tively unstable[39,55] and is consequently converted to the imido ligand by abstraction of a hydrogen atom from the solvent or adventitious water.

Acknowledgment. Support for this research by the National Science Foundation is gratefully appreciated. Special thanks are due to Dr. A. David Rae for helpful advice in the use of his crystallographic program RAELS, to Dr. Bruce R. Adams for valuable technical assistance in obtaining ^{15}N NMR spectra, and to Mr. Karl C. C. Kharas for a helpful discussion on the applications of electron-counting rules to metal clusters.

Registry No. $1 \cdot CH_2Cl_2$, 112068-76-5; **2**·hex, 112043-85-3; $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$, 12132-04-6; $Co(CO)_3NO$, 14096-82-3; Co, 7440-48-4; Mo, 7439-98-7; **1**, 112068-75-4; **2**, 112459-34-4.

Supplementary Material Available: For each of the two metal clusters, $(\eta^5\text{-}C_5Me_5)_3Mo_3Co_2(CO)_8(\mu_3\text{-}NH)(\mu_4\text{-}N) \cdot CH_2Cl_2$ ($1 \cdot CH_2Cl_2$) and $(\eta^5\text{-}C_5Me_5)_2Mo_2Co_3(CO)_{10}(\mu_5\text{-}N) \cdot C_6H_{14}$ (**2**·hex), tables presented with calculated positions for the hydrogen atoms and with thermal parameters for all atoms (5 pages); listings of observed and calculated structure factor amplitudes for $1 \cdot CH_2Cl_2$ and **2**·hex (57 pages). Ordering information is given on any current masthead page.

Structure of 2-Lithiophenyl *tert*-Butyl Thioether in Solution and in the Solid State. Detection of Agostic Li–H Interactions by NMR Spectroscopy

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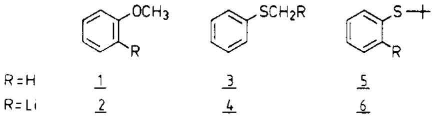
tert-Butyl phenyl thioether (**5**) in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) is deprotonated with *n*-butyllithium (*n*-BuLi) in hexane to give the ortho lithiation product **6**. X-ray analysis shows **6** to be an endless polymer with dimeric centrosymmetric subunits linked by TMEDA acting as a bridging ligand. The lithiated carbon atom tends toward planar tetracoordination. However, a different structure is present in solution. Structural assignments for **6** in tetrahydrofuran (THF) solution are made by one- and two-dimensional NMR spectroscopy. Complete dissociation into monomers is indicated by ^{13}C NMR (signal multiplicities and ^{13}C, ^{6}Li coupling constants). Close Li–H contacts (detected by ^{6}Li–^{1}H 2D heteronuclear Overhauser spectroscopy, HOESY) are observed for the aromatic hydrogen atom vicinal to the Li substituent and for the *tert*-butyl group. However, TMEDA apparently is not bound to lithium in THF solution.

The lithiation of aromatic compounds often is directed to specific positions by neighboring groups.[1] Ortho lithiation is usually observed when heteroatom substituents, e.g., OR, NR_2, and CH_2NR_2, are present.[2] However, different products are obtained for the pair **1** and **3**: whereas anisole **1** gives ortho metalation (**2**) upon treatment with *n*-BuLi,[3] thioanisole **3** is lithiated at the methyl group to give **4**.[4] However, when the aliphatic substituent in **3** is replaced by the *tert*-butyl group (which blocks α-lithiation), ortho metalation takes place. The lithiation of *tert*-butyl phenyl thioether (**5**) with *n*-butyllithium (*n*-BuLi) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) in hexane was reported by Horner and Lawson.[5] We were interested in comparing the structure of the lithiation product **6** in the solid state and in solution, e.g. with regard to differences in geometry and state of aggregation.



