Acta Cryst. (1975). B31, 30

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

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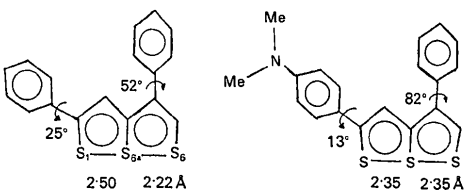
(*Received* 22 *July* 1974; *accepted* 24 *July* 1974)

2-(*p*-Dimethylanilino)-4-phenyl-6,6a-dithiafurophthene is monoclinic, space group $P2_1/c$, with $a=14{\cdot}180\ (3)$, $b=10{\cdot}265\ (2)$, $c=23{\cdot}322\ (5)$ Å, $\beta=93{\cdot}92\ (3)°$, $Z=8$. The structure was solved from counter data by direct methods and refined by full-matrix least-squares calculations to a final R of 0·044. The bond lengths in the dithiafurophthene system in the two crystallographically independent molecules are S(6)–S(6a) = 2·1045 (15) and 2·1101 (16), S(6a)–O = 2·441 (3) and 2·287 (3), O–C (2) = 1·255 (5) and 1·263 (5), S(6a)–C(3a) = 1·764 (4) and 1·758 (4), S(6)–C(5) = 1·720 (4) and 1·714 (4), C(2)–C(3) = 1·430 (5) and 1·428 (6), C(3)–C(3a) = 1·360 (5) and 1·377 (5), C(3a)–C(4) = 1·438 (5) and 1·444 (5), and C(4)–C(5) = 1·343 (5) and 1·345 (5) Å, respectively. The difference in S–O bond length is probably due to packing forces.

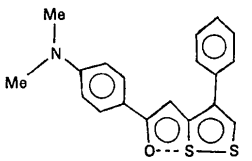
Introduction

Structural studies of 2,4-diphenyl-6a-thiathiophthene (I) (Hordvik, Sletten & Sletten, 1969*b*) and of 2-(*p*-dimethylanilino)-4-phenyl-6a-thiathiophthene (II) (Hordvik & Sæthre, 1972*b*) show that the introduction of a *p*-dimethylamino group in the 2-phenyl group of compound (I) causes a decrease in the S(1)–S(6a) bond length from 2·499 (3) in (I) to 2·348 (1) Å in (II), and an increase in S(6a)–S(6) from 2·218 (3) in (I) to 2·350 (1) Å in (II).



(I)

(II)



(III)

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 (II), and we have accordingly carried out an analysis of 2-(*p*-dimethylanilino)-4-phenyl-6,6a-dithiafurophthene (III). Preliminary results have been reported (Hordvik & Sæthre, 1972*a*).

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Crystal data

Crystals of 2-(*p*-dimethylanilino)-4-phenyl-6,6a-dithiafurophthene, $C_1\ H_{17}NOS_2$, recrystallized from 2-methoxyethanol (Klingsberg, 1963), are orange prisms, space group $P2_1/c$, with $a=14{\cdot}180\ (3)$, $b=10{\cdot}265\ (2)$, $c=23{\cdot}322\ (5)$ Å, $\beta=93{\cdot}92\ (3)°$, $V=3386{\cdot}8$ Å^3, $Z=8$, $D_x=1{\cdot}331$ g cm^{-3}, μ(Mo $K\alpha$) = 3·12 cm^{-1}.

Experimental

2θ values and intensities were measured on a paper-tape controlled Siemens AED diffractometer with Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å). Twenty 2θ values in the range $13° < 2\theta < 41°$ were measured at room temperature, $t=22$ °C, and the cell dimensions found by a least-squares procedure. The intensities were measured by the five-value scan technique (Troughton, 1970). 2951 out of 5959 reflexions for which the net count was greater than 2·5 times the respective standard deviations in the net count were accepted as observed ($\theta < 25°$). Unobserved reflexions were neglected.

Lp corrections were applied, but absorption corrections were ignored, the dimensions of the crystal being $0{\cdot}13 \times 0{\cdot}31 \times 0{\cdot}13$ mm.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1968) for the non-hydrogen and from Stewart, Davidson & Simpson (1965) for the hydrogen atoms.

The observed structure factors were put on an absolute scale (Wilson, 1942) and converted to normalized structure factors (Shiono, 1966).

Structure determination and refinement

The structure was solved by direct methods (Long, 1965). Three reflexions ($20\bar{6}, 506, 20\bar{4}$) with variable signs were chosen in addition to the origin-determining

ones ($30\bar{6}, 0\bar{3}\bar{3}, 7\bar{7}\bar{6}$), and reflexions with $|E| > 1{\cdot}45$ were included in the calculations. An E map with 400 terms, corresponding to the sign set with highest consistency index, showed maxima for the 46 non-hydrogen atoms. Structure-factor calculations based on these atomic positions, with scale and overall isotropic temperature factors from the Wilson statistics, gave an $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0·23.

Full-matrix least-squares refinement was performed, minimizing $\sum\omega(|F_o| - 1/k|F_c|)^2$ where k is the scale factor and $\omega = 1/\sigma^2_{F_o}$. Two cycles with individual isotropic temperature factors brought R down to 0·11. The sp^2 and sp^3 hydrogen positions were then estimated, the latter by assuming the dimethylamino groups to be the same as in compound (II) (Hordvik & Sæthre, 1972*b*). Anisotropic refinement of the temperature factors of the non-hydrogen atoms, keeping the hydrogen parameters fixed, reduced R to 0·054. From there on, hydrogen parameters plus phenyl-carbon parameters (245 parameters + scale) were refined alternately with the parameters of the other atoms in the molecules (307 parameters + scale). The refinement converged at $R = 0{\cdot}044$, with no shift at that stage greater than the corresponding standard deviation.

