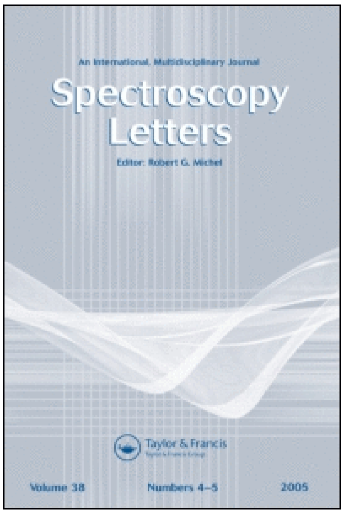

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Crystal Structures of Tetrakis-(4-chlorophenylthio)-butatriene and Tetrakis-(*tert*-butylthio)-butatriene

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Abstract: Tetrakis-(4-chlorophenylthio)-butatriene (**3a**) and tetrakis-(*tert*-butylthio)-butatriene (**3b**) were synthesized, and their crystal structures were determined. The compound **3a** is monoclinic, space group $P2_1/c$, $a = 6.9785(8)$, $b = 8.6803(9)$, $c = 22.884(2)$ Å, $\beta = 93.887(6)^o$, $V = 1383.0(3)$ Å^3, $Z = 2$. The compound **3b** is monoclinic, space group $P2_1/n$, $a = 11.0615(6)$, $b = 10.8507(4)$, $c = 11.2717(6)$ Å, $\beta = 116.427(2)^o$, $V = 1211.5(1)$ Å^3, $Z = 4$. The title compounds **3a** and **3b** reside on an inversion center so that only half of the molecule is crystallographically unique. Both compounds are not planar. The crystal structures of **3a** and **3b** have cumulated double bonds. The C7–C8–C8^i and C5–C6–C6^i angles that show the linearity in both structures, respectively, are $176.4(3)^\circ$ in **3a** and $175.6(2)^\circ$ in **3b**.

Keywords: Butatriene compounds, crystal structure, cumulated double bonds, linear configuration

INTRODUCTION

Compounds with cumulated double bonds, such as allene or ketene, are fairly reactive because of their strained structures; thus, effective synthesis of these compounds is still challenging in organic chemistry. Construction of three cumulated carbon–carbon double bonds is a more difficult problem, and the effective synthetic methods of butatrienes are still very rare.[1] In addition,

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1,2,3-butatrienes have long attracted organometallic chemists because of their highly unsaturated structure. Several investigations of the coordinated butatrienes on metal complexes have been described, and some of their reactions were reported.[2–6]

Tetrakis- and tris- (aryl and alkyl thio) diene compounds synthesized from polihalodienes and thiols have previously been reported.[7–11] S-, N,S-, and S,S-substituted 1,3-diene compounds have been synthesized extensively.[7–11] However, there are only a few reports on the 1,1,4,4-tetra-S-substituted butatriene compounds.[12,13] It is known that this type of compound shows isomerism in the presence of alkaline. The *tert*-butylthio substituted butatriene **3b** reacts with iodine, bromine, and hydrobromic acid to the thiophene derivatives respectively, under elimination of 1 mole of isobutene.[12,13] With the aim of gaining a deep insight into the structural aspect in the solid state, crystallographic analyses of the tetrakis-(4-chlorophenylthio)-butatriene **3a** and tetrakis-(*tert*-butylthio)-butatriene **3b** compounds were carried out, and the results are presented in this paper.

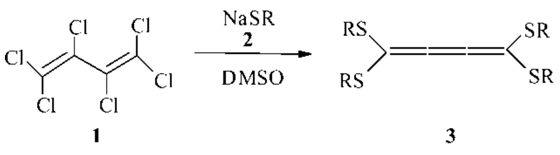
MATERIALS AND METHODS

Preparation

Tetrakis-(4-chlorophenylthio)-butatriene **3a** and tetrakis-(*tert*-butylthio)-butatriene **3b** compounds were prepared according to a method reported earlier[13] (Fig. 1).

3a; Suspension of sodium-*p*-chlorobenzenethiolate **2a** (6.0 g, 36 mmol) in DMSO (45 ml) was added dropwise to solution of hexachlorobutadiene **1** (2 g, 7.7 mmol) in DMSO (5 ml), and then the reaction mixture was stirred and extracted with benzene, organic layer was washed with distilled water and dried with $MgSO_4$.