Results and Discussion

Crystals of **6** containing TMEDA were obtained in hexane by deprotonation of **5** with *n*-BuLi.[5] However, as determined by ^{1}H NMR spectroscopy (see below) the TMEDA:**6** ratio in the crystals was 0.5 instead of the 1:1

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(3) (a) Glaze, W. H.; Ranade, A. C. *J. Org. Chem.* **1971**, *36*, 3331. (b) The X-ray structure of 2-lithioanisole–0.125-tetramethylethylenediamine has recently been solved: Brandsma, L., et al., to be submitted for publication. This structure is quite remarkable as it consists of tetrameric subunits linked by TMEDA analogous to **7**; the subunits are unusual in that sense that two lithium atoms of the Li_4 tetrahedron are complexed by a methoxy group each; one lithium atom is complexed by *two* OCH_3 groups, whereas the remaining Li atom carries the bridging ligand, TMEDA.

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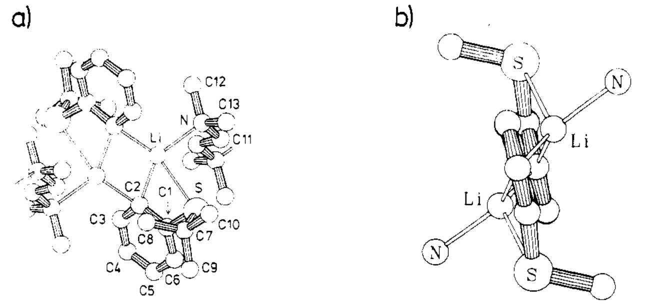
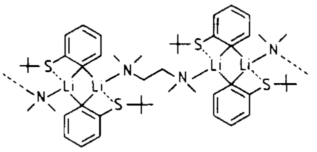


Figure 1. Crystal structure of 2-lithiophenyl *tert*-butyl thioether–0.5-tetramethylethylenediamine (**7**): (a) view perpendicular to the C_2Li_2 plane of the dimeric subunits; (b) view along the phenyl ring planes. For interatomic distances and angles see Table I.

ratio expected if TMEDA was acting as a chelate ligand.

X-ray analysis of the crystals revealed an endless polymer, **7** (Figure 1).[6] Dimeric subunits of 2-lithiophenyl *tert*-butyl thioether with a central C_2Li_2 four-membered ring are linked by TMEDA. Although this is unusual, there are other cases where TMEDA acts as a bridge, e.g., in methyllithium tetramer **8**,[7a] rather than as chelating ligand, e.g., in phenyllithium–TMEDA **9**[7b] and in numerous other examples.[8] Tetracoordination of each Li atom is achieved by additional complexation with sulfur.



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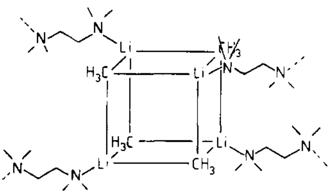

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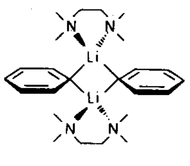

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Each dimeric subunit has a center of inversion at the midpoint of the Li–Li axis, and two dimeric subunits are related to each other by another center of inversion located at the midpoint of the CH_2–CH_2 axis in the TMEDA ligand. A striking feature is the magnitude of the angle between the plane of the central C_2Li_2 ring and the plane of the phenyl rings: whereas in dimeric phenyllithium (**9**) these planes are almost perpendicular,[7b] in **7** the angle is only 47.6° (Figure 1b). Thus promoted by the ortho sulfur substituent, the metalated ring carbon atom shows a tendency toward becoming planar tetracoordinate.[9] This is in agreement with theoretical predictions (MNDO) of our group for the geometry of (2,6-dihydroxyphenyl)lithium (**10**)[10a] and with the crystal structure of bis[(8-(dimethylamino)-1-naphthyl)lithium–diethyl ether] (**11**)[10b] which reveals a similar tendency towards planar tetracoordination of the lithiated carbon atom (interplanar angle 41.3°).

