2,4} indicate hindrance to the coplanarity of the phenyl substituent in the low-melting isomers and it was considered that such hindrance in appropriate phenyl derivatives of dibenzofuran and dibenzothiophen might lead to compounds having low melting points and high boiling points. The latter phenyl derivatives have not been described previously.

¹ Davies and Middleton, *J.*, 1958, 822.

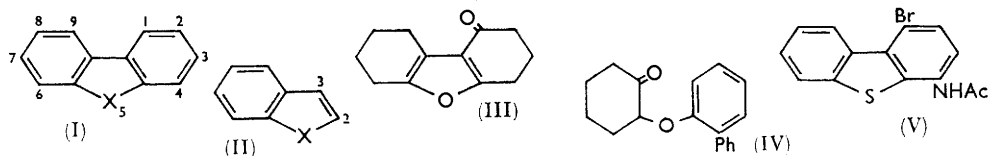
² Middleton, *Austral. J. Chem.*, 1959, **12**, 218.

³ Crowther, Mann, and Purdie, *J.*, 1943, 58.

⁴ Friedel, Orchin, and Regel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.

The present paper describes the synthesis and some of the properties of all the isomeric phenyl-dibenzofurans and -dibenzothiophens.

Syntheses.—There are no known electrophilic substitutions of dibenzofuran or dibenzothiophen which yield high proportions of the 1- and 4-derivatives. 1-Phenyldibenzofuran was therefore obtained from the octahydro-1-oxodibenzofuran (III) by an adaptation of the method⁵ used for 1-methyldibenzofuran. Lithiation^{6,7} of dibenzofuran takes place at the 4-position and provides a suitable route to 4-phenyldibenzofuran through the 4-bromo-derivative. Ebel's dibenzofuran synthesis⁸ with *o*-phenylphenol and 2-chlorocyclohexanone was used as an independent synthesis. Separate cyclisation of 2-*o*-phenylphenoxy-cyclohexanone (IV) was necessary and was accomplished in quantitative yield by using polyphosphoric acid. Substitution of dibenzofuran in the 2-position is readily brought about by molecular bromination⁹ and in the 3-position by nitration in acetic acid;¹⁰ these methods were used in the preparation of 2- and 3-phenyldibenzofuran.



All the phenyl derivatives of dibenzothiophen were obtained from the appropriate bromo-compounds. As in the case of dibenzofuran, dibenzothiophen is brominated largely in the 2-position.¹¹ Nitration, however, also yields the 2-derivative; it is necessary to use the 5-oxide to induce 3-substitution.¹² Lithiation occurs at the 4-position, and bromination of the lithio-compound provides the 4-bromo-derivative,¹³ whilst carboxylation allows the preparation of 4-acetamidodibenzothiophen¹⁵ in which the acetamido-group directs bromination into the 1-position (V). Deamination of this compound (V) affords 1-bromodibenzothiophen.¹⁶

Planar-projection diagrams with either van der Waals radii or double covalent radii¹⁷ indicate considerable overcrowding in 1-phenyl-dibenzofuran and -dibenzothiophen owing to overlap of hydrogen atoms on the substituent and the 9-hydrogen atom of the nucleus, and less crowding in the 4-phenyl derivatives owing to overlap with the neighbouring bulky heteroatoms. Analogy with similar systems such as biphenyl¹⁸ and the terphenyls¹⁹ suggests that such overcrowding and the accompanying strain are most likely to be relieved by rotation of the substituent phenyl group out of the main molecular plane. In the solid state this would probably mean that the 1- and the 4-phenyl derivatives would be non-planar (compare *o*-terphenyl¹⁹), and that the 2- and 3-derivatives would be planar (compare biphenyl^{18,19}). In the liquid state or in solution, non-planarity would be general

⁵ Chatterjea and Ray, *Chem. Ber.*, 1959, **92**, 998.

⁶ Gilman, *Org. Reactions*, 1954, **8**, 258.

⁷ Gilman, Parker, Baillie, and Brown, *J. Amer. Chem. Soc.*, 1939, **61**, 2836.

⁸ Ebel, *Helv. Chim. Acta*, 1929, **12**, 3.

