The Structure of 2-(*p*-Dimethylanilino)-4-phenyl-6,6a-dithiafurophthene

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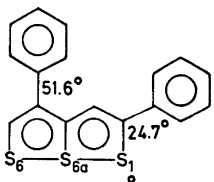
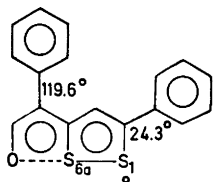


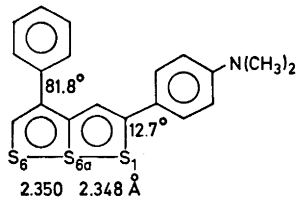
(I)



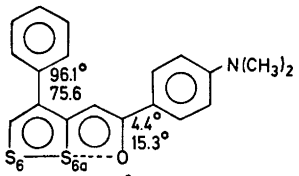
(II)

The length of the S(1)–S(6a) bond in 2,4-diphenyl-6a-thiathiophthene (I) and the length of the corresponding bond in 2,4-diphenyl-1,6a-dithiafurophthene are 2.499 and 2.106 ± 0.003 Å, respectively.[1,2] Thus, replacing S(6) in compound I by oxygen causes a decrease of 0.39 Å in the S(1)–S(6a) bond length.

A recent structure study of 2-(*p*-dimethylanilino)-4-phenyl-6a-thiathiophthene (III) shows that the sulphur-sulphur bonds in this compound are of equal length although the molecule has substituents



(III)



molecule A: 2.101 2.443 Å
molecule B: 2.111 2.284 Å

(IV)

in unsymmetrical positions; the S–S bonds in III were found to be 2.348 and 2.350 ± 0.0013 Å, respectively.[3]

We thought it might be of interest to look at the structure of a dithiafurophthene which had the same 2- and 4-substituents as compound III, and we have accordingly carried out an X-ray structure determination of 2-(*p*-dimethylanilino)-4-phenyl-6,6a-dithiafurophthene (IV). Preliminary results from this study are given.

The sulphur-sulphur distances as found in the two crystallographically non-equivalent 2-(*p*-dimethylanilino)-4-phenyl-6,6a-dithiafurophthene molecules A and B are 2.101 and 2.111 ± 0.002 Å, respectively, and the S(6a)–O distances, mentioned in the same order, are 2.443 and 2.284 ± 0.004 Å. The central ring system is planar in both molecules, and the twist angle of the phenyl group and that of the *p*-dimethylanilino group about the respective connecting bonds are 96.1 and 4.4° in molecule A, and 75.6 and 15.3° in molecule B.

The lengths found for the S–S bond in IV agree with the length 2.106 ± 0.003 Å of the S–S bond in compound II. One notes, however, that the S–O distance in molecule IV A is 0.16 Å longer than that in IV B, and that the shortest S–S bond length corresponds to the longest S–O distance.

A sample of 2-(*p*-dimethylanilino)-4-phenyl-6,6a-dithiafurophthene was generously supplied by Klingsberg.[4] The crystals are orange and belong to the monoclinic space group $P2_1/c$. The cell dimensions are $a = 14.180$ Å, $b = 10.265$ Å, $c = 23.321$ Å, and $\beta = 93.92°$. There are eight molecules per unit cell; density, calculated 1.331, found 1.33 g/cm³.

The structure analysis is based on X-ray data collected on a paper-tape controlled Siemens AED diffractometer using Mo$K\alpha$ radiation. 2951 reflections were observed within $\theta = 25°$.

The structure was solved by a symbolic addition procedure[5] and refined by full matrix least squares. The present R factor is 0.07.

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A Modified Synthesis of (±)-2,2′-Spirobi[indan]-1,1′-dione

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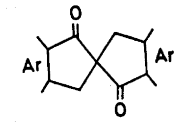
Aromatic spiro compounds of high symmetry and low overlap between the aromatic chromofores are of spectroscopic and theoretical interest.

One type of such compounds is derived from the spiro[4.4]nonane system. These compounds are usually synthesized according to the following route

$$ArCH_2CH(COOR)_2 \xrightarrow{1} (ArCH_2)_2C(COOR)_2$$

$$(ArCH_2)_2C(COX)_2 \xrightarrow{2}$$



The title spiro compound was previously synthesized by this method,[1] but the yield in step 2 was low.[2]

It has, however, been demonstrated that the unsymmetric spirodiketone 3′,4′-dihydrospiro[indan-2,2′(1′H)-naphthalene]-1,1′-dione could be prepared by cyclization of *o*-carboxy-α-phenethylhydrocinnamic acid.[3]

In the present communication it is demonstrated that this method can be successfully applied to the synthesis of the title spiro compound as outlined in Scheme 1.

The structures of the compounds II, IV, and VI were established by comparison of their NMR spetcra with those for the corresponding known compounds I, III, and V.

Physical data for the spiroketone VII (m.p. and CH-analysis) agreed with those previously reported.[1] Conclusive proof for the structure of VII, however, was afforded by means of the NMR spectrum, the aliphatic part of which displays an AB quartet, owing to the magnetic nonequivalence of the two hydrogens in the methylene groups of VII.

As expected the UV spectrum of VII shows a close resemblance to that of 1-indanone. The UV spectrum of 1-indanone in ethanol displays two absorption bands at 2460 and 2940 Å, respectively. The corresponding absorption bands for VII are positioned at 2520 and 2970 Å, but the extinction coefficients for VII at these two wavelengths are more than 2 times the values for 1-indanone indicating some electronic interaction between the two chromofores in VII.

Experimental. NMR spectra were recorded at 60 Mc/s on a Varian A-60 spectrometer. TMS was used as internal reference standard and the chemical shifts are expressed in τ-values. The coupling constants are expressed numerically in c/s. In the NMR data the notations for the hydrogen atoms according to Scheme 1 are used. The following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet. The UV-spectra were recorded on a Bausch and Lomb Spectronic 505 spectrometer.

(±)-*Triethyl benzyl-o-carboxybenzylmalonate* (II). To a stirred suspension of 0.12 mol sodium hydride (50 % in mineral oil) in 50 ml of dry DMF was added 27.43 g (0.11 mol) of diethyl benzylmalonate in an atmosphere of dry nitrogen. The internal temperature was maintained at 60° during 2 h. After formation of the sodium derivative, 26.7 g (0.11 mol) of ethyl α-bromo-*o*-toluate,[4] was added during 10 min, in which time the internal temperature rose to 90°. Stirring and heating was continued at 60° for 1.5 h. Most of the solvent was removed by distillation *in vacuo*. To the residue was added water (50 ml) and ether (90 ml). After extraction of the ethereal solution with sodium carbonate (5 %) and drying over calcium sulphate, the ether was evaporated *in vacuo*. The residue was distilled at 0.8 mm to give 34.9 g (75 %) of II with b.p. 200–210°. NMR