Final atomic coordinates and temperature parameters are given in Tables 1 and 2. The standard deviations, taken from the final least-squares cycles, are probably slightly too small because all parameters were not refined simultaneously.

Table 1. *Atomic coordinates in fractions of corresponding cell edges*

The standard deviations given in parentheses refer to the last digits of the respective values. The unprimed atoms belong to molecule (III*a*).

	x	*y*	*z*
O	0·26653 (20)	0·59087 (27)	0·29109 (11)
S(6a)	0·14003 (8)	0·54467 (11)	0·21769 (4)
S(6)	0·03840 (8)	0·48237 (11)	0·15365 (5)
C(2)	0·29868 (28)	0·47983 (41)	0·30318 (15)
C(3)	0·25720 (29)	0·37093 (35)	0·27289 (15)
C(3a)	0·18490 (27)	0·38727 (36)	0·23217 (15)
C(4)	0·14048 (27)	0·28613 (36)	0·19744 (15)
C(5)	0·06896 (29)	0·32092 (37)	0·15986 (16)
C(6)	0·37979 (27)	0·46273 (38)	0·34554 (15)
C(7)	0·42618 (31)	0·56995 (37)	0·37076 (17)
C(8)	0·50478 (31)	0·55799 (40)	0·40824 (17)
C(9)	0·54158 (29)	0·43418 (40)	0·42347 (16)
C(10)	0·49422 (31)	0·32649 (37)	0·39884 (16)
C(11)	0·41669 (31)	0·34169 (39)	0·36147 (16)
N	0·62051 (25)	0·42055 (33)	0·46027 (14)
C(12)	0·65980 (33)	0·29290 (47)	0·47291 (20)
C(13)	0·66947 (31)	0·53215 (43)	0·48581 (18)
C(14)	0·17440 (31)	0·14870 (42)	0·20303 (17)
C(15)	0·13151 (37)	0·06150 (52)	0·23780 (20)
C(16)	0·16238 (42)	−0·06647 (52)	0·24241 (23)
C(17)	0·23736 (44)	−0·10735 (55)	0·21312 (24)
C(18)	0·28062 (42)	−0·02137 (58)	0·17913 (24)
C(19)	0·25030 (41)	0·10698 (52)	0·17474 (22)
H(3)	0·2796 (21)	0·2858 (27)	0·2785 (11)
H(5)	0·0310 (22)	0·2578 (32)	0·1349 (12)
H(7)	0·3972 (23)	0·6580 (32)	0·3625 (13)
H(8)	0·5333 (24)	0·6344 (33)	0·4233 (13)
H(10)	0·5213 (22)	0·2399 (31)	0·4064 (12)
H(11)	0·3873 (23)	0·2672 (33)	0·3469 (13)
H(121)	0·6893 (29)	0·2567 (39)	0·4323 (16)
H(122)	0·6177 (30)	0·2463 (40)	0·4897 (16)
H(123)	0·7124 (31)	0·3038 (39)	0·4956 (17)
H(131)	0·6966 (26)	0·5915 (35)	0·4574 (15)
H(132)	0·6266 (30)	0·5810 (39)	0·5119 (17)
H(133)	0·7216 (28)	0·5056 (36)	0·5145 (15)
H(15)	0·0767 (28)	0·0904 (38)	0·2588 (16)
H(16)	0·1292 (29)	−0·1231 (40)	0·2682 (17)
H(17)	0·2581 (28)	−0·1944 (40)	0·2185 (16)
H(18)	0·3332 (31)	−0·0502 (43)	0·1611 (17)
H(19)	0·2807 (30)	0·1661 (41)	0·1505 (17)
O′	0·27093 (18)	0·17642 (26)	0·44330 (11)
S(6*a*)′	0·14260 (8)	0·25663 (11)	0·38988 (4)
S(6)′	0·01812 (9)	0·32990 (12)	0·34702 (4)
C(2)′	0·24344 (29)	0·15801 (35)	0·49292 (17)
C(3′)	0·14754 (28)	0·18906 (35)	0·50169 (15)
C(3*a*)′	0·09166 (27)	0·23587 (34)	0·45575 (15)
C(4)′	−0·00590 (28)	0·27517 (34)	0·45620 (15)
C(5)′	−0·04611 (29)	0·32037 (39)	0·40633 (17)
C(6)′	0·31147 (28)	0·11045 (37)	0·53859 (16)
C(7)′	0·40696 (32)	0·11476 (40)	0·52994 (17)
C(8)′	0·47534 (28)	0·07564 (39)	0·57090 (19)
C(9)′	0·45084 (30)	0·02791 (39)	0·62334 (17)
C(10)′	0·35428 (32)	0·01904 (45)	0·63270 (17)
C(11)′	0·28675 (28)	0·06054 (41)	0·59083 (17)
N′	0·51925 (25)	−0·01195 (37)	0·66469 (15)
C(12)′	0·49349 (38)	−0·04846 (67)	0·72056 (20)
C(13)′	0·61810 (32)	0·01486 (45)	0·65724 (20)
C(14)′	−0·06056 (28)	0·26315 (42)	0·50831 (16)
C(15)′	−0·09349 (34)	0·14320 (44)	0·52540 (20)
C(16)′	−0·14682 (34)	0·13310 (48)	0·57215 (21)
C(17)′	−0·16897 (32)	0·24158 (52)	0·60296 (20)
C(18)′	−0·13624 (35)	0·36150 (49)	0·58709 (21)
C(19)′	−0·08240 (34)	0·37242 (45)	0·53983 (20)
H(3)′	0·1230 (21)	0·1808 (28)	0·5388 (12)
H(5)′	−0·1089 (23)	0·3493 (31)	0·4038 (12)
H(7)′	0·4232 (24)	0·1468 (33)	0·4938 (13)
H(8)′	0·5419 (23)	0·0820 (30)	0·5641 (13)
H(10)′	0·3317 (25)	−0·0094 (33)	0·6678 (14)
H(11)′	0·2198 (23)	0·0531 (31)	0·5973 (13)
H(121)′	0·4635 (37)	0·0249 (50)	0·7425 (20)
H(122)′	0·4517 (35)	−0·1357 (49)	0·7171 (18)
H(123)′	0·5466 (36)	−0·0762 (47)	0·7482 (19)
H(131)′	0·6324 (28)	0·1089 (40)	0·6536 (16)
H(132)′	0·6417 (28)	−0·0334 (39)	0·6208 (16)
H(133)′	0·6608 (27)	−0·0238 (38)	0·6910 (16)
H(15)′	−0·0764 (25)	0·0685 (37)	0·5024 (14)
H(16)′	−0·1667 (27)	0·0553 (39)	0·5827 (15)
H(17)′	−0·2059 (25)	0·2380 (35)	0·6373 (14)
H(18)′	−0·1468 (27)	0·4431 (39)	0·6095 (15)
H(19)′	−0·0601 (26)	0·4601 (39)	0·5300 (15)