⁹ Mayer and Krieger, *Ber.*, 1922, **55**, 1659; Eaborn, *J.*, 1961, 5079.

¹⁰ Borsche and Bothe, *Ber.*, 1908, **41**, 1940; Cullinane, *J.*, 1930, 2267; Gilman, Bywater, and Parker, *J. Amer. Chem. Soc.*, 1935, **57**, 885; Dewar and Urch, *J.*, 1957, 345; Eaborn, *J.*, 1961, 4924.

¹¹ Cullinane, Davies, and Davies, *J.*, 1936, 1435; Eaborn, *J.*, 1961, 5079.

¹² Brown, Christiansen, and Sandin, *J. Amer. Chem. Soc.*, 1948, **70**, 1748.

¹³ Gilman and Esmay, *J. Amer. Chem. Soc.*, 1954, **76**, 5786.

¹⁴ Illuminati, Nobis, and Gilman, *J. Amer. Chem. Soc.*, 1951, **73**, 5887; Gilman and Ingham, *ibid.*, 1953, **75**, 3843.

¹⁵ Gilman and Esmay, *J. Amer. Chem. Soc.*, 1952, **74**, 2021.

¹⁶ Gilman and Jacoby, *J. Org. Chem.*, 1938, **3**, 108.

¹⁷ Braude and Sondheim, *J.*, 1955, 3574.

¹⁸ Coulson, "Steric Effects in Conjugated Systems," Butterworths Scientific Publns., London, 1958, p. 8; "Theoretical Organic Chemistry" (Kekulé Symposium), Butterworths Scientific Publns., London, 1959, p. 49.

¹⁹ Anderson and Ubbelohde, *Proc. Roy. Soc.*, 1955, *A*, **228**, 435; Ubbelohde, *Chem. and Ind.*, 1961, 186.

for all isomers but most severe for the 1-isomers. It was expected that such steric features would be observable in the melting points, complex formation, and absorption spectra.

Melting Points.—The melting process is not well understood,¹⁹⁻²¹ so that detailed discussion of the variation in melting points is not possible even among these closely related phenyl derivatives. Orchin and Friedel²² have stated that the non-planarity of 1-phenylnaphthalene probably explains the low melting point, compared with that of 2-phenylnaphthalene, and a similar effect has been noted for the phenyl-benzofurans and -benzothiophens.^{1,2} The striking facts in the present series (Table) are that 4-phenyldibenzofuran (m. p. 35°) melts at a lower temperature than the highly hindered 1-phenyldibenzofuran (63°), and that there is little difference between the melting points of the 1-, 2-, and 4-isomers in the dibenzothiophen series. In common with the phenyl derivatives of the simpler systems (II), there are generally lower melting points for the hindered compounds than for the 3-isomers. The rule cannot be taken further, however, and cannot be interpreted satisfactorily in the absence of knowledge about the heats and entropies of fusion. Similar considerations can be applied to the phenyl derivatives of phenanthrene.^{23,24}

Melting points (M. p.) of the phenyl-dibenzofurans and -dibenzothiophens. Melting points of trinitrofluorenone derivatives (T.N.F.), apparent association constants (K , l. mole⁻¹), and molar absorptivities (E , l. mole⁻¹ cm.⁻¹) of the 1:1 complexes with 2,4,7-trinitrofluorenone.

Subst.	Dibenzofuran				Dibenzothiophen			
	M. p.	T.N.F.	K	E	M. p.	T.N.F.	K	E
Parent	87°	163°	1.9	1125	99°	210°	4.4	1550
1-Ph	63	—	2.7	545	70	162	1.5	2037
2-Ph	100	161	1.8	1383	73	166	6.7	946
3-Ph	130	150	—	—	179	172	—	—
4-Ph	35	149	4.0	1027	69	144	—	—

Complex Formation.—The stabilities of complexes between aromatic compounds and nitro-compounds such as 1,3,5-trinitrobenzene, picric acid and 2,4,7-trinitrofluorenone have been related to steric effects in the donor molecule.²⁵ Quantitative evidence that such effects are important has been obtained for cyclohexenylnaphthalenes²⁶ and methylbenzanthracenes²⁷ with 2,4,7-trinitrofluorenone. Observations on compounds having non-planar phenyl substituents have been qualitative but suggestive, and notable examples are the inability of 3-phenyl-benzofuran¹ and -benzothiophen² to form isolable complexes with picric acid or 2,4,7-trinitrofluorenone.

