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Structure of 2-Lithiobenzofuran–tmeda and 2-Lithiobenzothiophene–tmeda in the Solid State and in Solution

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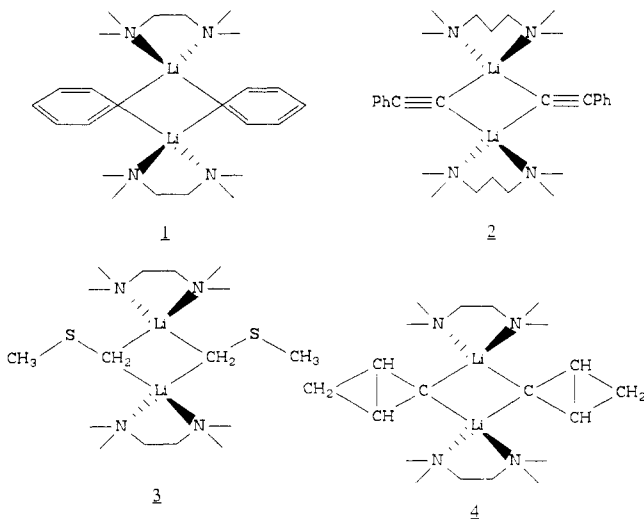
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The solid-state structure of 2-lithiobenzofuran–tmeda, determined by single-crystal X-ray diffraction, consists of dimeric species in which benzofuryl rings bridge the lithium atoms and tmeda acts as chelating ligand. The oxygen atom of one of the benzofuryl rings shows an interaction with lithium. The X-ray structure of 2-lithiobenzothiophene–tmeda dimer also shows chelating tmeda ligands to be present, but no sulfur–lithium contacts. The distortion of the C(ipso)–Li–C(ipso)′–Li′ ring, which also is found for dimeric phenyllithium–tmeda, is explained by steric effects. In solution (toluene) both species are revealed by NMR to have dimeric structures with C_{2v} symmetry. NMR shows the same to be true for 2-lithiobenzoselenophene–tmeda in toluene.
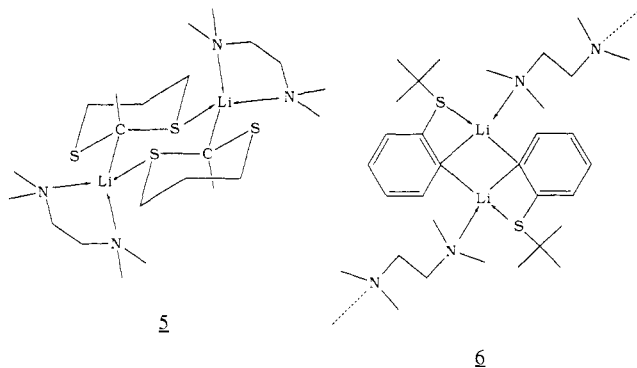
Introduction

Dimeric organolithium compounds with chelating ligands, e.g. *N,N,N′,N′*-tetramethylethylenediamine (tmeda), are well-known (1,[1] 2,[2] 3,[3] 4[4]) and have structures which

are all of the same type: two bridging organic groups of which the C(ipso) atoms participate in three-center, two-electron bonds and a chelating ligand complete the fourfold coordination of the lithium atoms. Dimeric organolithium compounds derived from organic ring systems containing a heteroatom (e.g. N, O, S) are interesting because their structures may differ from this common type. For example, no bridging carbon atoms occur in the crystal structure of 2-lithio-2-methyl-1,3-dithiane (5[5]), but a sulfur atom of the second dithiane molecule occupies the fourth coordination site. The lithium atoms form part of a six-membered ring in the chair conformation. In our recently published crystal structure of bis[2-lithiophenyl *tert*-butyl sulfide]–tmeda (6[6]), the chelating property of tmeda is not used: one nitrogen atom is displaced by the StBu substituent and sulfur acts as a ligand instead.

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Figure 1. ORTEP plot of the dimeric 2-lithiobenzofuran–tmeda. The tmeda ligands and hydrogen atoms have been omitted for clarity.

Figure 2. Plot of the dimeric 2-lithiobenzofuran–tmeda along one of the ring planes showing the steric interaction between the twisted benzofuryl ring and the tmeda ligand on the right. Oxygen atoms are indicated by black spheres and lithium atoms by speckled spheres. Hydrogen atoms have been omitted for clarity.

We wish to compare sulfur-containing aryllithium compounds with their oxygen analogues. This interest originates from the remarkable differences in reactivity between analogous aryllithium compounds with sulfur vs oxygen.[7] In this respect, one should distinguish between α-, β-, and γ-positioned heteroatoms. Because of the ease of five-membered ring formation, much is kn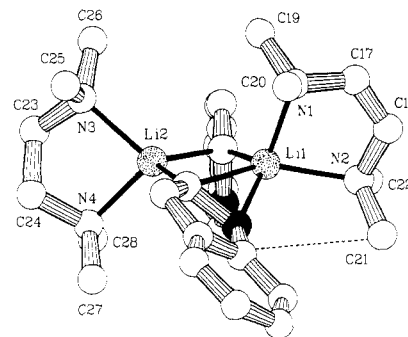own about organo-lithium compounds containing a γ-substituted oxygen function.[8,9] Recently we published the X-ray structures of aryllithium compounds with oxygen[10] and sulfur[6] in the β-position. Because of the lack of structural data on aryllithium compounds containing the heteroatom in the α-position, we now focus attention on this group. In this paper, the structures of 2-lithiobenzofuran–tmeda and 2-lithiobenzothiophene–tmeda are compared both in the solid state and in solution. We also describe the similar structure of 2-lithiobenzoselenophene in solution as deduced from NMR measurements.

Results and Discussion

The Solid-State Structure of 2-Lithiobenzofuran–tmeda. In the solid state, 2-lithiobenzofuran–tmeda is a dimer in which the benzofuryl rings bridge between the two lithium atoms; tmeda acts as a chelating ligand (Figure 1). Fractional coordinates of the non-hydrogen atoms are given in Table I, and Table II contains geometry data. The C–Li–C′–Li′ ring is nearly planar: the interplanar angle CLiLi′/C′LiLi′ is 7.7 (5)°. The twisting of one of the benzofuryl rings (the angle between the Li–Li′ vector and the ring plane is 39.1 (7)°) is remarkable (Figure 2). This results in a short Li–O contact of 2.09 (1) Å. As the rotation of aryl groups participating in electron-deficient bonds may require little energy,[11] such distortion could result from crystal packing effects. However, in this case the oxygen of the twisted ring displaces a tmeda molecule (Figure 2), as appears from short contacts; e.g., C(5)H···C(21)H₃ is 3.81 (1) Å. The somewhat elongated Li(1)–N(2) distance is another result of this steric interaction. Hence, the local dipole involving the oxygen atom due to the difference in electronegativity between oxygen and carbon must be the driving force for the Li–O interaction which gives the twisting. On first sight it seems strange that only Li(1) is stabilized by this extra Li–O contact. The lack of

Table I. Coordinates of the Non-Hydrogen Atoms in 2-Lithiobenzofuran–tmeda with Their Equivalent Thermal Parameters

