μ-1:2κ^2C^1-[5-ethoxy-1,2-bis(trifluoromethyl)penta-2,4-dienyl]-1$\kappa^2C^{2,3}$;2$\kappa^2C^{4,5}$-bis(tricarbonyliron)(*Fe–Fe*) (Ros, Commenges, Mathieu, Solans & Font-Altaba, 1985). The substitution of trifluoromethyl by the trimethylsilyl group produces slight differences between the two molecular structures. Thus, the Fe—Fe bond length [2·625 (1) Å] is intermeduate between those observed in the trifluoromethyl complex [2·617 (3) Å] and those obtained for the product resulting from the reaction of 2,7-dimethoxyepine with $Fe(CO)_5$ [2·642 (1) Å] (Aumann, Averbeck & Krüger, 1975), but this distance is quite long for an iron–iron single-bond distance (Krüger, Barnett & Brauer, 1978). The Fe(2) atom is asymmetrically bonded to the olefin part of the organic ligand with Fe(2)—C(5) [2·337 (6) Å] 0·163 Å longer than the Fe(2)—C(4) bond [2·174 (5) Å] [2·36 (1) and 2·21 (1) Å, respectively, in the trifluoromethyl complex].

C(1) is equidistant from Fe(1) and Fe(2) [average value 2·061 (1) Å] and Fe(1) is equidistant from C(1), C(2) and C(3) [average value 2·065 (13) Å]. The C(1)—O(6) chain gives evidence of extensive electronic delocalization with C—C lengths ranging from 1·415 (6) to 1·455 (7) Å and the C(5)—O(6) length shorter than the O(6)—C(7) length.

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Structure of Bis[*tert*-butyl (2-Lithiophenyl) Sulfide] [*N,N,N′,N′*-Tetramethylethylenediamine]

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Abstract. *catena*-Poly{[lithium-bis-μ-(*tert*-butylthiophenyl-*S*,μ-C)-lithium]-μ-(*N,N,N′,N′*-tetramethylethylenediamine-*N,N′*)}, $[\{Li(C_{10}H_{13}S)\}_2(C_6H_{16}N_2)]$, M_r = 460·64, triclinic, $P\bar{1}$, a = 7·832 (3), b = 9·419 (1), c = 10·771 (1) Å, α = 85·93 (1), β = 72·90 (2), γ = 69·64 (3)°, V = 711·6 (3) Å^3, Z = 1, D_x = 1·075 g cm^{-3} λ(Cu $K\alpha$) = 1·54184 Å, μ = 17·23 cm^{-1}, $F(000)$ = 250, T = 295 K, R = 0·055 for 2025 observed reflections. The structure consists of centrosymmetric *tert*-butyl (2-lithiophenyl) sulfide dimers [around ($\frac{1}{2}$00)] which are linked together by bridging centrosymmetric *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) molecules [around (000)] to form one-dimensional infinite chains. The Li atom has a distorted tetrahedral coordination sphere consisting of two C atoms of symmetry-related phenyl rings, one N atom and one S atom. The phenyl ring is distorted in a way which is common for all aryl groups bonded to electropositive elements.

Introduction. Whereas the activating and *ortho*-directing effect of several hetero substituents (*e.g.* —O*R*,

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$-CH_2NR_2$, $-SO_2NMe_2$, F) in the lithiation of benzene derivatives is well established (Gschwend & Rodriguez, 1979), the results reported on the metallation of alkyl aryl sulfides seem to conflict. Shirley & Reeves (1968) studied the reaction of PhSMe and PhSEt with butyllithium in Et_2O and found *ortho, meta* and *para* lithiation and some lithiation in the side chain. Recently, Horner, Lawson & Simons (1982) showed that *tert*-butyl phenyl sulfide is smoothly *ortho* lithiated with butyllithium.TMEDA in hexane. The present paper, which deals with the crystal-structure determination of *ortho*-lithiated *tert*-butyl phenyl sulfide, is part of a study on the relation between the structure and reactivity of polar organometallic compounds.

Experimental. Crystals were obtained by reacting *tert*-butyl phenyl sulfide in hexane at 313–323 K with one equivalent of butyllithium in the presence of two equivalents of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and subsequent cooling to room temperature. Rod-shaped yellowish crystal, 0·2 × 0·3 × 1·0 mm. Enraf–Nonius CAD-4 diffractometer. Cell constants from least-squares fit of the setting angles of 16 reflections with θ range 9·4–20·6°. ω–2θ scan, 2θ(max.) = 140°, $\omega = (0{\cdot}80 + 0{\cdot}15\tan\theta)°$, Ni-filtered Cu $K\alpha$ radiation. One half of the reflection sphere, index range $0 \le h \le 9$, $-11 \le k \le 11$, $-13 \le l \le 13$; 2700 reflections measured, 2025 considered observed [$I > 2{\cdot}5\sigma(I)$]. Two standard reflections ($1\bar{1}\bar{1}$: r.m.s.d. 0·58% and $1\bar{1}2$: r.m.s.d. 0·48%) measured every 50 reflections. Corrections for Lorentz–polarization effects and linear decay (4·5%). The structure was solved by direct methods. An absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied on isotropically refined data, min. and max. correction factors being 0·48 (2) and 1·26 (5) on F, respectively. H atoms were included in the refinement at calculated C(sp^3) and C(sp^2) positions (C–H 1·08 Å) riding on their bonded C atoms with an overall thermal parameter. Full-matrix refinement on F, function minimized $\sum w(|F_o|^2 - |F_c|^2)$, with 37 atoms and 146 parameters converged to $R(F) = 0{\cdot}055$ and $R(wF) = 0{\cdot}047$ with $w = 1/\sigma^2(F)$ and $S = 0{\cdot}53$. The overall temperature factor of the H atoms refined to 0·11 Å^2. The average shift-to-e.s.d. ratio (Δ/σ) is < 0·001. Max. and min. electron densities 0·23 and −0·33 e Å^{-3}, respectively.