In the present series, apparent spectrophotometric association constants²⁸ have been determined (see Table; the m. p.s of the isolated complexes are recorded to illustrate the lack of a parallel, noted previously,²⁷ with stability) in an attempt to explain the qualitative observation that 1-phenyldibenzofuran fails to give a solid complex with 2,4,7-trinitrofluorenone from a variety of solvents, whilst the sterically similar 1-phenyldibenzothiophen does so readily. Unfortunately, the charge-transfer absorption band for 1-phenyldibenzofuran with 2,4,7-trinitrofluorenone in chloroform is weak, so that the association constant may be unreliable. However, the value for 1-phenyldibenzothiophen in relation to the values for dibenzothiophen and 2-phenyldibenzothiophen seems to indicate a direct steric

²⁰ Ubbelohde, *Trans. Faraday Soc.*, 1957, **53**, 628; McLaughlin and Ubbelohde, *ibid.*, 1958, **54**, 1804.

²¹ Ubbelohde, *Quart. Rev.*, 1950, **4**, 356.

²² Orchin and Friedel, *J. Amer. Chem. Soc.*, 1949, **71**, 3002.

²³ Anderson, Campbell, and Leaver, *J.*, 1959, 3992.

²⁴ Beckwith and Thompson, *J.*, 1961, 73.

²⁵ Orchin, *J. Org. Chem.*, 1951, **16**, 165; Newman, "Steric Effects in Organic Chemistry," J. Wiley, 1956, p. 471; Andrews, *Chem. Rev.*, 1954, **54**, 713; McGlynn, *ibid.*, 1958, **58**, 1113.

²⁶ Klemm and Sprague, *J. Org. Chem.*, 1954, **19**, 1464; Klemm, Sprague, and Ziffer, *ibid.*, 1955, **20**, 200.

²⁷ Takemura, Cameron, and Newman, *J. Amer. Chem. Soc.*, 1953, **75**, 3280.

²⁸ Foster, *J.*, 1960, 1075.

effect which hinders the plane-to-plane approach of the two components of the complex. If the 1-phenyl substituent is perpendicular to the main molecular plane (the ultraviolet spectrum demonstrates severe hindrance), values of 1.39 and 1.08 Å for the C-C and

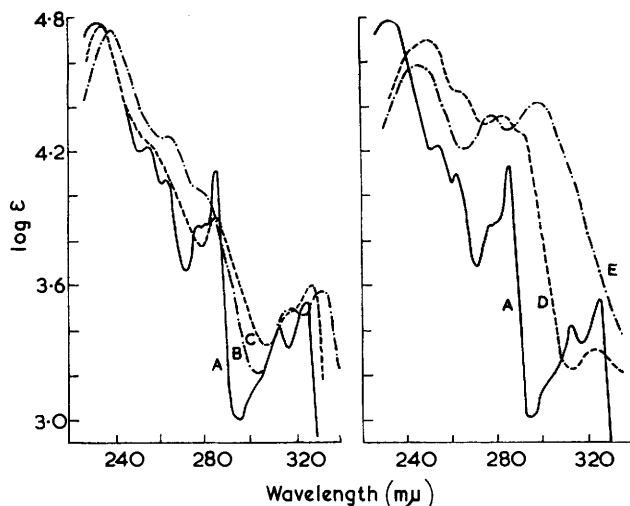


FIG. 1.

FIG. 2.

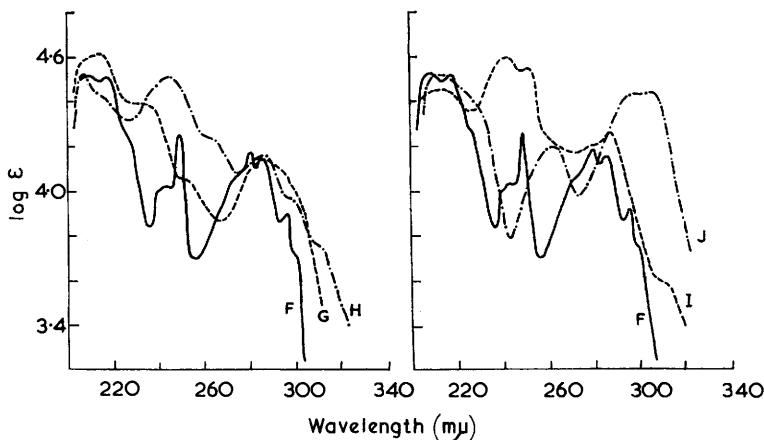


FIG. 3.