atom	x	y	z	$U(eq)$, Å^2
O(1)	0.3569 (3)	0.0056 (4)	0.3231 (4)	0.068 (2)
O(2)	0.2731 (3)	0.3287 (4)	0.5756 (4)	0.071 (2)
Li(1)	0.2418 (7)	0.0461 (10)	0.4028 (11)	0.072 (6)
Li(2)	0.2558 (6)	0.2434 (10)	0.2719 (10)	0.065 (6)
C(1)	0.3098 (4)	0.0600 (6)	0.2104 (7)	0.076 (4)
C(2)	0.3416 (5)	−0.0013 (7)	0.1003 (6)	0.085 (4)
C(3)	0.4072 (4)	−0.0890 (6)	0.1353 (6)	0.071 (4)
C(4)	0.4154 (4)	−0.0815 (5)	0.2743 (6)	0.061 (4)
C(5)	0.4739 (4)	−0.1484 (7)	0.3508 (7)	0.082 (4)
C(6)	0.5279 (5)	−0.2307 (7)	0.2790 (10)	0.098 (5)
C(7)	0.5211 (5)	−0.2418 (8)	0.1402 (11)	0.111 (6)
C(8)	0.4626 (5)	−0.1724 (8)	0.0662 (7)	0.102 (5)
C(9)	0.2035 (4)	0.2540 (6)	0.4683 (6)	0.069 (4)
C(10)	0.1268 (4)	0.3107 (6)	0.4901 (6)	0.067 (4)
C(11)	0.1444 (4)	0.4191 (6)	0.6069 (6)	0.061 (4)
C(12)	0.2358 (4)	0.4250 (6)	0.6546 (6)	0.061 (4)
C(13)	0.2822 (4)	0.5211 (7)	0.7651 (6)	0.076 (4)
C(14)	0.2323 (6)	0.6130 (7)	0.8296 (6)	0.085 (5)
C(15)	0.1401 (5)	0.6080 (7)	0.7860 (7)	0.085 (5)
C(16)	0.0956 (4)	0.5134 (7)	0.6755 (7)	0.078 (4)
C(17)	0.1022 (10)	−0.1574 (15)	0.4072 (14)	0.232 (14)
C(18)	0.1651 (8)	−0.1691 (11)	0.5205 (12)	0.156 (9)
C(19)	0.0534 (7)	−0.0236 (10)	0.2392 (12)	0.172 (9)
C(20)	0.1509 (7)	−0.1964 (8)	0.1842 (10)	0.150 (7)
C(21)	0.3246 (6)	−0.1208 (9)	0.6178 (9)	0.127 (7)
C(22)	0.2196 (6)	0.0371 (8)	0.6911 (7)	0.118 (6)
C(23)	0.2262 (6)	0.4635 (9)	0.1283 (9)	0.129 (7)
C(24)	0.3276 (7)	0.4554 (10)	0.1525 (8)	0.128 (7)
C(25)	0.1815 (6)	0.2395 (9)	−0.0228 (7)	0.127 (6)
C(26)	0.0823 (6)	0.3467 (10)	0.1241 (9)	0.139 (7)
C(27)	0.4481 (5)	0.3542 (10)	0.2835 (10)	0.143 (8)
C(28)	0.3580 (6)	0.5138 (7)	0.4071 (7)	0.117 (6)
N(1)	0.1275 (4)	−0.0981 (6)	0.2979 (6)	0.103 (4)
N(2)	0.2398 (4)	−0.0608 (4)	0.5730 (6)	0.091 (4)
N(3)	0.1775 (4)	0.3272 (6)	0.1119 (5)	0.085 (4)
N(4)	0.3575 (4)	0.4042 (6)	0.2833 (6)	0.092 (4)

a short O(2)–Li(2) contact can be explained by steric effects. The twisting of the second benzofuryl ring would result in a movement of the second tmeda ligand causing prohibitively short contacts between the tmeda methyl

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Table II. Bond Distances (Å) and Angles (deg) for 2-Lithiobenzofuran–tmeda

O(1)–C(1)	1.45 (1)	O(2)–C(9)	1.44 (1)
O(1)–C(4)	1.38 (1)	O(2)–C(12)	1.36 (1)
C(1)–C(2)	1.36 (1)	C(9)–C(10)	1.37 (1)
C(2)–C(3)	1.42 (1)	C(10)–C(11)	1.43 (1)
C(3)–C(4)	1.38 (1)	C(11)–C(12)	1.38 (1)
C(4)–C(5)	1.37 (1)	C(12)–C(13)	1.39 (1)
C(5)–C(6)	1.40 (1)	C(13)–C(14)	1.38 (1)
C(6)–C(7)	1.38 (1)	C(14)–C(15)	1.39 (1)
C(7)–C(8)	1.37 (1)	C(15)–C(16)	1.38 (1)
C(8)–C(3)	1.42 (1)	C(16)–C(11)	1.40 (1)
N(1)–C(17)	1.45 (2)	N(3)–C(23)	1.50 (1)
N(1)–C(19)	1.49 (1)	N(3)–C(25)	1.50 (1)
N(1)–C(20)	1.49 (1)	N(3)–C(26)	1.50 (1)
N(2)–C(18)	1.48 (2)	N(4)–C(24)	1.52 (1)
N(2)–C(21)	1.49 (1)	N(4)–C(27)	1.50 (1)
N(2)–C(22)	1.50 (1)	N(4)–C(28)	1.51 (1)
C(17)–C(18)	1.39 (2)	C(23)–C(24)	1.53 (2)
Li(1)–C(1)	2.39 (1)	Li(2)–C(1)	2.11 (1)
Li(1)–O(1)	2.09 (1)	Li(2)–C(9)	2.26 (1)
Li(1)–C(9)	2.23 (1)	Li(2)–N(3)	2.17 (1)
Li(1)–N(1)	2.18 (1)	Li(2)–N(4)	2.15 (1)
Li(1)–N(2)	2.20 (1)		
Li(1)–Li(2)	2.61 (2)		
C(1)–O(1)–C(4)	108.8 (4)	C(9)–O(2)–C(12)	108.6 (4)
O(1)–C(1)–C(2)	104.1 (5)	O(2)–C(9)–C(10)	104.9 (5)
C(1)–C(2)–C(3)	112.2 (6)	C(9)–C(10)–C(11)	111.3 (5)
C(2)–C(3)–C(4)	105.7 (5)	C(10)–C(11)–C(12)	104.4 (5)
C(4)–C(3)–C(8)	117.8 (6)	C(12)–C(11)–C(16)	118.2 (5)
C(3)–C(4)–O(1)	109.1 (5)	C(11)–C(12)–O(2)	110.7 (5)
C(3)–C(4)–C(5)	124.9 (6)	C(11)–C(12)–O(13)	123.6 (6)
C(4)–C(5)–C(6)	115.9 (6)	C(12)–C(13)–C(14)	116.8 (6)
C(5)–C(6)–C(7)	120.9 (8)	C(13)–C(14)–C(15)	121.0 (7)
C(6)–C(7)–C(8)	121.9 (8)	C(14)–C(15)–C(16)	121.3 (7)
C(7)–C(8)–C(3)	118.5 (7)	C(15)–C(16)–C(11)	119.1 (6)
C(19)–N(1)–C(20)	108.2 (7)	C(25)–N(3)–C(26)	110.6 (6)
C(21)–N(2)–C(22)	109.4 (6)	C(27)–N(4)–C(28)	111.4 (6)
N(1)–C(17)–C(18)	121.5 (12)	N(3)–C(23)–C(24)	110.7 (7)
N(2)–C(18)–C(17)	118.1 (10)	N(4)–C(24)–C(23)	109.7 (7)
N(1)–Li(1)–C(1)	98.0 (5)	N(3)–Li(2)–C(1)	117.0 (5)
N(1)–Li(1)–C(9)	113.2 (5)	N(3)–Li(2)–C(9)	117.0 (5)
N(1)–Li(1)–N(2)	84.5 (4)	N(3)–Li(2)–N(4)	85.9 (4)
N(2)–Li(1)–C(1)	143.8 (5)	N(4)–Li(2)–C(1)	107.5 (5)
N(2)–Li(1)–C(9)	107.9 (5)	N(4)–Li(2)–C(9)	112.8 (5)
C(1)–Li(1)–C(9)	104.2 (5)	C(1)–Li(2)–C(9)	113.1 (5)
Li(1)–C(1)–O(1)	60.1 (4)	Li(2)–C(1)–O(1)	114.1 (5)
Li(1)–C(1)–C(2)	150.0 (6)	Li(2)–C(1)–C(2)	137.0 (6)
Li(1)–C(9)–O(2)	109.4 (5)	Li(2)–C(9)–O(2)	106.3 (4)
Li(1)–C(9)–C(10)	136.4 (5)	Li(2)–C(9)–C(10)	123.2 (5)
Li(1)–C(1)–Li(2)	70.8 (4)	Li(2)–C(9)–Li(1)	71.2 (4)
Li(1)–O(1)–C(1)	82.7 (4)		