Rigid-body analyses for certain parts of the molecules have been carried out (Schomaker & Trueblood, 1968). The parts of the molecules treated in this way are the 6,6a-dithiafurophthene system plus C(6) and C(14), the *p*-dimethylanilino group plus C(2), and the phenyl group plus C(4). The librational tensors, $\mathbf{L}_F$, $\mathbf{L}_A$, and $\mathbf{L}_P$, are listed in Table 3. One notes that the libration of the *p*-dimethylanilino and the phenyl groups is rather anisotropic in (III*a*) as well as (III*b*). Furthermore, in both molecules the *p*-dimethylanilino group has maximum libration about an axis which

Table 2. *Temperature parameters U_{ij} (Å^2) for sulphur, oxygen, nitrogen and carbon, and U (Å^2) for hydrogen*

The expressions used are $\exp[-2\pi^2(h^2a^{*2}U_{11}\ldots 2hka^*b^*U_{12}+\ldots)]$ and $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$. Values for sulphur, nitrogen, oxygen and carbon are multiplied by 10^4; values for hydrogen are multiplied by 10^3. Standard deviations in parentheses refer to the last digits of the respective values. The unprimed atoms belong to molecule (III*a*).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
O	590 (21)	477 (19)	638 (19)	83 (17)	−95 (15)	−87 (16)
S(6a)	492 (7)	480 (7)	562 (7)	64 (6)	−54 (6)	−1 (6)
S(6)	462 (7)	638 (8)	600 (7)	106 (7)	−43 (6)	−60 (6)
C(2)	440 (27)	523 (29)	388 (23)	16 (25)	−14 (22)	90 (21)
C(3)	553 (30)	357 (24)	398 (23)	29 (22)	−46 (19)	18 (22)
C(3a)	420 (26)	467 (25)	327 (21)	2 (22)	−1 (19)	75 (20)
C(4)	378 (25)	480 (26)	398 (21)	−34 (22)	21 (19)	48 (20)
C(5)	464 (28)	519 (27)	511 (25)	−31 (24)	−29 (21)	28 (22)
C(6)	462 (27)	400 (25)	382 (22)	−7 (23)	−64 (20)	55 (20)
C(7)	632 (32)	395 (26)	623 (29)	69 (25)	−80 (22)	−97 (25)
C(8)	615 (32)	466 (27)	581 (28)	−49 (26)	−111 (23)	−107 (25)
C(9)	505 (29)	470 (28)	422 (23)	−29 (24)	−1 (21)	9 (22)
C(10)	616 (32)	390 (25)	523 (25)	−52 (25)	25 (21)	−90 (23)
C(11)	573 (31)	456 (27)	509 (25)	−111 (25)	−58 (23)	−56 (23)
N	597 (26)	497 (23)	616 (23)	−5 (21)	−43 (19)	−143 (20)
C(12)	705 (37)	705 (36)	1036 (39)	−35 (30)	100 (29)	−257 (30)
C(13)	682 (34)	628 (32)	742 (30)	−150 (28)	−151 (26)	−160 (27)
C(14)	405 (28)	502 (29)	410 (24)	−65 (25)	−42 (23)	26 (22)
C(15)	553 (34)	650 (37)	584 (32)	−53 (31)	53 (27)	125 (28)
C(16)	678 (40)	523 (38)	732 (36)	−109 (33)	120 (29)	9 (32)
C(17)	748 (44)	478 (36)	761 (38)	−2 (36)	14 (31)	−132 (33)
C(18)	800 (44)	713 (44)	878 (41)	125 (37)	−74 (34)	286 (36)
C(19)	879 (44)	477 (33)	723 (35)	60 (33)	43 (28)	281 (33)
O′	505 (20)	672 (20)	501 (17)	−3 (16)	27 (15)	96 (15)
S(6a)′	584 (8)	546 (7)	460 (6)	−40 (7)	12 (6)	69 (6)
S(6)′	733 (9)	717 (8)	483 (7)	46 (8)	71 (6)	−38 (6)
C(2)′	481 (29)	341 (23)	482 (25)	−73 (22)	−60 (21)	67 (24)
C(3)′	417 (26)	423 (24)	416 (23)	−14 (23)	−55 (19)	80 (21)
C(4)′	449 (26)	321 (23)	506 (25)	−15 (21)	−41 (19)	−61 (21)
C(5)′	553 (31)	577 (28)	591 (27)	56 (25)	−32 (23)	−5 (24)
C(6)′	391 (27)	406 (24)	469 (25)	21 (23)	−60 (20)	56 (22)
C(7)′	512 (30)	551 (28)	581 (28)	20 (27)	64 (22)	149 (25)
C(8)′	384 (27)	560 (30)	677 (30)	9 (24)	36 (24)	94 (25)
C(9)′	416 (27)	548 (28)	513 (27)	85 (25)	−137 (23)	32 (24)
C(10)′	548 (30)	872 (36)	477 (25)	154 (30)	10 (24)	95 (24)
C(11)′	404 (26)	678 (31)	537 (27)	74 (25)	−20 (23)	68 (23)
N′	495 (25)	930 (31)	586 (24)	146 (24)	−64 (22)	23 (21)
C(12)′	864 (43)	2169 (69)	596 (32)	422 (46)	116 (40)	−13 (31)
C(13)′	538 (33)	748 (35)	1021 (38)	29 (30)	−72 (28)	−107 (30)
C(14)′	324 (25)	404 (27)	512 (26)	−0 (24)	−37 (23)	−13 (21)
C(15)′	504 (33)	378 (29)	568 (31)	10 (26)	−61 (25)	18 (26)
C(16)′	514 (34)	430 (33)	656 (33)	−45 (27)	56 (27)	−15 (27)
C(17)′	396 (30)	631 (36)	515 (29)	34 (30)	−12 (29)	3 (24)
C(18)′	565 (37)	484 (33)	636 (33)	−0 (28)	−121 (28)	71 (28)
C(19)′	558 (35)	387 (30)	683 (32)	−107 (27)	−74 (25)	118 (27)