3b; Suspension of sodium-2-methyl-2-propanthiolate **2b** (6.0 g, 53.7 mmol) in DMSO (45 ml) was added dropwise to solution of hexachlorobutadiene **1**



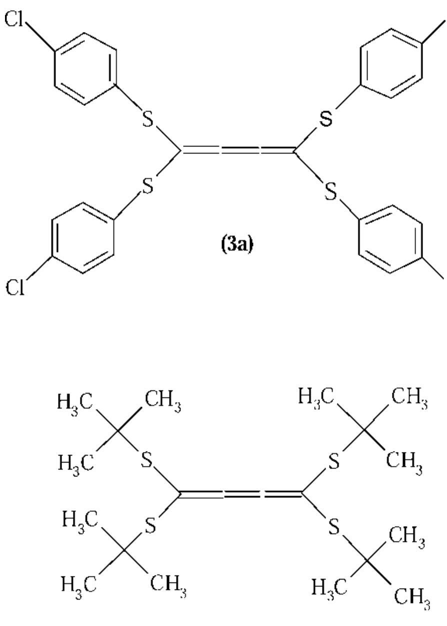
2, 3	R
a	p-Cl-C_6H_4-
b	(CH_3)C-

Figure 1. Synthesis schema of **3a** and **3b**.

(2 g, 7.7 mmol) in DMSO (5 ml), and then the reaction mixture was stirred and extracted with benzene, organic layer was washed with distilled water and dried with $MgSO_4$.

All chemicals and solvents were obtained commercially and used without purification. TLC was performed on precoated aluminum plates (Silicagel 60 $F_{254,}$ Merck-Merck KGaA, Darmstadt, Germany). The structures of **3a** and **3b** (Fig. 2) were determinated by microanalysis and spectroscopic data. Melting points were measured on a Buchi B-540 melting point apparatus (BÜCHI Labortechnik, AG, Switzerland) and uncorrected. Elemental analyses were performed by Carlo Erba 1106 Elemental analyzer (Strada Rivoltana 20090, Milano, Italy). Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Shimadzu FTIR-8101 spectrometer (Shimadzu Corporation Analytical Instruments). Ultraviolet (UV) spectra were recorded on a Beckman DB-GT spectrometry (Beckman Coulter, Inc., 4300 N. Harbor Boulevard, P.O. Box 3100, Fullerton, CA 92834-3100 USA). ^1H and ^{13}C NMR spectra were recorded on Varian^{UNITY} INOVA (Yarian AG NMR Systems Choilerstrasse, 38 Postfach CH-6303 Zug.-Switzerland) operating at 500 MHz.

3a; Yield 66% (0.8 g) m.p. = 161–162.5°C (EtOH). IR (KBr): $\nu = 3050$ (C–H), 1555 (C=C); (Benzene): 2032 cm^{-1}(C=C=C). ^1H-NMR (DMSO): $\delta = 7.35$ (AA'BB' system, 8H, J = 8.3 Hz, CH_{arom}), 7.40 (AA'BB' system, 8H, J = 8.8 Hz, CH_{arom}). UV (*n*-Heptane): λ_{max} 195 (l g ε 4.88), 224



(3a)

(3b)

Figure 2. The chemical diagrams of **3a** and **3b**.

(4.59), 401 nm (4.31). ^{13}C-NMR (CDCl$_3$): 149.9 ($>C{=}\mathbf{C}{=}\mathbf{C}{=}C<$), 110.0 ($>\mathbf{C}{=}C{=}C{=}\mathbf{C}<$), 133.9, 132.7, 130.0, 128.3 (Ar-**C**). $C_{28}H_{16}Cl_4S_4$ (622.6): calcd. C 54.03, H 2.59, Cl 22.78, S 20.60; found C 54.08, H 2.67, Cl 22.73, S 20.58.

3b; Yield 71% (2.2 g) m.p. = 170–171°C (EtOH). IR (KBr): $\nu = 2900$ (C–H), 1550 (C=C); (Benzene): 2022 cm^{-1}(C=C=C). ^{1}H-NMR (CDCl$_3$): $\delta = 1.44$ (s, 36H,–C–C**H**$_3$). UV (*n*-Heptane): $\lambda_{\max}$ 205 (1 g ε 4.53), 233 (4.22), 314 (3.91), 392 nm (4.54). ^{13}C-NMR (CDCl$_3$): 155.1 ($>{=}\mathbf{C}{=}\mathbf{C}{=}C<$), 107.7 ($>\mathbf{C}{=}C{=}C{=}\mathbf{C}<$), 49.5 (–**C**–CH$_3$), 31.0 (–C–**C**H$_3$). $C_{20}H_{36}S_4$ (404.8): calcd. C 59.35, H 8.97, S 31.69; found C 59.18, H 8.86, S 31.58.

Spectroscopic analysis of **3a** and **3b** are found to be in good agreement with the relevant literature.[12]

X-Ray Structure Determination

Crystals of **3a** and **3b** were mounted on an Rigaku R-AXIS Rapid-S diffractometer with a graphite monochromatized MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å).