Table III. Coordinates of All Non-Hydrogen Atoms in 2-Lithiobenzothiophene–tmeda with Their Equivalent Thermal Parameters

atom	x/a	y/b	z/c	$U_{eq},^a$ Å^2
S(1)	0.2217 (2)	0.17121 (4)	0.9389 (1)	0.0700 (6)
S(2)	−0.3038 (2)	0.05852 (4)	0.6036 (1)	0.0863 (6)
Li(1)	0.0382 (9)	0.1016 (2)	0.6987 (7)	0.062 (3)
Li(2)	−0.1437 (9)	0.1438 (2)	0.8045 (7)	0.064 (3)
C(11)	0.0951 (5)	0.1574 (2)	0.7985 (4)	0.060 (2)
C(12)	0.0858 (5)	0.1907 (2)	0.7216 (4)	0.058 (2)
C(13)	0.1741 (5)	0.2259 (2)	0.7700 (4)	0.053 (2)
C(14)	0.1838 (6)	0.2637 (2)	0.7161 (5)	0.075 (3)
C(15)	0.2738 (7)	0.2942 (2)	0.7815 (6)	0.082 (3)
C(16)	0.3558 (6)	0.2876 (2)	0.9014 (5)	0.077 (3)
C(17)	0.3476 (6)	0.2510 (2)	0.9578 (5)	0.064 (2)
C(18)	0.2558 (5)	0.2201 (1)	0.8930 (4)	0.050 (2)
C(21)	−0.2195 (6)	0.1072 (1)	0.6324 (5)	0.068 (2)
C(22)	−0.2667 (5)	0.1320 (2)	0.5244 (4)	0.056 (2)
C(23)	−0.3693 (6)	0.1098 (2)	0.4248 (5)	0.056 (2)
C(24)	−0.4398 (7)	0.1241 (2)	0.3057 (5)	0.076 (3)
C(25)	−0.5353 (8)	0.1000 (2)	0.2239 (5)	0.091 (3)
C(26)	−0.5649 (6)	0.0606 (2)	0.2536 (5)	0.083 (3)
C(27)	−0.4987 (6)	0.0447 (2)	0.3675 (5)	0.070 (2)
C(28)	−0.4012 (5)	0.0698 (2)	0.4527 (4)	0.056 (2)
N(31)	0.1464 (5)	0.0896 (1)	0.5533 (4)	0.079 (2)
N(32)	0.1462 (5)	0.0446 (1)	0.7810 (4)	0.085 (2)
N(41)	−0.2672 (5)	0.1969 (1)	0.8340 (4)	0.088 (2)
N(42)	−0.1972 (6)	0.1206 (1)	0.9728 (4)	0.096 (2)
Atoms with sof^b 0.49				
C(311)	0.283 (1)	0.1170 (3)	0.578 (1)	0.1046 (9)
C(321)	0.051 (1)	0.0958 (4)	0.4297 (8)	0.1046 (9)
C(331)	0.196 (2)	0.0468 (3)	0.5740 (8)	0.1046 (9)
C(341)	0.264 (1)	0.0389 (4)	0.7099 (8)	0.1046 (9)
C(351)	0.228 (1)	0.0509 (4)	0.9133 (7)	0.1046 (9)
C(361)	0.047 (1)	0.0091 (3)	0.774 (1)	0.1046 (9)
Atoms with sof 0.56				
C(411)	−0.421 (1)	0.1945 (4)	0.7482 (9)	0.1046 (9)
C(421)	−0.199 (1)	0.2361 (3)	0.814 (1)	0.1046 (9)
C(431)	−0.282 (1)	0.1940 (3)	0.9613 (7)	0.1046 (9)
C(441)	−0.325 (1)	0.1502 (2)	0.980 (1)	0.1046 (9)
C(451)	−0.259 (1)	0.0787 (2)	0.951 (1)	0.1046 (9)
C(461)	−0.073 (1)	0.1228 (3)	1.0809 (9)	0.1046 (9)
Atoms with sof 0.51				
C(312)	0.228 (1)	0.1229 (3)	0.510 (1)	0.1046 (9)
C(322)	0.028 (1)	0.0747 (4)	0.4446 (9)	0.1046 (9)
C(332)	0.251 (1)	0.0554 (3)	0.602 (1)	0.1046 (9)
C(342)	0.174 (2)	0.0248 (3)	0.6696 (9)	0.1046 (9)
C(352)	0.286 (1)	0.0551 (4)	0.873 (1)	0.1046 (9)
C(362)	0.040 (1)	0.0182 (3)	0.830 (1)	0.1046 (9)
Atoms with sof 0.44				
C(412)	−0.379 (1)	0.2124 (4)	0.7281 (9)	0.1046 (9)
C(422)	−0.166 (1)	0.2306 (4)	0.893 (1)	0.1046 (9)
C(432)	−0.345 (1)	0.1819 (4)	0.931 (1)	0.1046 (9)
C(442)	−0.238 (2)	0.1582 (3)	1.0304 (9)	0.1046 (9)
C(452)	−0.322 (1)	0.0915 (4)	0.944 (1)	0.1046 (9)
C(462)	−0.060 (1)	0.1020 (4)	1.057 (1)	0.1046 (9)

$^a U_{eq} = \frac{1}{3}\{\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j\}$. ^{b} Sof = site-occupation factor.

groups (C(25)···C(20) and C(26)···C(29)). As a result of the twisting of the ring, C(1) bridges the two lithium atoms asymmetrically. The C–Li distances in dimeric organolithium compounds are normally in the range of 2.20–2.30 Å,[12] but C(1) has C–Li bond distances of 2.38 (1) and 2.11 (1) Å to Li(1) and Li(2), respectively. The average value of 2.25 (1) Å fits in the normal range. Thus the positive charge of Li(2) is stabilized by its short contact with C(1).

One of the tmeda ligands has an apparently very short C–C distance (C(17)–C(18) = 1.39 (2) Å). This is due to disorder of the same type as found in the crystal structure of 2-lithiobenzothiophene–tmeda, as confirmed by the small torsion angle N(1)–C(17)–C(18)–N(2) = 34.2 (9)°. The bridging of the first benzofuryl group is intermediate between the usual bridging (e.g. as in 1, 2, 3, 4) and that exhibited by 5.
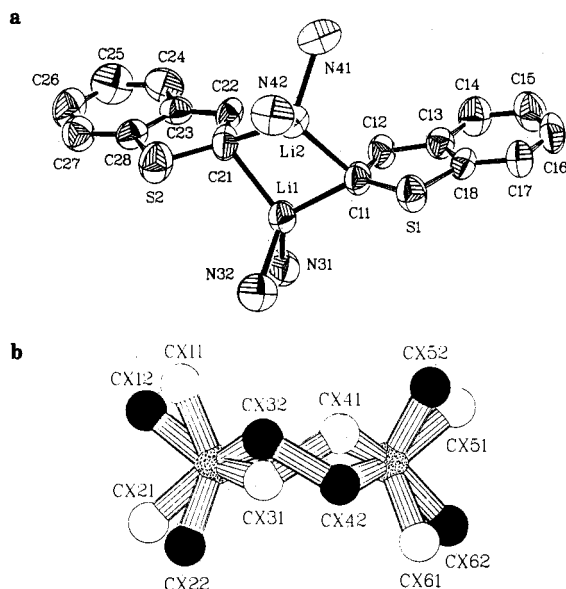
(12) Harder, S.; Brandsma, L.; Spek, A. L.; Smeets, W. J. J., unpublished results: space group triclinic, P1̄; cell parameters, a = 10.091 (9) Å, b = 10.285 (9) Å, c = 14.34 (3) Å, α = 93.1 (1)°, b = 107.1 (1)°, γ = 109.72 (7)°; current $R(F)$ = 0.104.

The Solid-State Structure of 2-Lithiobenzothiophene–tmeda. The solid-state structure of 2-lithiobenzothiophene–tmeda also consists of a dimeric unit in which the benzothienyl groups are bridging and tmeda acts as chelating ligand (Figure 3a). Fractional coordinates of the non-hydrogen atoms are given in Table III, and Table IV contains geometry data. The tmeda molecules are disordered as is described in the Experimental Section and is depicted in Figure 3b. The Li(1)–C(11) and Li(2)–C(11) twist angles with the plane of the first benzothiophene moiety are 21.5 (3)° and 53.0 (3)°, respectively. The Li(1)–C(21) and Li(2)–C(21) twist angles with the plane of the second benzothiophene moiety are 49.8 (2)° and 21.5 (3)°, respectively, so the benzothiophene groups are nearly coplanar but are slipped ca. 1.1 Å relative to

Figure 3. a. ORTEP plot of the dimeric 2-lithiobenzo-thiophene–tmeda. Hydrogen and disordered tmeda atoms have been omitted for clarity. b. Plot of the disorder model found for the tmeda ligands in 2-lithiobenzothiophene–tmeda showing the systematic numbering. X defines the molecule (i.e. 3 or 4), the second number designates the atom, and the third marks the conformation (i.e. 1 for white and 2 for black). The speckled nitrogen atoms are not disordered.