Table 2 (*cont.*)

	U		U
H(3)	26 (9)	H(131)	87 (13)
H(5)	57 (10)	H(132)	126 (15)
H(7)	64 (11)	H(133)	100 (14)
H(8)	63 (11)	H(15)	71 (14)
H(10)	56 (11)	H(16)	82 (15)
H(11)	68 (11)	H(17)	60 (15)
H(121)	113 (14)	H(18)	84 (16)
H(122)	112 (15)	H(19)	102 (16)
H(123)	117 (15)		
H(3)′	39 (9)	H(131)′	106 (14)
H(5)′	49 (11)	H(132)′	109 (14)
H(7)′	62 (12)	H(133)′	98 (14)
H(8)′	50 (11)	H(15)′	47 (12)
H(10)′	76 (12)	H(16)′	51 (13)
H(11)′	54 (11)	H(17)′	49(12)
H(121)′	164 (19)	H(18)′	73 (13)
H(122)′	150 (18)	H(19)′	68 (13)
H(123)′	136 (18)		

runs roughly in the C(2)–N direction, and the phenyl group has maximum libration about an axis which almost follows the C(4)–C(14)–C(17) sequence.

All calculations were carried out on an IBM 360/50H computer. The programs, with a few exceptions, originate from the Weizmann Institute of Science, Rehovoth, Israel, and have been modified by D. Rabinovich, L. M. Milje and K. Åse. The diffractometer programs were written by K. Maartmann-Moe.

Description and discussion of the structure

Bond lengths and angles with standard deviations are listed in Tables 4 and 5. According to Hamilton & Abrahams (1970) a more realistic estimate of the standard deviations might be obtained by doubling those given. The numbering of the atoms and the

Table 3. *Librational tensors from the rigid-body analysis of certain parts of the 2-(p-dimethylanilino)-4-phenyl-6,6a-dithiafurophthene molecule*

$\mathbf{L}_F$ refer to the 6,6a-dithiafurophthene system plus C(6) and C(14), $\mathbf{L}_A$ refer to the *p*-dimethylanilino group plus C(2), and $\mathbf{L}_P$ refer to the phenyl group plus C(4).

	Eigenvalues	Eigenvectors: Direction cosines $\times 10^4$ relative to *a*, *b*, and *c**, respectively.		
Molecule (IIIa)				
$\mathbf{L}_F$	11·9 (°)²	8324	−791	5485
	2·1	3252	−7317	−5991
	0·8	4487	6770	−5834
$\mathbf{L}_A$	62·3	−7802	−268	−6250
	7·1	−5468	−4560	7022
	3·2	−3038	8896	3410
$\mathbf{L}_P$	85·6	−2819	9589	−321
	15·4	−7905	−2511	−5586
	1·4	−5437	−1321	8288
Molecule (IIIb)				
$\mathbf{L}'_F$	10·6 (°)²	5959	−3484	7235
	6·2	4856	−5611	−6703
	2·9	6396	7508	−1652
$\mathbf{L}'_A$	86·6	−8163	3795	−4354
	8·9	−4930	−8506	1830
	1·4	−3009	3641	8814
$\mathbf{L}'_P$	56·7	−6103	−0051	7921
	9·1	−6871	5009	−5263
	3·1	−3941	−8655	−3092

designation of various parts of the molecule are given in Fig. 1.

The bond lengths between non-hydrogen atoms have been corrected for rigid-body libration (Cruickshank, 1956, 1961) according to the libration tensors given in Table 3. The C(2)–C(6) and C(4)–C(14) lengths were corrected according to $\mathbf{L}_A$ and $\mathbf{L}_P$, respectively, as well as according to $\mathbf{L}_F$, and the mean value of the results are given in Table 4.

There is a significant difference between the S(6a)–O distance of 2·441 (3) Å in (III*a*) and that of 2·291 (3) Å in (III*b*). The other lengths, as found in (III*a*) and (III*b*), agree closely.

C(2)–C(3), C(3)–C(3a), C(3a)–C(4) and C(4)–C(5) are alternating 'long' and 'short' bonds as usually found in 6,6a-dithiafurophthenes (Mammi, Bardi, Traverso & Bezzi, 1961; Hordvik, Sletten & Sletten, 1969*a*), and the lengths of the O–S and the S–C bonds are equal to those in 2,4-diphenyl-1,6a-dithiafurophthene (Hordvik, Sletten & Sletten, 1969*a*).