Scattering factors from Cromer & Mann (1968). Anomalous-dispersion corrections from Cromer & Liberman (1970). Calculations were performed with *SHELXS*86 (direct methods) (Sheldrick, 1986), *SHELX*76 (refinement) (Sheldrick, 1976), *DIFABS* (absorption correction) (Walker & Stuart, 1983) and *EUCLID* (illustrations and molecular geometry) (Spek, 1982) on the Cyber 180–855 of the University of Utrecht.

Discussion. Atomic coordinates, bond lengths and angles are given in Tables 1 and 2.* The structure of the title compound, illustrated in Fig. 1, consists of two *tert*-butyl phenyl sulfide fragments each three-centre two-electron bonded *via* C(6) to two Li atoms and *via* the S atom lone pair to one of these Li atoms. These centrosymmetric dimeric species are linked together by the TMEDA ligands, which possess a centre of inversion in the middle of the C–C bond. This results in one-dimensional chains of aggregates in the [100] direction. The geometry of the Li coordination is given in Table 3. The Li atom has a distorted tetrahedral coordination sphere and Li–C, Li–N and Li–Li distances are comparable with values found in other dimeric aryllithium compounds: in [PhLi.TMEDA]$_2$ these distances are Li–C 2·208 (6) and 2·278 (6), Li–N 2·177 (4) and 2·208 (4), Li–Li 2·490 (6) Å (Thoennes & Weiss, 1978); in 8-(dimethylamino)-1-naphthyllithium (Jastrzebski & van Koten, 1983) these distances are Li–C 2·232 (4) and 2·224 (4), Li–N 2·136 (4), Li–Li 2·366 (5) Å.

The S–Li distance of 2·712 (5) Å is remarkably long compared with the only other example of S–Li coordination found in 2-lithio-2-methyl-1,3-dithiane–tetramethylethylenediamine (Amstutz, Seebach, Seiler, Schweizer & Dunitz, 1980) with S–Li distance of 2·516 Å. Nevertheless, we believe there must be a coordinative interaction between S and Li, because the C(6)Li$_2$C(6′) plane is tilted towards the phenyl-ring plane, as is illustrated in Fig. 2, with an interplanar angle of 47·9 (3)°. In most aryllithium compounds with an electron-deficient (three-centre two-electron) CLi_2 bond, this angle deviates only slightly from 90°, *e.g.* 2·3 (2)° for [Li(THF)$_2$mesityl]$_2$ (Beno, Hope, Olmstead & Power, 1985). The same holds for organoaluminium compounds bridged by an aryl group, *e.g.* Ph_6Al_2 (Malone & McDonald, 1972). However, the structure of 8-(dimethylamino)-1-naphthyllithium.Et_2O (Jastrzebski & van Koten, 1983), which shows an Li coordination which is similar to that of the title compound, is even more flattened [interplanar angle 41·3 (3)°].

The phenyl ring is planar [σ(plane) = 0·011 (4) Å], but is distorted in a way which is common for all aryl groups taking part in an electron-deficient bonding system. The C atom which is bonded to the metal has a small C–C–C angle [112·0 (3)°] while the neighbouring C atoms in the ring have large C–C–C angles [both 125·0 (3)°]. This distortion has already been mentioned by Thoennes & Weiss (1978) in the

* Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms and bond lengths, angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43918 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

description of the structure of $(PhLi.TMEDA)_2$. The reason for this distortion is unclear. It may be a change of hybridization at C(6) or the electron-withdrawing effect of the electron-deficient bond. The same sort of distortion is also found in the phenyl groups of Ph_2In and Ph_3Ga (Malone & McDonald, 1970) which possess no bridging phenyl groups, so it seems to be a general feature of phenyl groups bonded to electropositive elements.