each other (Figure 5a). The lack of short Li–S distances (S(1)–Li(1) = 3.592 (7) Å, S(1)–Li(2) = 3.401 (8) Å, S-(2)–Li(1) = 3.311 (8) Å, and S(2)–Li(2) = 3.644 (7) Å) is remarkable and contrasts with the oxygen analogue. The symmetry (not crystallographic) of this dimer is of interest. In principle there are two possibilities: C_{2h} or C_{2v} (Figure 4). These symmetry assignations are made on the average structures of the compound, i.e. structures containing chelating tmeda ligands with an N–C–C–N torsion angle of 0°, because on the NMR time scale one can make no distinction between the tmeda conformations depicted in Figure 3b. The C_{2v} symmetry of 2-lithiobenzothiophene–tmeda observed in the solid state is retained in toluene solution as shown by NMR studies (see below). Hence, crystal packing forces are ruled out. The structural details of the C–Li–C′–Li′ ring suggest an explanation. The distortion of the four-membered ring is apparent from plots along the Li–Li′ vector and along the ring planes (Figure 5). The lithium atoms seem to bend toward the sulfur atoms, but actually the benzothiophene rings are rotated on the Li–Li′ vector (the Li–Li′ vector acts as a hinge). The interplanar angle CLiLi′/C′LiLi′ is 32.7 (4)°. From an electrostatic point of view a planar geometry for the C–Li–C′–Li′ ring would be best. Hence, the asymmetry in the bridging aryl groups, due to the presence of the sulfur atoms, could be responsible for the distortion.

Surprisingly, the X-ray structure of dimeric phenyl-lithium–tmeda (1[1]) shows a similar CLiLi′/C′LiLi′ inter-
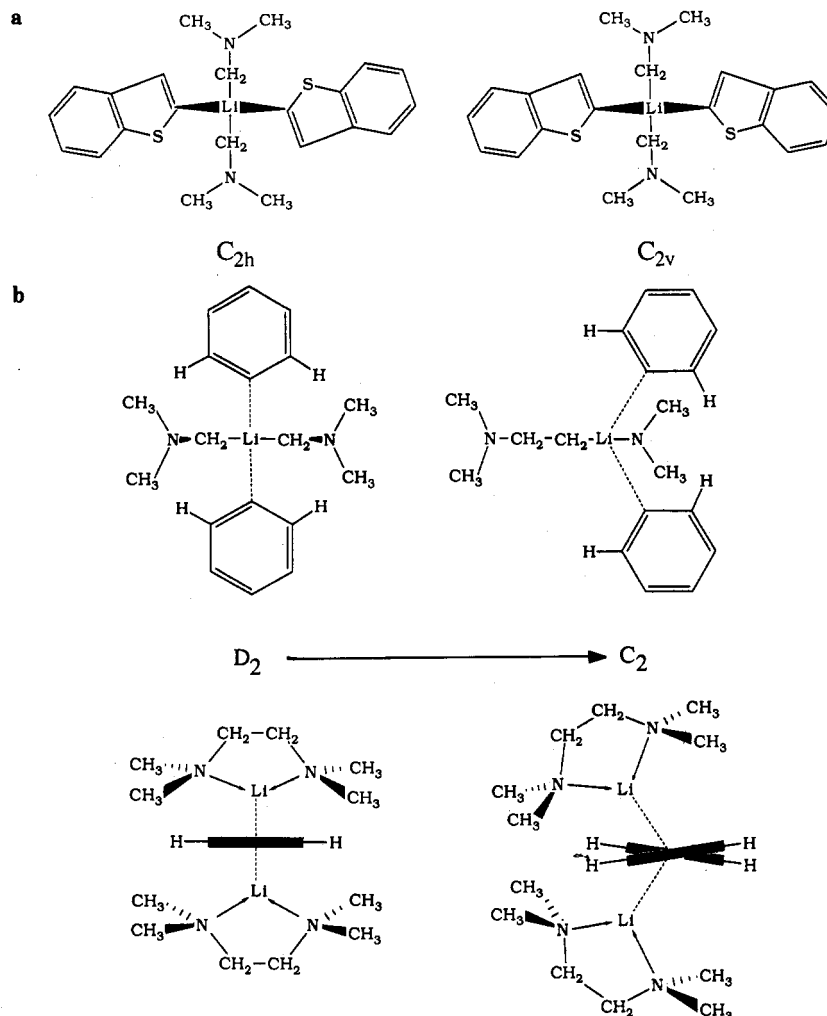
Figure 4. a. Two possible symmetries for the 2-lithiobenzothiophene–tmeda dimer drawn along the LiLi′ vector. The tmeda ligands above the projection plane have been omitted. b. Representation of the change from the sterically unfavorable D_2 symmetry to C_2 for the phenyllithium–tmeda dimer.

**Table IV. Bond Distances (Å) and Angles (deg) for
2-Lithiobenzothiophene–tmeda**

S(1)–C(11)	1.756 (5)	S(2)–C(21)	1.759 (4)
S(1)–C(18)	1.728 (4)	S(2)–C(28)	1.735 (5)
C(11)–C(12)	1.374 (8)	C(21)–C(22)	1.426 (7)
C(12)–C(13)	1.428 (8)	C(22)–C(23)	1.454 (8)
C(13)–C(18)	1.401 (6)	C(23)–C(28)	1.390 (9)
C(13)–C(14)	1.385 (9)	C(23)–C(24)	1.403 (8)
C(14)–C(15)	1.377 (9)	C(24)–C(25)	1.346 (9)
C(15)–C(16)	1.376 (8)	C(25)–C(26)	1.371 (9)
C(16)–C(17)	1.361 (9)	C(26)–C(27)	1.366 (8)
C(17)–C(18)	1.391 (7)	C(27)–C(28)	1.393 (8)
N(31)–C(311)	1.50 (1)	N(41)–C(411)	1.49 (1)
N(31)–C(321)	1.45 (1)	N(41)–C(421)	1.46 (1)
N(31)–C(331)	1.47 (1)	N(41)–C(431)	1.461 (9)
N(32)–C(341)	1.49 (1)	N(42)–C(441)	1.53 (1)
N(32)–C(351)	1.492 (9)	N(42)–C(451)	1.476 (8)
N(32)–C(361)	1.46 (1)	N(42)–C(461)	1.43 (1)
C(331)–C(341)	1.51 (1)	C(431)–C(441)	1.51 (1)
N(31)–C(312)	1.46 (1)	N(41)–C(412)	1.44 (1)
N(31)–C(322)	1.49 (1)	N(41)–C(422)	1.48 (1)
N(31)–C(332)	1.48 (1)	N(41)–C(432)	1.51 (1)
N(32)–C(342)	1.48 (1)	N(42)–C(442)	1.47 (1)
N(32)–C(352)	1.46 (1)	N(42)–C(452)	1.45 (1)
N(32)–C(362)	1.49 (1)	N(42)–C(462)	1.49 (1)
C(332)–C(342)	1.52 (2)	C(432)–C(442)	1.50 (2)
C(11)–S(1)–C(18)	95.7 (3)	C(21)–S(2)–C(28)	94.5 (3)
S(1)–C(11)–C(12)	106.2 (4)	S(2)–C(21)–C(22)	109.5 (4)
C(11)–C(12)–C(13)	117.3 (4)	C(21)–C(22)–C(23)	111.3 (5)
C(14)–C(13)–C(18)	118.0 (5)	C(24)–C(23)–C(28)	116.9 (5)
C(12)–C(13)–C(18)	111.9 (5)	C(22)–C(23)–C(28)	115.3 (5)
C(13)–C(14)–C(15)	120.5 (5)	C(23)–C(24)–C(25)	120.9 (6)
C(14)–C(15)–C(16)	120.5 (6)	C(24)–C(25)–C(26)	121.1 (5)
C(15)–C(16)–C(17)	120.5 (6)	C(25)–C(26)–C(27)	120.9 (6)
C(16)–C(17)–C(18)	119.4 (5)	C(26)–C(27)–C(28)	118.0 (6)
S(1)–C(18)–C(13)	108.9 (4)	C(23)–C(28)–C(27)	122.2 (5)
C(13)–C(18)–C(17)	120.9 (4)	S(2)–C(28)–C(23)	109.4 (4)
C(311)–N(31)–C(321)	111.3 (7)	C(411)–N(41)–C(421)	108.2 (7)
N(31)–C(331)–C(341)	110.7 (8)	N(41)–C(431)–C(441)	106.5 (7)
C(351)–N(32)–C(361)	108.2 (7)	C(451)–N(42)–C(461)	111.9 (6)
N(32)–C(341)–C(331)	110.1 (9)	N(42)–C(441)–C(431)	111.6 (7)
C(312)–N(31)–C(322)	107.2 (7)	C(412)–N(41)–C(422)	109.6 (7)
N(31)–C(332)–C(342)	110.3 (9)	N(41)–C(432)–C(442)	111.5 (9)
C(352)–N(32)–C(362)	113.9 (7)	C(452)–N(42)–C(462)	110.7 (7)
N(32)–C(342)–C(332)	108.9 (8)	N(42)–C(442)–C(432)	107.2 (8)
Li(1)–C(11)	2.131 (9)	Li(2)–C(21)	2.220 (9)
Li(1)–C(21)	2.28 (1)	Li(2)–C(11)	2.23 (1)
N(31)–Li(1)	2.127 (9)	N(41)–Li(2)	2.133 (8)
N(32)–Li(1)	2.196 (8)	N(42)–Li(2)	2.185 (9)
Li(1)–Li(2)	2.64 (1)		
N(31)–Li(1)–C(11)	117.2 (4)	N(41)–Li(2)–C(11)	113.2 (4)
N(32)–Li(1)–C(11)	118.8 (4)	N(42)–Li(2)–C(11)	121.2 (4)
C(11)–Li(1)–C(21)	101.4 (3)	C(11)–Li(2)–C(21)	100.2 (4)
N(31)–Li(1)–N(32)	85.4 (3)	N(41)–Li(2)–N(42)	85.0 (3)
N(31)–Li(1)–C(21)	113.4 (4)	N(41)–Li(2)–C(21)	120.6 (4)
N(32)–Li(1)–C(21)	121.3 (4)	N(42)–Li(2)–C(21)	117.9 (4)
S(1)–C(11)–Li(1)	134.9 (4)	S(1)–C(11)–Li(2)	116.8 (3)
S(2)–C(21)–Li(1)	110.6 (3)	S(2)–C(21)–Li(2)	132.2 (3)
Li(1)–C(11)–Li(2)	74.5 (3)	Li(1)–C(21)–Li(2)	71.9 (3)
Li(1)–C(11)–C(12)	112.4 (4)	Li(2)–C(11)–C(12)	105.4 (4)
Li(1)–C(21)–C(22)	112.9 (4)	Li(2)–C(21)–C(22)	112.8 (3)