C(4)–C(14) = 1·497 (6) Å and C(4)′–C(14)′ = 1·494 (6) Å agree with the length of the central C–C bond in diphenyl, 1·494 Å (Robertson, 1961). C(2)–C(6) = 1·476 (5) Å and C(2)′–C(6)′ = 1·474 (5) Å are somewhat shorter, in agreement with the quinoid structure of the *p*-dimethylanilino group; the mean value of the C(7)–C(8) and the C(10)–C(11) lengths in (III*a*) and (III*b*) is 1·378 Å, while that of the other bonds in this ring is 1·406 Å. The C(9)–N bonds, 1·373 (5) Å in (III*a*) and 1·386 (5) in (III*b*), are shorter than a C–N single bond (Pauling, 1960) but somewhat longer than the C–N bond in pyridine, 1·340 Å (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958).

Table 4. *Bond lengths (l) in 2-(p-dimethylanilino)-4-phenyl-6,6a-dithiafurophthene in molecules* (III*a*) *and* (III*b*)

The standard deviations given in parentheses refer to the last digits of the respective values. Bond lengths (*l*′) with corrections for rigid-body libration are given for the S–S, S–O, S–C, N–C and C–C bonds.

	Molecule (III*a*)		Molecule (III*b*)	
	l′ (Å)	*l* (Å)	*l*′ (Å)	*l* (Å)
S(6)—S(6a)	2·1045	2·1028 (15)	2·1101	2·1070 (16)
S(6a)—O	2·441	2·440 (3)	2·291	2·287 (3)
O——C(2)	1·255	1·253 (5)	1·263	1·260 (5)
S(6a)–C(3a)	1·764	1·761 (4)	1·758	1·755 (4)
S(6)—C(5)	1·720	1·717 (4)	1·714	1·710 (4)
C(2)—C(3)	1·430	1·428 (5)	1·428	1·425 (6)
C(3)—C(3a)	1·360	1·359 (5)	1·377	1·375 (5)
C(3a)–C(4)	1·438	1·436 (5)	1·444	1·442 (5)
C(4)—C(5)	1·343	1·343 (5)	1·345	1·342 (5)
C(2)—C(6)	1·476	1·474 (5)	1·474	1·471 (5)
C(6)—C(7)	1·402	1·392 (5)	1·393	1·383 (6)
C(7)—C(8)	1·376	1·374 (6)	1·378	1·374 (6)
C(8)—C(9)	1·423	1·410 (6)	1·402	1·384 (6)
C(9)—C(10)	1·406	1·396 (6)	1·415	1·404 (6)
C(10)–C(11)	1·367	1·364 (6)	1·391	1·387 (6)
C(11)–C(6)	1·401	1·389 (6)	1·407	1·389 (6)
C(9)—N	1·373	1·370 (5)	1·386	1·382 (5)
N——C(12)	1·460	1·446 (6)	1·446	1·427 (6)
N——C(13)	1·457	1·447 (5)	1·464	1·450 (6)
C(4)—C(14)	1·497	1·493 (6)	1·494	1·491 (6)
C(14)–C(15)	1·394	1·377 (7)	1·397	1·385 (6)
C(15)–C(16)	1·391	1·386 (8)	1·375	1·373 (7)
C(16)–C(17)	1·385	1·368 (9)	1·383	1·373 (7)
C(17)–C(18)	1·377	1·360 (8)	1·386	1·375 (7)
C(18)–C(19)	1·391	1·388 (8)	1·390	1·387 (7)
C(19)–C(14)	1·385	1·369 (7)	1·398	1·388 (6)
C(3)—H(3)		0·94 (3)		0·96 (3)
C(5)—H(5)		1·00 (3)		0·94 (3)
C(7)—H(7)		1·01 (3)		0·95 (3)
C(8)—H(8)		0·94 (3)		0·97 (3)
C(10)–H(10)		0·98 (3)		0·95 (3)
C(11)–H(11)		0·92 (3)		0·97 (3)
C(12)–H(121)		1·12 (4)		1·02 (5)
C(12)–H(122)		0·88 (4)		1·07 (5)
C(12)–H(123)		0·89 (4)		1·00 (5)
C(13)–H(131)		1·00 (4)		0·99 (4)
C(13)–H(132)		1·02 (4)		1·06 (4)
C(13)–H(133)		1·00 (4)		1·04 (4)
C(15)–H(15)		0·99 (4)		0·97 (4)
C(16)–H(16)		0·98 (4)		0·89 (4)
C(17)–H(17)		0·95 (4)		0·99 (4)
C(18)–H(18)		0·93 (4)		1·00 (4)
C(19)–H(19)		0·95 (4)		0·99 (4)

Atomic distances from the least-squares planes for certain parts of (III*a*) and (III*b*) are given in Table 6. The equations for these planes have been calculated with weights equal to the atomic weights; the planes *C* and *B*+*C* comprise the atoms of rings *C* and *B*+*C*, respectively (*cf.* Fig. 1).

The values in Table 6 show that the central ring system, *B*+*C*, is very nearly planar in both molecules.

One notes, however, a small difference in the orientation of the C(3)–C(2)–O groups.

The C(2)–C(6)–C(9)–N and the C(4)–C(14)–C(17) sequences point out of the plane of the central-ring system in (III*a*) as well as in (III*b*); the sequences lie on the same side of the plane in (III*a*) and on opposite sides in (III*b*).

Phenyl group *D* of (III*a*) is twisted 75·6° about the C(4)–C(14) bond. This angle was taken between the normal to the plane through C(3a), C(4), C(5), and C(14), and the normal to the plane through C(4), C(14), C(15), and C(19). Similarly the twist angle of the *p*-dimethylanilino group *A* about C(2)–C(6) is 4·3°. The corresponding values for (III*b*) are 84·1 and 15·3°, and for (II) they are 81·8 and 12·7°.