Table I. Interatomic Distances (Å) and Angles (deg) in [2-Lithiophenyl *tert*-Butyl Thioether–0.5-Tetramethylethylenediamine]$_\infty$ (7)

S–C(1)	1.801 (3)	C(2)–C(3)	1.404 (4)
S–C(7)	1.843 (4)	C(7)–C(9)	1.509 (3)
N–C(11)	1.475 (3)	C(7)–C(10)	1.516 (3)
N–C(12)	1.476 (2)	C(7)–C(8)	1.504 (4)
N–C(13)	1.475 (2)	C(11)–C(11i)	1.506 (1)
C(1)–C(2)	1.407 (4)	Li–C(2)	2.247 (6)
C(1)–C(6)	1.389 (4)	Li–C(2ii)	2.193 (7)
C(5)–C(6)	1.381 (5)	Li–N	2.157 (7)
C(4)–C(5)	1.381 (5)	Li–S	2.712 (5)
C(3)–C(4)	1.391 (5)	Li–Li(ii)	2.455 (9)
C(1)–S–C(7)	107.8 (2)	Li(ii)–C(2)–C(1)	137.6 (3)
Li–N–C(11)	107.8 (2)	Li–C(2)–C(3)	143.6 (3)
Li–N–C(12)	113.4 (2)	S–C(7)–C(10)	104.3 (2)
Li–N–C(13)	109.1 (2)	S–C(7)–C(8)	110.9 (2)
C(11)–N–C(12)	111.4 (2)	S–C(7)–C(9)	110.8 (2)
C(11)–N–C(13)	108.1 (2)	C(9)–C(7)–C(10)	109.4 (2)
C(12)–N–C(13)	107.0 (1)	C(8)–C(7)–C(9)	110.4 (2)
S–C(1)–C(6)	117.1 (2)	C(8)–C(7)–C(10)	111.0 (2)
S–C(1)–C(2)	117.6 (2)	N–C(11)–C(11i)	112.1 (1)
C(2)–C(1)–C(6)	125.0 (3)	C(2)–Li–C(2ii)	112.9 (3)
C(1)–C(6)–C(5)	119.6 (3)	C(2)–Li–S	66.6 (2)
C(6)–C(5)–C(4)	118.9 (3)	C(2ii)–Li–S	135.1 (3)
C(3)–C(4)–C(5)	119.5 (3)	C(2)–Li–N	129.9 (3)
C(2)–C(3)–C(4)	125.0 (3)	C(2ii)–Li–N	112.5 (3)
C(1)–C(2)–C(3)	112.0 (3)	S–Li–N	94.7 (2)
Li–C(2)–Li(ii)	67.1 (2)		
Li(ii)–C(2)–C(3)	98.1 (3)		
Li–C(2)–C(1)	99.6 (2)		

Table II. ¹H Chemical Shifts (δ, Diagonal) and Coupling Constants (Hz, Off-Diagonal) of 6•0.5TMEDA in THF-d_8 at 0 °C

H3	H4	H5	H6	$C(CH_3)_3$	TMEDA CH_2	TMEDA CH_3
7.74	6.5	1.5				
	6.75	7.5	1.2			
		6.68	7.5			
			7.2			
				1.27		
					2.17	
						2.31

In the planar phenyl ring of **7** the C1–C2 and C2–C3 bonds are longer than the remaining carbon–carbon bonds. The C1–C2–C3 angle is small (112.0°) whereas the "adjacent" angles C2–C3–C4 and C2–C1–C6 are large (both 125.0°). This behavior also was found in dimeric phenyllithium **9**.[6]

NMR Studies. For NMR analysis of **6** (carried out prior to the X-ray analysis), crystals of **6**·0.5TMEDA prepared with 96% ^6Li were dissolved in THF-d_8. The stoichiometry of **6**:TMEDA is determined by integration of the ¹H NMR signals. As was observed for 1-lithionaphthalene (**12**),[11a] for 2-lithio-*N*-phenylpyrrole (**13**),[11b] and for several other lithiated aromatic compounds,[11c] the ¹H NMR signals of the vicinal proton H3 in **6** appears