planar angle of 33.4°. The similarity of this structural feature may be explained in the following way. The structure of the phenyllithium–tmeda dimer in its unfavorable D_2 symmetry (Figure 4b) would have short distances between the ortho protons of the phenyl groups and the tmeda methyl groups. These repulsive interactions could be overcome by an elongation of the N–Li coordination bond, but this would result in poor lithium coordination. Therefore the symmetry is reduced to C_2 by phenyl ring rotation on the Li–Li' vector. By an additional small rotation of the phenyl rings toward each other, strong internuclear repulsions between the ortho protons of the different rings are prevented. The tmeda ligands, rotated
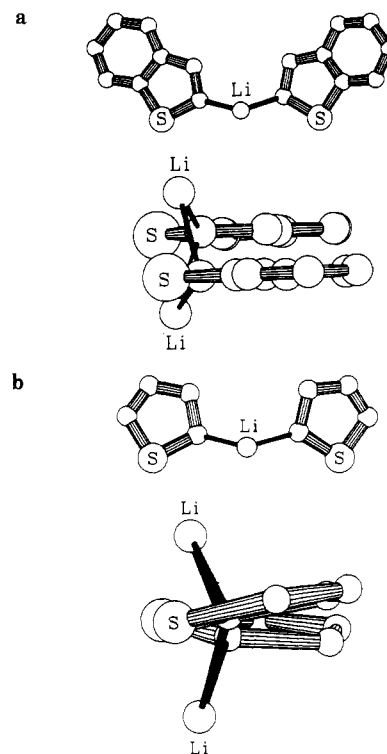
Figure 5. Plots showing the distortion of the C(ipso)–Li–C'-(ipso)–Li' ring in (a) 2-lithiobenzothiophene–tmeda and (b) 2-lithiothiophene–tmeda.[12]

on the C(ipso)–C(ipso)' vector by 46.8°, seek to balance their internuclear repulsions with one another and with the ortho protons. The structure of 2-lithiobenzothiophene can be explained analogously. Both structures have many features in common. The rotation of the benzothiophene rings on the Li–Li' vector is 32.7 (4)°. The tmeda ligands are rotated on the C(ipso)–C(ipso)' vector by 41.5 (5)°. In order to minimize internuclear repulsions between the ortho protons of both benzothiophene groups, the rings are slipped relative to each other (Figure 5a). An alternative way to minimize these internuclear repulsions might involve rotation of the rings on the Li–Li' vector in the other direction. Ortho proton interactions would be absent, but electron-electron repulsions between the sulfur lone pairs would discourage this conformation.

Evidence that these distortions are not due primarily to crystal packing effects is provided by the X-ray structure of 2-lithiothiophene–tmeda.[12] In the solid state, this compound forms dimers isostructural to those described for 2-lithiobenzothiophene–tmeda (Figure 5b). The thiophene rings are rotated on the Li–Li' vector by 30.30 (7)°, the tmeda ligands are rotated on the C(ipso)–C(ipso)' vector by 40.50 (9)°, and the thiophene rings are rotated relative to each other in order to prevent internuclear repulsion between their ortho protons.

NMR Data for 2-Lithiobenzofuran–tmeda. ^{1}H and ^{13}C NMR spectra of crystals of 2-lithiobenzofuran–tmeda (enriched 96% with [6]Li, spin $I = 1$) dissolved in toluene-d_8 show only one set of signals for the aromatic hydrogen and carbon atoms, respectively, even at –90 °C. This indicates that only one species is present under these conditions. [13]C,[6]Li coupling constants and multiplicities characterize the aggregation state of organolithium compounds.[13,14]

(13) (a) Fraenkel, G.; Fraenkel, A. M.; Geckle, M. J.; Schloss, F. J. *J. Am. Chem. Soc.* **1979**, *101*, 4745. (b) Fraenkel, G.; Henrichs, M.; Hewitt, J. M.; Su, B. M.; Geckle, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 3345. (c) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308.

Table V. ^{13}C NMR Chemical Shifts (δ_{TMS}) of Benzofuran, Lithiobenzofuran–tmeda, Benzothiophene,
Lithiobenzothiophene–tmeda, Benzoselenophene, and Lithiobenzoselenophene–tmeda (Numbering, cf. Figure 8)

C	benzofuran	lithiobenzofuran[a]	benzothiophene	lithiobenzo-thiophene[a]	benzoselenophene	lithiobenzo-selenophene[b]
2	144.8	215.6[c]	126.2	181.4[d]	127.2	192.0[e]
3	106.5	120.6	123.8	134.2	128.6	138.5
4	121.1	118.9	123.6	121.0	125.6	122.6
5	122.7	120.7	124.1	122.5	124.3	123.2
6	124.2	120.2	124.2	120.9	124.4	121.3
7	111.4	109.8	122.4	121.7	125.3	125.8
8	155.0	160.9	139.7	149.3	141.9	148.6
9	127.4	131.9	139.6	144.5	141.2	147.1
tmeda CH$_3$		46.2		46.5		48.7, 44.1
tmeda CH$_2$		56.9		56.9		55.8
ref	28	this work	29	this work	this work	this work

[a] Dissolved crystals of tmeda-containing dimer, toluene-d_8, +10 °C. [b] Dissolved crystals of tmeda-containing dimer, toluene-d_8, –90 °C. [c] $^1J_{^{13}C,^6Li}$ = 7.7 Hz (–90 °C). [d] $^1J_{^{13}C,^6Li}$ = 8.2 Hz (–90 °C). [e] $^1J_{^{13}C,^6Li}$ = 7.8 Hz (–90 °C).
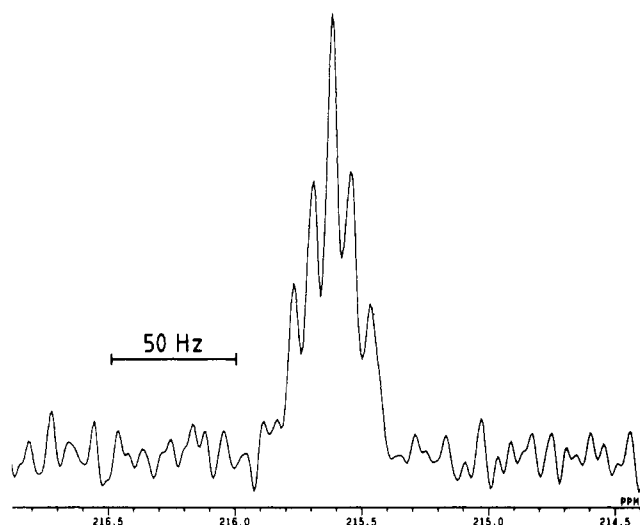
Figure 6. ^{13}C NMR signal for C2 of 2-(lithio-^6Li)benzofuran–tmeda (crystals dissolved in toluene-d_8, T = –90 °C, with slight resolution enhancement).