FIG. 4.

FIGS. 1—4. Absorption spectra of: (A) dibenzothiophen; (B) 4-, (C) 1-, (D) 2-, and (E) 3-phenyldibenzothiophen; (F) dibenzofuran; (G) 1-, (H) 4-, (I) 2-, and (J) 3-phenyldibenzofuran.

C-H bond lengths and 1.2 Å for the van der Waals radius of hydrogen indicate a closest approach of 3.34 Å. This is of the same order as the perpendicular separation found in solid complexes.²⁹

Absorption Spectra.—The commonest effects of the non-coplanarity of substituents on ultraviolet spectra are^{30,31} (a) in the case of moderate hindrance, a hypsochromic shift, and/or a decreased intensity of some characteristic longwave absorption band relative to a

²⁹ Wallwork, *J.*, 1961, 494.

³⁰ "Steric Effects in Conjugated Systems," Butterworths Scientific Publns., London, 1958.

³¹ Jaffe and Orchin, *J.*, 1960, 1078.

suitable reference compound, and (b) in the case of severe hindrance, degeneration of the spectrum towards that of the parent substance. Effect (a) can be shown to result when the bond order of the bond joining a substituent to a parent aromatic ring increases as the result of excitation.

Ultraviolet spectra in the present series can be partly interpreted on the basis that there is hindrance to conjugation in the 1- and 4-phenyl derivatives. In the case of the dibenzothiophen derivatives, it appears that effect (b) is under observation. For both the 1- and 4-phenyl compounds, there is a strong resemblance between the spectra and that of the unsubstituted parent compound (Fig. 1). By contrast, the 2- and 3-phenyl derivatives demonstrate the bathochromic shifts of absorption bands expected for compounds in which there is enhanced conjugation (Fig. 2). For the dibenzofuran derivatives, the position is less clear but there is a very close resemblance between the 2- and the 4-phenyl derivative (Figs. 3 and 4), and the 1-phenyl derivative shows some of the characteristics of the parent. Hindrance in the 4-phenyl compound is apparently not sufficient to produce a large effect on the ultraviolet absorption though there is a decreased intensity relative to the 2-phenyl isomer for both of the long-wavelength absorption bands. Hindrance appears to be considerably greater for 1-phenyldibenzofuran.

EXPERIMENTAL

Ultraviolet spectra (ethanol solutions) were obtained by using a Unicam S.P. 700 spectrometer (ϵ are given below in parentheses). Association constants were determined by Foster's method²⁸ with a fixed concentration of 2,4,7-trinitrofluorenone (*ca.* $8 \times 10^{-4}M$) and varying concentrations of the heterocyclic compounds (0.03—0.15*M*) in spectroscopic chloroform. Measurements were made beyond 440 $m\mu$ and only small corrections were necessary for absorption due to the components of the complexes. Linear plots indicated the formation of 1:1 complexes and this was confirmed by analysis of the solids isolated from xylene-ethanol (1:1) solutions. All the phenyl derivatives were checked for purity by gas chromatography and are thought to be at least 99% pure.