Table 1. *Fractional atomic coordinates of the non-*H *atoms with their equivalent isotropic thermal parameters* (Å^2)

	x	y	z	U_{eq}*
S	0·2886 (1)	0·8607 (1)	0·2617 (1)	0·0585 (3)
N	0·2209 (3)	0·8257 (2)	−0·0498 (2)	0·0446 (8)
Li	0·4013 (8)	0·9215 (5)	0·0067 (5)	0·052 (2)
C(1)	0·2511 (4)	1·0605 (3)	0·2599 (3)	0·047 (1)
C(2)	0·1368 (5)	1·1455 (4)	0·3732 (3)	0·062 (1)
C(3)	0·0889 (5)	1·3011 (4)	0·3737 (3)	0·077 (1)
C(4)	0·1531 (5)	1·3689 (4)	0·2602 (4)	0·074 (2)
C(5)	0·2647 (5)	1·2794 (3)	0·1485 (3)	0·061 (1)
C(6)	0·3236 (4)	1·1206 (3)	0·1409 (3)	0·049 (1)
C(7)	0·4853 (5)	0·7663 (3)	0·3329 (3)	0·056 (1)
C(8)	0·6620 (2)	0·7985 (1)	0·2576 (1)	0·118 (2)
C(9)	0·4299 (2)	0·8151 (1)	0·4738 (1)	0·093 (2)
C(10)	0·5149 (2)	0·5991 (1)	0·3234 (1)	0·106 (2)
C(11)	0·0216 (2)	0·9174 (1)	0·0151 (1)	0·046 (1)
C(12)	0·2570 (2)	0·8157 (1)	−0·1919 (1)	0·062 (1)
C(13)	0·2554 (2)	0·6701 (1)	−0·0028 (1)	0·061 (1)

* $U_{eq} = \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

Table 2. *Interatomic distances* (Å) *and angles* (°)

S–C(1)	1·801 (3)	C(3)–C(4)	1·381 (5)
S–C(7)	1·843 (4)	C(4)–C(5)	1·391 (5)
N–C(11)	1·475 (3)	C(5)–C(6)	1·404 (4)
N–C(12)	1·476 (2)	C(7)–C(9)	1·509 (3)
N–C(13)	1·475 (2)	C(7)–C(10)	1·516 (3)
C(1)–C(6)	1·407 (4)	C(7)–C(8)	1·504 (4)
C(1)–C(2)	1·389 (4)	C(11)–C(11^i)	1·506 (1)
C(2)–C(3)	1·381 (5)		

C(1)–S–C(7)	107·8 (2)	Li–C(6)–Li^{ii}	67·1 (2)
Li–N–C(11)	107·8 (2)	Li^{ii}–C(6)–C(5)	98·1 (3)
Li–N–C(12)	113·4 (2)	Li–C(6)–C(1)	99·6 (2)
Li–N–C(13)	109·1 (2)	Li^{ii}–C(6)–C(1)	137·6 (3)
C(11)–N–C(12)	111·4 (2)	Li–C(6)–C(5)	143·6 (3)
C(11)–N–C(13)	108·1 (2)	S–C(7)–C(10)	104·3 (2)
C(12)–N–C(13)	107·0 (1)	S–C(7)–C(8)	110·9 (2)
S–C(1)–C(2)	117·1 (2)	S–C(7)–C(9)	110·8 (2)
S–C(1)–C(6)	117·6 (2)	C(9)–C(7)–C(10)	109·4 (2)
C(2)–C(1)–C(6)	125·0 (3)	C(8)–C(7)–C(9)	110·4 (2)
C(1)–C(2)–C(3)	119·6 (3)	C(8)–C(7)–C(10)	111·0 (2)
C(2)–C(3)–C(4)	118·9 (3)	N–C(11)–C(11^i)	112·1 (1)
C(3)–C(4)–C(5)	119·5 (3)		
C(4)–C(5)–C(6)	125·0 (3)		
C(1)–C(6)–C(5)	112·0 (3)		

Table 3. *The lithium coordination* (Å,°)

Li···C(6)	2·247 (6)	C(6)···Li···C(6^{ii})	112·9 (3)
Li···C(6^{ii})	2·193 (7)	C(6)···Li···S	66·6 (2)
Li···N	2·157 (7)	C(6^{ii})···Li···S	135·1 (3)
Li···S	2·712 (5)	C(6)···Li···N	129·9 (3)
Li···Li^{ii}	2·455 (9)	C(6^{ii})···Li···N	112·5 (3)
		S···Li···N	94·7 (2)

Symmetry code: (i) $-x, 2-y, -z$; (ii) $1-x, 2-y, -z$.

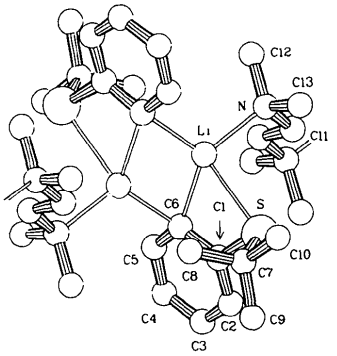

Fig. 1. Perspective view of the dimer with atom numbering. H atoms have been omitted for clarity.

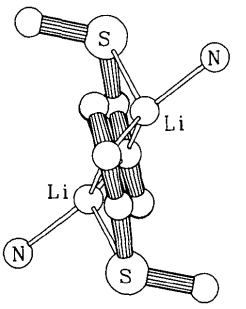

Fig. 2. View of the dimeric unit along the aryl-ring plane showing the tilt of the $C(6)Li_2C(6')$ plane with respect to the aryl planes. (Three C atoms of the *tert*-butyl group and the C atoms of TMEDA are not shown.)

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