Figure 7. ^{13}C NMR spectrum of 2-(lithio-^6Li)benzofuran–tmeda: tmeda carbon signals; crystals dissolved in toluene-d_8; exponential line broadening (BF 1.6); x = signals of nonchelating tmeda from small amounts of hydrolysis product; numbers above signals represent half-height widths in hertz.

The ^{13}C signal of the lithiated carbon of 2-lithiobenzofuran is split into a 1/2/3/2/1 quintet ($^1J_{^{13}C,^6Li}$ = 7.7 Hz; Figure 6) due to coupling of ^{13}C to two equivalent ^6Li atoms. The magnitude of $^1J_{^{13}C,^6Li}$ is typical for dimers.[14] Thus the solid-state dimer structure is retained in solution under these conditions. However, the chemical equivalence of corresponding hydrogen and carbon positions indicates the C_1 symmetry of the solid-state species to be converted to higher symmetry on the NMR time scale (even at –90 °C). For this species a distinction between C_{2v} or C_{2h} symmetry (analogous to Figure 4a) can be made by NMR; in C_{2v} symmetry, the methyl groups of tmeda attached to the *same* nitrogen atom are enantiotopic and thus isochronous under the nonchiral conditions. However, the two N(CH$_3$)$_2$ groups of a tmeda molecule are diastereotopic. On the other hand, in C_{2h} symmetry the N(CH$_3$)$_2$ groups are homotopic whereas the methyl groups attached to the same nitrogen are diastereotopic. Thus unisochronicity of the tmeda methyl signals in the ^{1}H and ^{13}C NMR spectra is consistent with either possibility.

However, unisochronicity and therefore diastereotopicity of the tmeda methylene carbon atoms would indicate C_{2v} symmetry; in C_{2h} symmetry these positions are homotopic.
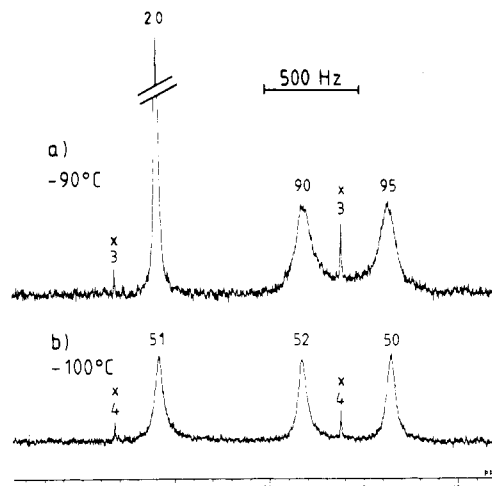
Figure 7 shows the tmeda ^{13}C signals of crystals dissolved in toluene-d_8. At –90 °C (Figure 7a) the N(CH$_3$)$_2$ ^{13}C signals are unisochronous and two broadened singlets due to exchange are observed. The N(CH$_2$) signal appears as a singlet with half-height width of 20 Hz. The natural half-height width, indicated by the signals of nonchelating tmeda (resulting from small amounts of hydrolysis product), is 3 Hz. Further cooling to –100 °C (Figure 7b) *decreases* the line width of the N(CH$_3$)$_2$ signals; therefore, these are before coalescence. In contrast, in the same experiment the line width of the N(CH$_2$) signals *increases*. This temperature dependence indicates exchanging methylene groups after coalescence. Hence, the NCH$_2$ carbon atoms must be diastereotopic. We conclude that 2-lithiobenzofuran–tmeda in toluene-d_8 is a dimer with average C_{2v} symmetry.

In the ^{1}H spectrum at +10 °C, both the methyl and the methylene group signals tmeda appear at a higher field than those of free tmeda, but the order is reversed; i.e., the methyl group signals now appear at the lower field. This exchange in order is due to tmeda chelation[14,15] and results from the electric field effects induced by lithium.[16]

The proton and carbon resonances of 2-lithiobenzofuran were assigned by combined one- and two-dimensional

(14) (a) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371. (b) Bauer, W.; Müller, G.; Pi, R.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.*, **1986**, *25*, 1103. (c) Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970. (d) Boersma, J. Ph.D. Thesis, Utrecht, the Netherlands, 1968. (e) A paper on this subject will be published (Bauer et al.).

(15) (a) Koga, N.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4625. (b) Erker, G.; Frömberg, W.; Angermund, K.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 372. (c) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(16) Musher, J. I. *J. Chem. Phys.* **1962**, *37*, 34.

Table VI. ¹H NMR Chemical Shifts of 2-Lithiobenzofuran–tmeda, 2-Lithiobenzothiophene–tmeda, and 2-Lithiobenzoselenophene–tmeda[a] (Numbering, cf. Figure 8)

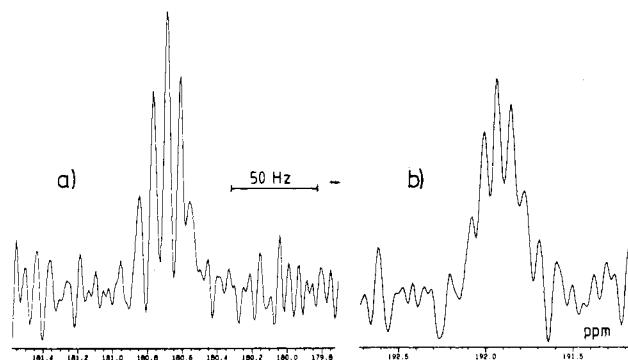| H	2-lithiobenzo-furan[b]	2-lithiobenzo-thiophene[b]	2-lithiobenzo-selenophene[c]
3	6.98 s	7.92 s	8.52 s
4	7.69 d, 7.6	7.95 d, 7.9	8.04 d, 7.6
5	7.22 dd, 7.6, 7.9	7.31 dd, 7.9, 7.9	7.41 dd, 7.3, 7.6
6	7.14 dd, 7.9, 7.9	7.14 dd, 7.9, 7.9	7.15 dd, 7.3, 7.6
7	7.58 d, 7.9	7.95 d, 7.9	8.27 d, 7.6
tmeda CH₃	1.93 s	1.87 s	1.99, 1.70 s, s
tmeda CH₂	1.72 s	1.57 s	1.70, 0.89 s, s

[a] δ (ppm); multiplicities; coupling constants (Hz). [b] In toluene-d_8, +10 °C. [c] In toluene-d_8, –90 °C.
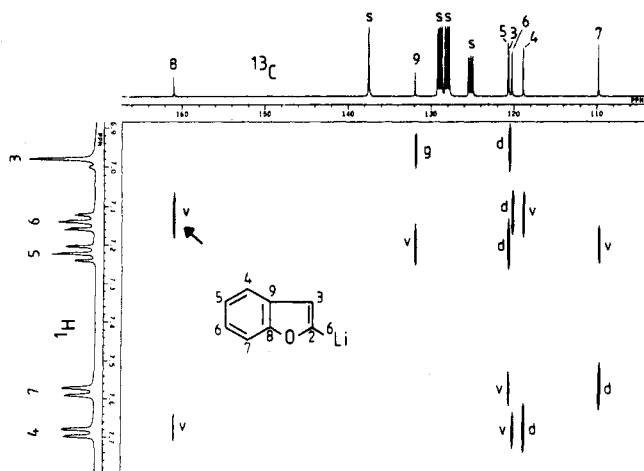
Figure 8. COLOC (C,H correlation via long-range couplings[17]) contour plot of 2-(lithio-⁶*Li*)benzofuran–tmeda: crystals dissolved in toluene-d_8; T = +10 °C; s = solvent, d = direct coupling ($^1J_{^{13}C,^1H}$), g = geminal coupling ($^2J_{^{13}C,^1H}$), v = vicinal coupling ($^3J_{^{13}C,^1H}$); selected parameters are given in the Experimental Section.