1-Phenyldibenzofuran.—1,2,3,4,6,7,8,9-Octahydro-1-oxodibenzofuran, m. p. 54.5—57.5°, prepared in 62% yield from dihydroresorcinol and 2-chlorocyclohexanone,⁵ condensed with phenylmagnesium bromide in ether to give a yellow oil, b. p. 158—190°/2.5 mm., which was heated with 40% of its weight of 5% palladium-charcoal at 310° for 6 hr. The *product*, after distillation (b. p. 152—158°/0.4 mm.), crystallised from light petroleum and had m. p. 63—64° (Found: C, 88.2; H, 5.0. $C_{18}H_{12}O$ requires C, 88.5; H, 4.9%), λ_{max} 238 (23,300) and 287 $m\mu$ (13,630). A *complex*, m. p. 96—97°, with 1,3,5-trinitrobenzene crystallised from ethanol (Found: C, 63.3; H, 3.2; N, 9.7. $C_{18}H_{12}O, C_6H_3N_3O_6$ requires C, 63.0; H, 3.3; N, 9.2%). The compound did not form a complex with picric acid in ethanol, or with 2,4,7-trinitrofluorenone in xylene-ethanol (1:1), acetic acid, or chloroform.

2-Phenyldibenzofuran.—2-Bromodibenzofuran,⁹ m. p. 101—105°, formed a Grignard compound in tetrahydrofuran and this with cyclohexanone yielded a pale yellow oil, b. p. 196—208/1.5 mm., which, after reaction with 5% palladium-charcoal at 310° for 13 hr. gave *2-phenyldibenzofuran*, b. p. 188—192°/1.2 mm., which crystallised from acetic acid and then had m. p. 99—100° (Found: C, 88.7; H, 5.0%), λ_{max} 244 (38,500) and 289 $m\mu$ (17,900). It formed a *complex*, m. p. 160—161°, with 2,4,7-trinitrofluorenone (Found: C, 66.5; H, 3.0; N, 7.3. $C_{18}H_{12}O, C_{13}H_5N_3O_7$ requires C, 66.5; H, 3.1; N, 7.5%).

3-Phenyldibenzofuran.—3-Nitrodibenzofuran, m. p. 181—182°, was prepared in 67% yield by the method of Borsche and Bothe¹⁰ and was reduced to 3-aminodibenzofuran (65% yield). 3-Bromodibenzofuran (57% yield¹²) formed a Grignard derivative in tetrahydrofuran that on condensation with cyclohexanone and dehydrogenation as above gave *3-phenyldibenzofuran*, m. p. 130—131° (from acetic acid) (Found: C, 87.8; H, 5.0%), λ_{max} 263 (16,000) and 303 $m\mu$ (26,300). It gave a *2,4,7-trinitrofluorenone derivative*, m. p. 148—149.5° (Found: C, 66.6; H, 2.8; N, 7.6%).

4-Phenyldibenzofuran.—(a) Dibenzofuran was metallated with *n*-butyl-lithium in ether and converted into 4-bromodibenzofuran by the method of Gilman *et al.*⁷ (yield 17%; m. p. 57.5—59°). Conversion into *4-phenyldibenzofuran*, b. p. 157—159°/0.2 mm., was effected as above.

Gas-chromatography indicated the presence of a minor proportion of impurity having a retention volume equal to that for 1-phenyldibenzofuran. Purification by decomposition of the trinitrofluorenone derivative on activated alumina gave a colourless liquid (Found: C, 88.4; H, 5.1%; λ_{\max} , 244 (31,850) and 289 μ (14,430) [2,4,7-trinitrofluorenone derivative, m. p. 147.5—148.5° (Found: C, 65.7; H, 3.0; N, 7.35%)]).

(b) Condensing sodium *o*-phenylphenoxide and 2-chlorocyclohexanone by Ebel's procedure⁸ gave a mixture containing a major proportion of 2-*o*-phenylphenoxycyclohexanone (Found: C, 83.6; H, 6.9. Calc. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8%), which gave a 2,4-dinitrophenylhydrazone, m. p. 160—161° (Found: C, 64.1; H, 4.7; N, 12.7. $C_{24}H_{22}N_4O_5$ requires C, 64.6; H, 5.0; N, 12.55%). Cyclisation of the ketone (71.9 g., 0.27 mole) with phosphorus pentoxide (1438 g.) and phosphoric acid (719 ml.; *d* 1.75) for 3 hr. at 100° gave 1,2,3,4-tetrahydro-6-phenyldibenzofuran (69 g., 100%), m. p. 43—45° (Found: C, 86.8; H, 6.5%; *M*, 266. $C_{18}H_{16}O$ requires C, 87.0; H, 6.45%; *M*, 248). Dehydrogenation with 100% excess of selenium at 330° gave 4-phenyldibenzofuran identical (infrared spectra, gas-chromatography) with the product obtained by method (a). It crystallised from ethanol initially at -40° and subsequently at room temperature and had m. p. 34—35°.