The different S(6a)–O distances as well as the different orientation of substituents in (III*a*) and (III*b*)

Table 5. *Bond angles* (°) *in* 2-(*p-dimethylanilino*)-4-*phenyl*-6,6*a-dithiafurophthene in molecules* (III*a*) and (III*b*)

The standard deviations given in parentheses refer to the last digits of the respective values.

	Molecule (III*a*)	Molecule (III*b*)
O———S(6a)–S(6)	173·05 (8)	175·16 (8)
C(2)—O——S(6a)	102·7 (2)	105·6 (2)
O———S(6a)–C(3a)	78·8 (1)	80·7 (1)
C(3a)—S(6a)–S(6)	94·5 (1)	94·4 (1)
S(6a)—S(6)—C(5)	94·4 (1)	94·1 (1)
O———C(2)—C(3)	118·0 (3)	117·1 (3)
C(2)—C(3)—C(3a)	121·0 (3)	118·1 (3)
C(3)—C(3a)–C(4)	125·9 (3)	126·5 (3)
C(3a)—C(4)—C(5)	117·3 (3)	116·2 (3)
C(4)—C(5)—S(6)	119·1 (3)	120·2 (3)
C(3)—C(3a)–S(6a)	119·5 (2)	118·3 (3)
C(4)—C(3a)–S(6a)	114·6 (2)	115·2 (2)
O———C(2)—C(6)	121·0 (3)	119·1 (3)
C(3)—C(2)—C(6)	121·0 (3)	123·7 (3)
C(2)—C(6)—C(7)	120·9 (3)	118·9 (3)
C(6)—C(7)—C(8)	122·5 (3)	122·7 (3)
C(7)—C(8)—C(9)	120·7 (3)	120·7 (3)
C(8)—C(9)—C(10)	116·8 (3)	117·8 (3)
C(9)—C(10)–C(11)	121·1 (3)	120·3 (3)
C(10)—C(11)–C(6)	123·1 (3)	121·8 (3)
C(11)—C(6)—C(7)	115·8 (3)	116·6 (3)
C(11)—C(6)—C(2)	123·2 (3)	124·4 (3)
C(8)—C(9)—N	121·5 (3)	121·0 (3)
C(10)—C(9)—N	121·7 (3)	121·2 (3)
C(9)—N——C(12)	120·5 (3)	120·2 (3)
C(9)—N——C(13)	121·7 (3)	119·9 (3)
C(12)—N——C(13)	117·8 (3)	118·0 (3)
C(3a)—C(4)—C(14)	120·5 (3)	120·4 (3)
C(5)—C(4)—C(14)	122·2 (3)	121·4 (3)
C(4)—C(14)–C(15)	120·9 (4)	120·8 (3)
C(14)—C(15)–C(16)	120·8 (4)	120·7 (4)
C(15)—C(16)–C(17)	120·3 (5)	120·8 (4)
C(16)—C(17)–C(18)	119·3 (5)	119·4 (4)
C(17)—C(18)–C(19)	120·6 (5)	120·0 (4)
C(18)—C(19)–C(14)	120·8 (4)	120·7 (4)
C(19)—C(14)–C(15)	118·3 (4)	118·3 (4)
C(19)—C(14)–C(4)	120·8 (4)	120·8 (3)
C(2)—C(3)—H(3)	123 (2)	121 (2)
H(3)—C(3)—C(3a)	116 (2)	121 (2)
C(4)—C(5)—H(5)	124 (2)	121 (2)
H(5)—C(5)—S(6)	117 (2)	119 (2)
C(6)—C(7)—H(7)	117 (2)	116 (2)
H(7)—C(7)—C(8)	120 (2)	121 (2)
C(7)—C(8)—H(8)	118 (2)	121 (2)
H(8)—C(8)—C(9)	121 (2)	118 (2)
C(9)—C(10)–H(10)	118 (2)	123 (2)
H(10)—C(10)–C(11)	121 (2)	117 (2)
C(10)—C(11)–H(11)	118 (2)	120 (2)
H(11)—C(11)–C(6)	119 (2)	118 (2)
C(14)—C(15)–H(15)	119 (2)	116 (2)
H(15)—C(15)–C(16)	120 (2)	123 (2)
C(15)—C(16)–H(16)	117 (2)	119 (2)
H(16)—C(16)–C(17)	123 (2)	120 (2)
C(16)—C(17)–H(17)	118 (2)	123 (2)

Table 5 (*cont.*)

	Molecule (III*a*)	Molecule (III*b*)
H(17)—C(17)–C(18)	123 (2)	117 (2)
C(17)—C(18)–H(18)	118 (3)	123 (2)
H(18)—C(18)–C(19)	122 (3)	117 (2)
C(18)—C(19)–H(19)	120 (3)	117 (2)
H(19)—C(19)–C(14)	119 (3)	122 (2)
N———C(12)–H(121)	107 (2)	114 (3)
N———C(12)–H(122)	109 (3)	109 (2)
N———C(12)–H(123)	108 (3)	116 (3)
N———C(13)–H(131)	114 (2)	114 (2)
N———C(13)–H(132)	110 (2)	112 (2)
N———C(13)–H(133)	112 (2)	111 (2)
H(121)–C(12)–H(122)	120 (3)	114 (4)
H(122)–C(12)–H(123)	112 (4)	101 (4)
H(123)–C(12)–H(121)	101 (3)	102 (4)
H(131)–C(13)–H(132)	112 (3)	108 (3)
H(132)–C(13)–H(133)	100 (3)	103 (3)
H(133)–C(13)–H(131)	108 (3)	109 (3)