Figure 9. ¹³C NMR signal of C2 of 2-(lithio-⁶*Li*)benzo-thiophene–tmeda (a) and of 2-(lithio-⁶*Li*)benzoselenophene–tmeda (b): crystals dissolved in toluene-d_8, T = –90 °C, with slight resolution enhancement.

NMR techniques. NMR data for 2-lithiobenzofuran are listed in Tables V and VI. The connectivity pattern of the ¹H resonances can be obtained by selective irradiation of the two low-field doublets at 7.69 and 7.58 ppm; this converts both the 7.22 and 7.14 ppm triplets to doublets. C3 can be assigned from the C,H-shift correlation spectrum via the cross peak with the ¹H singlet at 6.98 ppm. The chemical shift of C8 at 160.9 ppm is found at low field due to its oxygen substituent. The COLOC[17] contour plot (Figure 8), which provides information about long-range ¹³C,¹H couplings, exhibits an intense cross peak due to $^3J_{^{13}C,^1H}$ coupling of C8 (arrow in Figure 8) to the ¹H triplet of H6 at 7.14 ppm. The alternative assignment of this triplet to H5 can be ruled out as the $^4J_{^{13}C,^1H}$ coupling constant should be less than 2 Hz[18] and thus would not appear in the COLOC spectrum under these conditions. The assignment of the remaining positions follows easily from the C,H-shift correlation spectrum. As is usual in lithiated aromatic compounds, the ¹³C resonance of the lithiated carbon atom is shifted considerably downfield as compared to the protonated precursor. This has been attributed to low mean excitation energy for magnetic mixing of the ground state into higher energy state levels.[19] However, the π-electrons are polarized away from the

(17) (a) Kessler, H.; Griesinger, C.; Zarbock, J.; Loosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331. (b) Kessler, H.; Griesinger, C.; Lautz, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 444.

(18) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; VCH Publishers: New York, 1987.

(19) Jones, A. J.; Grant, D. M.; Russell, J. G.; Fraenkel, G. *J. Chem. Phys.* **1969**, *73*, 1624.

lithiated carbon due to the σ-negative charge, and this provides a simpler explanation. This chemical shift behavior is also found for C3 in 2-lithiobenzofuran.

NMR Data for 2-Lithiobenzothiophene–tmeda. NMR spectra of crystals of 2-lithiobenzothiophene–tmeda (enriched with 96% ⁶Li) dissolved in toluene-d_8 under the same conditions resemble those of 2-lithiobenzofuran–tmeda. Also here the ¹³C signal of the lithiated carbon is split into a quintet (intensity ratio 1/2/3/2/1) expected for a dimer (Figure 9). The ¹³C,⁶Li coupling constant of 8.2 Hz is only 0.5 Hz larger than the corresponding value for 2-lithiobenzofuran, indicating that the influence of the heteroatom is small. Moreover, the temperature dependence of the ¹³C NMR signals is identical with that of 2-lithiobenzofuran (cf. Figure 7). Hence, our arguments for a dimer with average C_{2v} symmetry in solution also apply to 2-lithiobenzothiophene. As is described for 2-lithiobenzofuran, assignments of the carbon and proton resonances were achieved by selective decoupling, C,H-shift correlation, and COLOC experiments. These are summarized in Tables V and VI. The changes in ¹³C chemical shifts in going from the protonated to the lithiated species are the same for benzofuran and for benzothiophene. The methyl signals of tmeda in the ¹H spectrum of 2-lithiobenzothiophene–tmeda again appear downfield from the methylene group resonance. 2-Lithiobenzofuran and 2-lithiobenzothiophene must be chelated similarly by tmeda.

The chemical shift of H3 (the proton vicinal to the lithium substituent) was evaluated by using increment rules:[20] for furan and thiophene chemical shifts of 5.49 and 6.40 ppm, respectively, are calculated. The shift of H3 in furan, 0.91 ppm upfield relative to thiophene, is caused by the better π-donor properties of oxygen as compared with sulfur. This behavior is also found in 2-lithiobenzofuran and 2-lithiobenzothiophene: H3 in the oxygen compound resonates 0.96 ppm upfield from H3 in the sulfur compound. However, the presence of lithium produces a high frequency shift: in both lithiated species H3 appears ca. 1.5 ppm downfield from the values calculated for furan and thiophene.

NMR Data for 2-Lithiobenzoselenophene–tmeda. Crystals of 2-lithiobenzoselenophene dissolved in toluene-d_8 give NMR spectra which are qualitatively identical with the spectra described above for the oxygen and sulfur analogues. The spectral assignments, made by selective decoupling experiments and by C,H-shift correlation spectroscopy, are summarized in Tables V and VI.

The temperature behavior of the tmeda ¹³C NMR signals is the same as that shown in Figure 7. The lithiated carbon atom shows a 1/2/3/2/1 quintet with $^1J_{^{13}C,^6Li}$ = 7.8 Hz (Figure 9b). This is nearly identical with the value

found for 2-lithiobenzofuran. Thus like 2-lithiobenzofuran-tmeda and 2-lithiobenzothiophene-tmeda, 2-lithiobenzoselenophene-tmeda is a syn dimer in toluene-d_8 solution with average C_{2v} symmetry. A remarkable α-effect is found for C2 in 2-lithiobenzoselenophene which resonates 10.6 ppm at lower field than the corresponding atom in 2-lithiobenzothiophene. This anomaly in the series oxygen-sulfur-selenium is also observed in the hydrogenated starting compounds (Table V) and can be rationalized by the electronegativities of the involved elements[21] (oxygen, 3.50; sulfur, 2.44; selenium, 2.48; tellurium, 2.01).

In both the ^{1}H and ^{13}C NMR spectra the positions 3 and 7 which are connected to the heteroatom via two (^{13}C) and three (^{1}H) bonds, respectively, show a pronounced downfield shift in the series oxygen-sulfur-selenium (Tables V and VI). This can be rationalized by two opposing effects: the electronegative oxygen atom is a good π-donor, thus increasing electron density at these positions as compared to the weaker π-donor sulfur. The downfield shift for selenium again reflects the higher electronegativity and/or the poorer π-donor character of selenium as compared to sulfur.

Experimental Section

General Conditions. All manipulations were carried out in an inert-nitrogen or -argon atmosphere, using Schlenk techniques. Solvents used were distilled from sodium prior to use.

Preparation. 2-Lithiobenzofuran was synthesized by deprotonating 725 mg (6.14 mmol) of benzofuran in 22 mL of diethyl ether in presence of 1.0 mL (6.65 mmol) of tmeda with 2.45 mL (6.08 mmol, 2.48 M) of n-Bu[6]Li in hexane at room temperature. Orange crystals can be obtained by cooling to -78 °C.

2-Lithiobenzothiophene was synthesized by direct metallation of benzothiophene (2.19 g, 16.3 mmol) dissolved in hexane (ca. 50 mL) and tmeda (4.9 mL, 32.0 mmol). Crystals were obtained by recrystallization from diethyl ether in the presence of 2 equiv of tmeda.

2-Lithiobenzoselenophene was synthesized by direct metallation of benzoselenophene[22] (133 mg, 0.71 mmol) dissolved in pentane (3.0 mL) containing 0.15 mL of tmeda (0.99 mmol) by adding 1 equiv of butyllithium at -25 °C. The white needles formed after ca. 30 s are washed twice with pentane at -50 °C and dried in vacuo.