1-Phenyldibenzothiophen.—4-Acetamidodibenzothiophen,¹⁵ m. p. 196—198°, was brominated¹⁶ in acetic acid. Deamination by nitrosylsulphuric acid¹⁶ gave 1-bromodibenzothiophen m. p. 82—83° (Found: C, 55.1; H, 2.4; S, 12.2; Br, 29.85. Calc. for $C_{12}H_7BrS$: C, 54.7; H, 2.7; S, 12.2; Br, 30.4%). A Grignard reaction with cyclohexanone in tetrahydrofuran gave an oil, b. p. 216—226°/1.5 mm., which on dehydrogenation as above, distillation (b. p. 200—203°/1.5 mm.), sublimation, and recrystallisation from acetic acid gave 1-phenyldibenzofuran, m. p. 68.5—70° (Found: C, 82.9; H, 4.6; S, 12.0. $C_{18}H_{12}S$ requires C, 83.1; H, 4.6; S, 12.3%), λ_{\max} , 234 (56,900) and 286 μ (7950). The 5,5-dioxide had m. p. 137—138° (from acetic acid) (Found: C, 73.7; H, 4.15; S, 10.7. $C_{18}H_{12}O_2S$ requires C, 74.0; H, 4.1; S, 10.95%). The 2,4,7-trinitrofluorenone derivative had m. p. 160.5—162° (Found: C, 64.4; H, 3.0; S, 5.6; N, 7.4. $C_{18}H_{12}S, C_{13}H_5N_3O_7$ requires C, 64.7; H, 3.0; S, 5.6; N, 7.3%).

2-Phenyldibenzothiophen.—The method of Cullinane, Davies, and Davies¹¹ gave 2-bromodibenzothiophen, m. p. 115—117° (yield 77%). 2-Phenyldibenzothiophen, prepared from the 2-bromo-compound as in the preceding case and crystallised from acetic acid, had m. p. 73—74° (Found: C, 83.2; H, 5.0; S, 12.0%), λ_{\max} , 247 (46,000) and 282 μ (21,700) [5,5-dioxide, m. p. 173—174° (from acetic acid) (Found: C, 74.1; H, 4.6; S, 10.85%); 2,4,7-trinitrofluorenone derivative, m. p. 164—166° (Found: C, 64.7; H, 3.2; S, 5.8; N, 7.3%)].

3-Phenyldibenzothiophen.—3-Aminodibenzothiophen, m. p. 119—121°, obtained from 3-nitrodibenzothiophen 5-oxide by the method of Brown *et al.*,¹² was converted into 3-bromodibenzothiophen, m. p. 97—98.5°, as described by Illuminati *et al.*¹⁴ Condensation of the Grignard compound with cyclohexanone as usual gave 3-phenyldibenzothiophen, m. p. 178.5—179.5° (from acetic acid) (Found: C, 83.1; H, 4.7; S, 11.9%), λ_{\max} , 247 (35,600), 278 (21,700), and 299 μ (25,300) [5,5-dioxide, m. p. 208.5—209.5° (Found: C, 73.5; H, 4.3; S, 11.2%); 2,4,7-trinitrofluorenone derivative, m. p. 170.5—172° (Found: C, 64.5; H, 2.8; S, 5.4; N, 7.2%)].

4-Phenyldibenzothiophen.—4-Dibenzothiophenyl-lithium was converted into 4-bromodibenzothiophen, m. p. 75—79° (cf. Gilman and Esmay¹³), and gave 4-phenyldibenzothiophen, m. p. 63—64.5° (Found: C, 83.3; H, 4.8; S, 11.65%), λ_{\max} , 239 (54,100) and 282 μ (9750) [5,5-dioxide, m. p. 203—205° (Found: C, 73.7; H, 4.2; S, 11.05%); 2,4,7-trinitrofluorenone derivative, m. p. 142—143.5° (Found: C, 64.0; H, 3.0; S, 5.7; N, 7.6%)].