Table 6. *Atomic distances* (Å × 10^3) *from least-squares planes*

	Plane *C* (III*a*)	Plane *C'* (III*b*)	Plane *B*+*C*	Plane *B'*+*C'*
S(6)	2	−3	5	0
S(6*a*)	0	3	−16	−2
C(3*a*)	−7	−11	−14	−17
C(4)	13	5	22	3
C(5)	−12	4	4	7
C(3)	−4	11	−20	0
C(2)	34	21	2	6
O	66	18	28	3
C(6)	95	79	54	58
C(9)	338	289	280	257
N	479	397	412	360
C(14)	76	−18	94	−19
C(17)	197	−90	232	−90

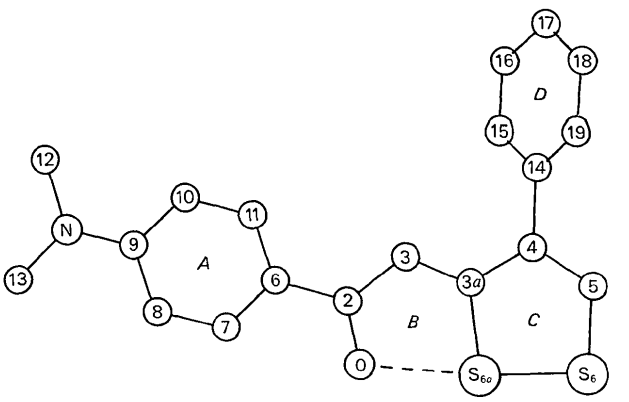

Fig. 1. 2-(*p*-Dimethylanilino)-4-phenyl-6,6a-dithiafurophthene with numbering of atoms and designation of various parts.

reflect the versatility of such molecules in a crystal. Similar differences between two crystallographically independent 6a-thiathiophthene molecules have been reported by Johnson, Newton & Paul (1969).

The S(6)–S(6a) bonds in (III*a*) and (III*b*) are 2·1045 (15) and 2·1101 (16) Å, respectively, and the corresponding S(6a)–O distances are 2·441 (3) and 2·291 (3) Å. Thus, the longer S–S bond corresponds to the shorter S–O distance. The difference in S–S length is small and hardly significant, but in the direc-

Table 7. *Observed and calculated structure factors for* 2-(*p-dimethylanilino*)-4-*phenyl*-6,6*a*-*dithiafurophthene*

The values given are ten times the absolute values. Unobserved reflexions are not included.

Table 7 (*cont.*)

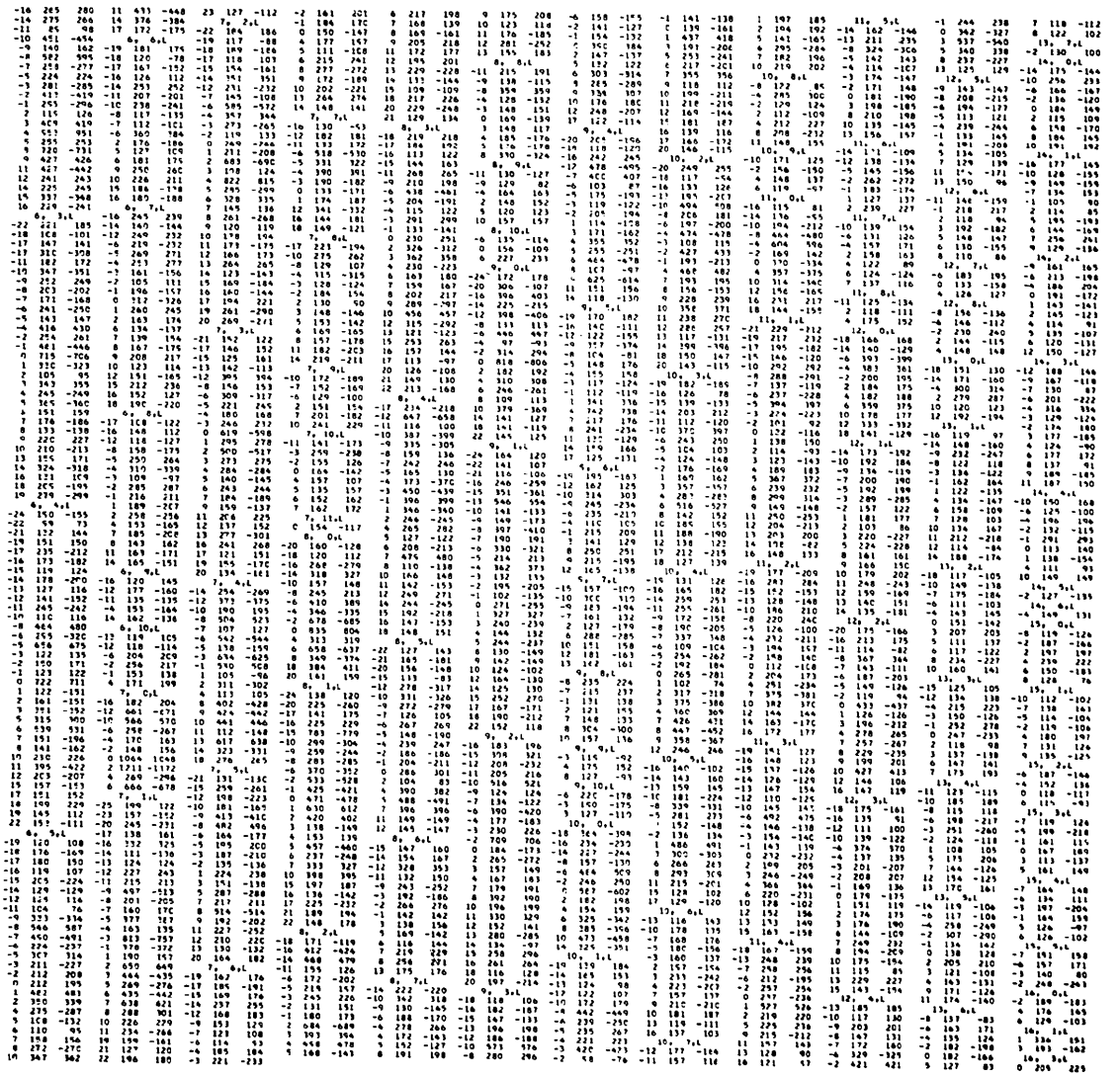

Fig. 2. A stereoscopic view of the molecular packing in the unit cell of 2-(*p*-dimethylanilino)-4-phenyl-6,6*a*-dithiafurophthene.