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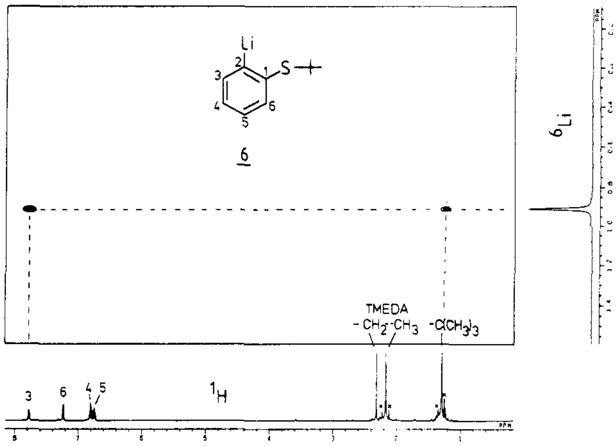
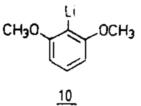


Figure 2. ^{6}Li–^{1}H 2D HOESY of 6·0.5TMEDA: contour plot; THF-d_8; +23 °C; mixing time[11a,b,19] 2.4 s; dissolved crystals of 6·0.5TMEDA enriched with 96% ^{6}Li; the asterisk indicates spinning sidebands due to recording of the one-dimensional ^{1}H spectrum on a broad-band probe.

shifted downfield ($\Delta\delta$ = 0.25 ppm) relative to the ortho protons in the starting material, **5**. This can be explained by the electric field produced by Li.[12] The assignment of the other three ^{1}H resonances can be made easily by analyzing the expanded one-dimensional spectrum (cf. Figure 3). The ^{1}H chemical shifts and coupling constants of **6** are shown in Table II.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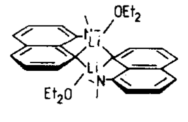
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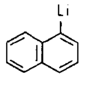
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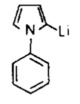
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As with 1-lithionaphthalene (**12**), the vicinal coupling constant $^3J_{H3,H4}$ in **6** is smaller than that between both H4,H5 and H5,H6. This is due to the reduced π-bond order. Indeed, the X-ray data shows an increased C2C3 bond length.[13] Another striking feature in the ^{1}H NMR spectrum of **6** is the downfield shift ($\Delta\delta$ = 0.03 ppm) of the *tert*-butyl resonances as compared to those in **5**.[14] This downfield shift, also due to the electric field of Li, indicates the spatial proximity between Li and the *tert*-butyl hydrogen atoms in solution. Close lithium–hydrogen contacts ("agostic interactions"[15]) have been recognized in the crystal state, e.g. in [Li(Mn(N(SiMe$_3$)$_2$)(OC-*t*-Bu$_3$)$_2$)][16] and in lithium tetrakis((di-*tert*-butylmethylene)amino)aluminate.[17] In solution, we have observed such contacts by means of ^{6}Li–^{1}H 2D heteronuclear Overhauser spectroscopy (HOESY).[11a,b,18] This NMR technique allows short ^{6}Li–^{1}H distances (<ca. 3.5 Å) to be detected due to dipolar relaxation between the nearby nuclei. Figure 2 shows the ^{6}Li–^{1}H 2D HOESY experiment applied to 6·0.5TMEDA.

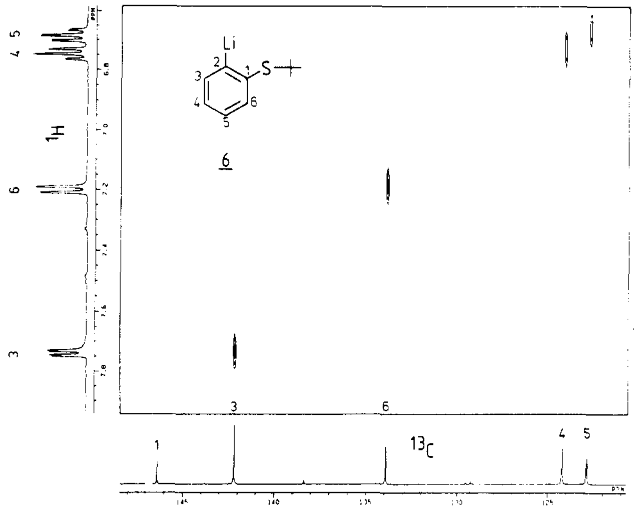


Figure 3. ^{13}C–^{1}H shift correlated spectrum of **6**: dissolved crystals; THF-d_8; 0 °C; only the relevant part of the ring atom resonances is depicted.