Structure Determination of 2-Lithiobenzofuran-tmeda. Crystals of 2-lithiobenzofuran-tmeda, [Li(C$_8$H$_5$O)]$_2$·[C$_6$H$_{16}$N$_2$]$_2$, are colorless and of isomeric habitus. They are very air-sensitive. A crystal fragment of dimensions 0.16 × 0.30 × 0.35 mm was mounted under argon in a Lindemann glass capillary. The X-ray measurements employed a Philips PW1100 diffractometer and graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). The following cell parameters of the triclinic cell were determined by a least-squares procedure from 22 high-angle reflections: a = 15.202 (6) Å, b = 10.138 (3) Å, c = 10.129 (4) Å, α = 100.64 (4)°, β = 100.14 (4)°, and γ = 93.44 (3)°. The space group is $P\bar{1}$ (confirmed by determination and refinement in this space group): D_{calcd} = 1.062 g·cm^{-3} for Z = 2 and M_r = 480.54. Intensity data were measured at room temperature; $\omega/2\theta$ scan method; $2\theta_{max}$ = 44°; reflections measured: $-15 \le h \le 15$, $-10 \le k \le 10$, $0 \le l \le$ 10. Three standard reflections were monitored periodically during data collection. There was a 9% decay indicated by the change in intensity of the standard reflections. Decay and Lorentz-polarization corrections were applied. A total of 3679 independent reflections were obtained. In subsequent calculations a set of 2652 reflections with $I > 2.5\sigma(I)$ was used. The structure was solved by direct methods.[23] The non-hydrogen atoms were refined with anisotropic temperature factors. One of the tmeda ligands proved

to be disordered in the same way as in the structure of 2-lithiobenzothiophene-tmeda. Resolution of this disorder was not attempted. Hence, only the average structure of this group was obtained. The hydrogen atoms of the benzofuryl groups were included in the refinement at their calculated positions (C-H 1.00 Å). Least-squares refinement using unit-weights converged to $R(F)$ = 0.91. Δ/σ is less than 0.005 for all parameters. The maximum residual density in a final ΔF map is 0.34 e Å^{-3}. Scattering factors for neutral atoms were taken from Cromer and Mann.[24] The refinement calculations were done with the SHELX-76 program system.[25]

Structure Determination of 2-Lithiobenzothiophene-tmeda. A rod-shaped, colorless crystal, 0.3 × 0.6 × 1.0 mm, was sealed in a capillary under nitrogen because of its high sensitivity to oxygen and water. An Enraf-Nonius Cad 4 diffractometer was employed. Cell constants from least-squares fit of the setting angles of 12 reflections (SET 4 method) with a θ range of 8.4-13.6°: monoclinic, a = 9.064 (3) Å, b = 32.657 (4) Å, c = 11.144 (2) Å, and β = 104.29 (2)°; space group $P2_1/c$; D_{calcd} = 1.065 g·cm^{-3} for Z = 4 and M_r = 512.67; $\omega/2\theta$ scan method with $2\theta_{max}$ = 50° and ω = (0.55 + 0.35 tan θ)°; Zr-filtered Mo Kα radiation (λ = 0.71073 Å); T = 295 K; one-fourth of the reflection sphere; index range, $0 \le h \le 10$, $0 \le k \le 38$, $-13 \le l \le 13$. A total of 5599 independent reflections were measured, of which 2706 were considered observed [$I > 2.5\sigma(I)$]. Two standard reflections (200, rmsd. 0.37%, and 040, rmsd. 0.69%) were measured after every 50 reflections. Corrections for Lorentz-polarization effects and linear decay were made. The structure was solved by direct methods (SHELXS-86).[26] During isotropic refinement it became clear that the tmeda ligands are disordered. This was concluded from the short CH$_2$-CH$_2$ and NCH$_2$ distances, a torsion angle approaching 0°, large isotropic thermal parameters, and the appearance of many electron density peaks around the tmeda molecule. The nature of the disorder became clear by fixing the tmeda molecule in an ideal restrained geometry with a certain tolerance. The following distances were imposed: CH$_2$-CH$_2$ (1.51 ± 0.01 Å), N-CH$_2$ and NCH$_3$ (1.48 ± 0.01 Å), CH$_3$···N···CH$_2$ and CH$_3$···N···CH$_3$ (2.415 ± 0.03 Å), and CH$_2$···CH$_2$···N (2.44 ± 0.03 Å). By fixing the nonbonded distances a tetrahedral geometry was preserved. When this model was refined with an occupation of 0.5, a second model emerged in the difference Fourier map. Both molecules were refined with a variable occupation resulting in the disorder model which is illustrated in Figure 2; the nitrogen atoms are not disordered while carbon atoms between the nitrogen atoms possess two possible conformations which are correlated to two possible positions of each of the terminal carbon atoms. The occupation of both conformations was refined to ca 0.5. During further refinement the two models were kept fixed and the disordered atoms were refined with an overall isotropic thermal parameter which converged to 0.105 Å^2. Hydrogen atoms were included in the refinement at calculated C(sp^3) and C(sp^2) positions (C-H = 1.00 Å) riding on their bonded C atoms. The hydrogens on the ordered atoms were refined with an overall thermal parameter which converged to 0.071 Å^2. Full-matrix refinement on F, function minimized $\sum w(|F_o|^2 - |F_c|^2)$, with 122 atoms and 293 parameters converged to $R(F)$ = 0.052 with w = $1/\sigma^2(F)$. The average shift to error ratio (Δ/σ) is 0.040. Maximum and minimum electron densities were 0.26 and 0.33 e Å^{-3}, respectively. Scattering factors from Cromer and Mann.[24]

Calculations were performed with SHELXS-86 (direct methods),[26] SHELX-76 (refinement),[25] and EUCLID (illustrations and molecular geometry),[27] on the CYBER 180-855 of the University of Utrecht.

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2-(lithio-^6Li)benzofuran–tmeda, 2-(lithio-^6Li)benzothiophene–tmeda, and 2-(lithio-^6Li)benzoselenophene–tmeda were prepared by dissolving crystals (prepared in the manner as described above using [(lithio-^6Li)-n-butyl]lithium[13c]) in dry 5-mm tubes in 0.5 mL of toluene-d_8.

NMR spectra were recorded on a JEOL GX400 spectrometer (^{1}H, 400 MHz) on a 5-mm dual ^{1}H/^{13}C probehead. The 90° pulse lengths are as follows: ^{1}H, 15 μs; ^{13}C, 9 μs. One-dimensional ^{13}C spectra were recorded with a 25 000 Hz frequency width, 32K data points, a 3.2-s repetition time, and 30° pulses. Zero filling to 64K and Gaussian apodization was carried out before Fourier transformation to give the spectra in Figures 6 and 9.

Selected parameters of the COLOC[17] spectrum in Figure 8 are as follows: ^{1}H frequency width, 363 Hz; ^{13}C frequency width, 6353 Hz; 1024 data points in t_2 with zero filling to 2048; 16 increments in t_1 with zero filling to 64; Gaussian apodization in t_2 (GF 12, BF-5) and in t_1 (GF 25, BF-15); 512 scans per t_1 increment; $Δ_1$ = 25 ms, $Δ_2$ = 30 ms.

Supplementary Material Available: Tables of thermal parameters, fractional coordinates, bond distances, bond angles, and torsion angles (11 pages); listings of structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

Crystal Structure of [2,6-Bis(dimethylamino)phenyl]lithium: The First Trimeric Organolithium Compound

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The X-ray structure of [2,6-bis(dimethylamino)phenyl]lithium reveals the first trimeric organolithium species. This trimer is retained in apolar solvents like benzene or toluene. On the basis of NMR data a monomer–trimer equilibrium is proposed in THF solution.

Introduction

Organolithium compounds can exist in a variety of aggregation states.[1] Monomers (1), dimers (2), tetramers, (3), and hexamers (4) are common and polymers are also known.[2,3] Since the nature of the C–Li bond is largely ionic,[4–7] high aggregation states containing a maximum of C⁻–Li⁺ contacts are favored. According to high level ab initio calculations,[7] association of methyllithium monomers into dimers, trimers, or tetramers yields 22.2, 26.3, and 30.7 kcal/mol energy per monomer, respectively.
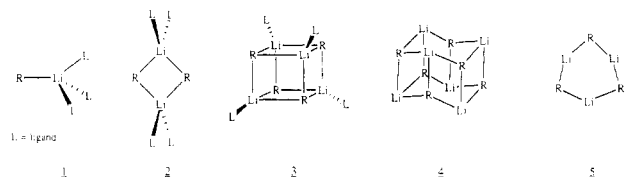
However, in solution entropy and solvation effects also are important. In the absence of solvent ligands, dissociation of tetramers into trimers is calculated to be favored over dissociation into dimers, but this preference reverses when solvation is included.[7] These calculations are consistent with the numerous tetramer–dimer equilibria found in solution.[8] Two dimers may be stacked to give a tet-

ramer.[9,10] The X-ray[11a,b] and solution[11b] structure of tetrakis[(2,6-dimethoxyphenyl)lithium] show this stacking concept nicely.

Hexameric organolithium compounds (4) are formally comprised of two stacked trimers.[10,12] NMR studies of alkyllithium compounds in solution, however, show hexamer/dimer + tetramer equilibria to be present.[13,14] Although the dissociation of hexameric aggregates into trimers is not excluded,[10,14,15] the existence of trimeric aggregates in solution has never been proven. This work reports the first trimeric organolithium compound in the solid state as well as in solution.

Results and Discussion

X-ray Structure. The X-ray structure of [2,6-bis(dimethylamino)phenyl]lithium (7) reveals a trimeric aggre-

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