tion one would expect. In 2,3-tetramethylene-4-phenyl-6,6a-dithiafurophthene (Pinel, Mollier, Llaguno & Paul, 1971) the S(6)–S(6a) and S(6a)–O distances are 2·126 (4) and 2·255 (8) Å, respectively, and in 2,3-benzo-5-phenyl-6,6a-dithiafurophthene (Llaguno, Paul, Pinel & Mollier, 1972) they are 2·137 (3) and 2·184 (7) Å. The S(1)–S(6a) and S(6a)–O distances in 2-phenyl-4-benzoyl-5-aza-1,6a-dithiafurophthene, which Johnson, Reid & Paul (1971) reported to be 2·178 (2) and 2·034 (6) Å, respectively, show clearly that the sulphur–oxygen interaction in such molecules can affect the sulphur–sulphur bonding. The lengthening of the S–S bond seems to be detectable for S–O contacts shorter than 2·30 Å.

A stereoscopic view of the molecular packing is given in Fig 2. There are no intermolecular contacts shorter than the corresponding van der Waals distances.

The authors are indebted to Dr E. Klingsberg, American Cyanamid Co., for providing a sample of 2-(*p*-dimethylanilino)-4-phenyl-6,6a-dithiafurophthene.

One of us (A. H.) wishes to thank the Norwegian Research Council for Science and the Humanities for financial aid.

References

BAK, B., HANSEN-NYGAARD, L. & RASTRUP-ANDERSEN, J. (1958). *J. Mol. Spectrosc.* **2**, 361–368.
CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757–758.
CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896–898.
HAMILTON, W. C. & ABRAHAMS, S. C. (1970). *Acta Cryst.* A**26**, 18–24.
HORDVIK, A., SLETTEN, E. & SLETTEN, J. (1969*a*). *Acta Chem. Scand.* **23**, 1377–1388.
HORDVIK, A., SLETTEN, E. & SLETTEN, J. (1969*b*). *Acta Chem. Scand.* **23**, 1852–1870.
HORDVIK, A. & SÆTHRE, L. J. (1972*a*). *Acta Chem. Scand.* **26**, 849–850.
HORDVIK, A. & SÆTHRE, L. J. (1972*b*). *Acta Chem. Scand.* **26**, 3114–3130.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., pp. 202–206. Birmingham: Kynoch Press.
JOHNSON, P. L., REID, K. I. G. & PAUL, I. C. (1971). *J. Chem. Soc.* (*B*), pp. 946–952.
JOHNSON, S. M., NEWTON, M. G. & PAUL, I. C. (1969). *J. Chem. Soc.* (*B*), pp. 986–993.
KLINGSBERG, E. (1963). *J. Amer. Chem. Soc.* **85**, 3244–3246.
LLAGUNO, E. C., PAUL, I. C., PINEL, R. & MOLLIER, Y. (1972). *Tetrahedron Lett.* pp. 4687–4690.
LONG, R. E. (1965). Ph. D. Dissertation, Univ. of California, Los Angeles.
MAMMI, M., BARDI, R., TRAVERSO, G. & BEZZI, S. (1961). *Nature, Lond.* **192**, 1282–1283.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd. ed. New York: Cornell Univ. Press.
PINEL, R., MOLLIER, Y., LLAGUNO, E. C. & PAUL, I. C. (1971). *Chem. Commun.* pp. 1352–1353.
ROBERTSON, G. B. (1961). *Nature, Lond.* **191**, 593–594.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
SHIONO, R. (1966). *Normalized Structure Factors Program.* The Department of Crystallography, Univ. of Pittsburgh.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
TROUGHTON, P. G. H. (1970). *Siemens Rev.* XXXVII, Fourth Special Issue: X-ray and Electron Microscopy News.
WILSON, A. J. C. (1942), *Nature, Lond.* **150**, 151–152.

Acta Cryst. (1975). B**31**, 37

The Crystal Structure of Lithium Hydrogen Maleate Dihydrate, $LiC_4H_3O_4.2H_2O$

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(*Received* 4 *July* 1974; *accepted* 29 *July* 1974)

The crystal structure of lithium hydrogen maleate dihydrate has been determined by X-ray diffraction and refined by least-squares calculations to $R = 0{\cdot}078$. The molecules are arranged in layers, hydrogen-bonded *via* the water molecules. There is also a short intramolecular hydrogen bond of 2·46 Å which may be 'statistically symmetrical'. The lithium ion has fourfold coordination.

The title compound was studied because of interest in the dimensions of the maleate ion. The hydrogen maleate ion (HM) has been found to have somewhat different dimensions in sodium hydrogen maleate (Gupta, Prasad & Yadav, 1972) and potassium hydrogen maleate (Darlow & Cochran, 1961). In sodium hydrogen maleate the HM ion has no symmetry, in potassium hydrogen maleate it has a crystallographic plane of symmetry perpendicular to the central C=C bond and the plane of the molecule. The e.s.r. and n.m.r. spectra of the two compounds are also different (Toriyama & Iwasaki, 1971; Iwasaki & Itoh, 1964; Iwasaki & Toriyama, private communication).

Experimental

Crystals of lithium hydrogen maleate dihydrate (LiHM) grow as long rods and are hygroscopic, tending