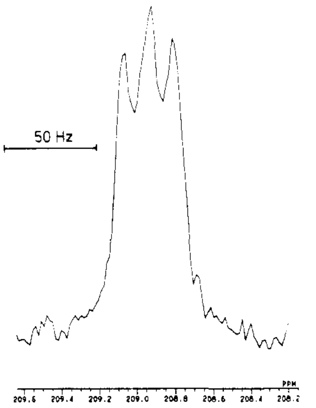
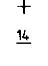


Figure 4. ^{13}C NMR signal of C2 in 6·0.5TMEDA: 96% enriched with ^{6}Li; crystals dissolved in THF-d_8; −101 °C.

Table III. ^{13}C Chemical Shifts (δ_{TMS}) of 6 and 5:[14] 6•0.5TMEDA Crystals Dissolved in THF-d_8 at −101 °C

C	5	6
1	138.8	145.8
2	129.6	208.9
3	130.0	142.4
4	132.7	129.5
5	130.0	123.7
6	129.6	134.7
7	46.0	43.7
8–10	30.7	31.5
TMEDA CH$_2$		58.3
TMEDA CH$_3$		46.6

As was expected from the chemical shift differences and from the X-ray analysis, an intense cross peak between ^{6}Li and H3 and a weaker cross peak between ^{6}Li and the *tert*-butyl ^{1}H resonance is found. This demonstrates close contacts between these nuclei. However, a cross peak between ^{6}Li and the TMEDA CH$_3$ resonances is missing. This suggests that TMEDA is *not* attached to Li under these conditions (THF solution, room temperature). This conclusion is in accord with observations made for TMEDA-containing THF solutions of *tert*-butyllithium and of "supermesityllithium" (**14**). In both cases TMEDA–Li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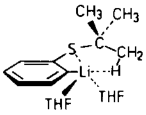
interactions were unimportant.[20] The ^{13}C NMR signals of **6** are assigned unambiguously by means of $^{13}C-^{1}H$ shift correlation spectroscopy (Figure 3). The ^{13}C chemical shifts of **6** and the educt **5**[14] are summarized in Table III. Due to reduced π-electron density, the signal of the metalated carbon atom in **6** is shifted strongly downfield and appears at 208.9 ppm. This behavior is found for other lithiated aromatic compounds.[11a,b,20,21] At low temperatures with a ^{6}Li-enriched sample, this carbon signal is split into a 1:1:1 triplet (J = 13.0 Hz, Figure 4). This indicates coupling of ^{13}C to only *one* ^{6}Li nucleus (spin $I = 1$).

Hence, the geometry of **6** in THF solution cannot be similar to that found in the solid state (**7**), where carbon is bonded to *two* lithium atoms. In that case, a ^{6}Li-enriched sample should show a 1:2:3:2:1 quintet for the C2 signal. Instead, a species with intramolecular sulfur coordination and two additional THF ligands as in **15** seems likely under these measuring conditions, as only a monomer is visible by NMR at low temperatures.



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Hence, as found by cryoscopic investigations of other lithio organic species for which X-ray structures are available,[22] the crystal and THF solution compositions of **6** differ. The magnitudes of $^{13}C,^{6}Li$ coupling constants in lithioorganic compounds have been found to be rather constant within a given state of aggregation and are largely independent of carbon hybridization.[20] The general equations (1) and (2) are satisfied for a large number of literature values for $J_{^{13}C,^{6,7}Li}$ (n = number of lithium atoms directly bonded to carbon in terms of the NMR time scale).

$$J_{^{13}C,^{6}Li} = 1/n(17 \pm 2)\ \text{Hz} \qquad (1)$$

$$J_{^{13}C,^{7}Li} = 1/n(45 \pm 5)\ \text{Hz} \qquad (2)$$

Monomeric aryllithium compounds studied so far show values of $J_{^{13}C,^{6}Li}$ ranging from 15.3 to 16.1 Hz.[20] The significantly lower value of 13.0 Hz found for **6** in THF is apparently due to the geminal heteroatom substitution of the lithiated carbon atom.

Experimental Section

Crystals were obtained[5] by reacting *tert*-butyl phenyl thioether (**5**) in hexane at 40–50 °C with 1 equiv of butyllithium in the presence of 2 equiv of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and subsequent cooling to room temperature: rod-shaped, yellowish crystal, 0.2 × 0.3 × 1.0 mm.

$[Li(C_{10}H_{13}S)]_2[(C_6H_{16}N_2)]$: M_r 460.64: triclinic: $P\bar{1}$, a = 7.832 (3) Å, b = 9.419 (1) Å, 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_{calcd} = 1.075 g·cm^{-3}, λ(Cu Kα) = 1.54184 Å, μ = 17.23 cm^{-1}, T = 295 K, $F(000)$ = 250, R = 0.055 for 2025 observed reflections; 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°; ω = (0.80 + 0.15 tan θ)°; Ni-filtered Cu Kα radiation; one-half of the reflection sphere, index range $0 \leq h \leq 9$, $-11 \leq k \leq 11$, $-13 \leq l \leq 13$; 2700 reflections measured, 2025 considered observed [$I > 2.50\sigma(I)$]; two standard reflections (1,-1,-1, rmsd 0.58%; 1,-1,-2, rmsd 0.48%), measured every 50 reflections; corrections for Lorentz polarization effects and linear decay (4.5%). The structure was solved by direct methods (SHELXS 86; SHELX 76 refinement). An absorption correction following the DIFABS procedure was applied on isotropically refined data, minimum and maximum 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 refinements on F, function minimized $\sum w(|F_o|^2 - |F_c|^2)$, with 37 atoms and 146 parameters converged to $R(F)$[24] = 0.055 and $R(wF)$[24] = 0.047 with $w = 1/\sigma^2(F)$ and S = 0.53. The overall temperature factor of the H atoms refined to 0.11 Å^2. The average shift to error ratio (Δ/σ) is <0.001. Maximum and minimum electron densities 0.23 and 0.33 e A^{-3}, respectively. Calculations were performed on the CYBER 180-855 of the University of Utrecht.[25]

NMR spectra were recorded on a JEOL GX 400 spectrometer under conditions described previously.[11a] Chemical shifts are reported in δ values downfield from TMS and are based on the solvent (THF-d_8) signals: ^1H, 3.58 ppm; ^{13}C, 67.4 ppm. ^6Li shifts are relative to 1 M LiBr in THF at room temperature. THF-d_8 (Aldrich) was dried over Na/Pb alloy. Selected parameters of the $^6Li-^1H$ 2D HOESY are as follows: sequence,[19] 5-mm tube, 10-mm broad-band probe, pulse widths,[11a] 0.5 mL of THF-d_8, +23 °C, dissolved crystals of **6**·0.5TMEDA, 96% ^6Li enrichment, ca. 30 mg, spectral widths 100 Hz (f_2) and 3197 Hz (f_1), 512 data points in t_2, 64 increments in t_1 with 16 scans per increment, zero filling to 128 data points, pulse delay 7.7 s, mixing time 2.4 s, exponential line broadening in t_2 (BF 0.4), Lorentzian to Gaussian transformation in t_1 (CBF-60, CGF 60). The CH shift correlated spectrum was recorded under standard conditions,[23] using Lorentzian to Gaussian transformation in both dimensions.

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(24) $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(wF) = [\{\sum[w(|F_o| - |F_c|)^2]/\sum[wF_o^2]\}]^{1/2}$ and $S = [\{\sum[w(|F_o| - |F_c|)^2]/(m - n)\}]^{1/2}$.

(25) Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms, and bond lengths, bond angles, and torsion angles have been deposited British Library Document Supply Centre as Supplementary Publication No. SUP 43918 (18 pages). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH12HU, England.