Table 1. Crystallographic data and structure refinement for **3a** and **3b**

	3a	3b
Sum formula	$C_{28}H_{16}Cl_4S_4$	$C_{20}H_{36}S_4$
f_w (g mol^{-1})	622.49	404.76
Crystal system	Monoclinic	Monoclinic
Space group	P2$_1$/c	P2$_1$/n
a (Å)	6.9785(8)	11.0615(6)
b (Å)	8.6803(9)	10.8507(4)
c (Å)	22.884(2)	11.2717(6)
α (°)	90.00	90.00
β (°)	93.887(6)	116.427(12)
γ (°)	90.00	90.00
Vol [Å^3]	1383.0(3)	1211.51(10)
Z	2	4
D_{calc} (g cm^{-3})	1.495	2.219
μ (cm^{-1})	7.47	7.86
F(000)	632.00	880.00
Index ranges, h, k, l	0/8	−13/13
	0/10	−12/12
	−27/27	−13/13
Reflections collected	5356	25978
Independent reflections	2678 [*R*(int) = 0.021]	2267 [*R*(int) = 0.013]
Data/restraints/parameters	1889/0/171	2009/0/127
Goodness-of-fit on F^2	1.189	1.149
Final *R* indices [I > 2σ (I)]	$R = 0.023$, $wR = 0.094$	$R = 0.033$, $wR = 0.081$
Largest diff. peak and hole	0.51 and −0.43 e. Å^{-3}	0.34 and −0.43 e. Å^{-3}

Experimental conditions of **3a** and **3b** are summarized in Table 1. The structures were solved by SIR 92 [14] and refined with CRYSTALS.[15] The positions of the H atoms bonded to C atoms were calculated (C–H distance 0.96 Å), and refined using a riding model. The H atom displacement parameters were restricted to be $1.2U_{eq}$ of the parent atom. All calculations were performed using the crystallographic software package.[16] Selected bond distances and bond angles for **3a** and **3b** are listed in Tables 2 and 3. ORTEP-III views of the molecular structures of **3a** and **3b** are given in Figs. 3 and 4[17] and crystal packing diagrams in Figs. 5 and 6.[18] Crystallographic data (excluding structures factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-246711 for **3a** and CCDC-251072 for **3b**.[19]

RESULTS AND DISCUSSION

In the solid state, the compound **3a** resides on an inversion center so that only half of the molecule is crystallographically unique. Compound **3a** is

Table 2. Selected bond lengths [Å] and angles [°] with electrostatic discharge in parentheses for **3a**

Cl 2–C12	1.736(3)	Cl1–C3	1.741(3)
S2–C9	1.782(3)	S2–C7	1.747(3)
S1–C6	1.791(3)	S1–C7	1.768(3)
C1–C2	1.384(4)	C1–C6	1.381(4)
C2–C3	1.372(4)	C9–C14	1.380(4)
C9–C10	1.389(4)	C8–C7	1.324(4)
C12–C13	1.388(4)	C11–C12	1.367(5)
C6–C5	1.372(4)	C13–C14	1.377(4)
C11–C10	1.356(5)	C3–C4	1.361(5)
C5–C4	1.379(4)	C8–C8^{i}	1.260(3)
C9–S2–C7	103.0(1)	C6–S1–C7	102.8(1)
C2–C1–C6	119.0(3)	C3–C2–C1	119.7(3)
C14–C9–C10	119.5(3)	C14–C9–S2	121.0(2)
C10–C9–S2	119.5(2)	C7–C8–C8^{i}	176.7(3)
C13–C12–C11	122.2(3)	C13–C12–Cl2	118.3(3)
C11–C12–Cl 2	119.5(2)	C5–C6–S1	115.4(2)
C5–C6–C1	120.8(3)	S1–C6–C1	123.7(2)
C14–C13–C12	117.4(3)	C9–C14–C13	121.0(3)
C14–C13–C9	119.5(3)	C9–C10–Cl1	120.2(3)
S2–C7–S1	112.6(1)	S2–C7–C8	125.3(2)
S1–C7–C8	122.0(2)	C4–C3–C11	120.8(2)
C4–C3–C2	121.1(3)	Cl1–C3–C2	118.1(2)
C4–C5–C6	119.5(3)	C3–C4–C5	119.9(3)

(i) $+1 + x,\ 1/2 + 1 - y,\ 1/2 - 1 + z$.

Table 3. Selected bond lengths [Å] and angles [°] with electrostatic discharge in parentheses for **3b**

S1–C5	1.770(3)	C7–C8	1.531(3)
S1–C1	1.852(3)	C7–C9	1.514(4)
S2–C5	1.756(2)	C1–C3	1.527(3)
S2–C7	1.834(3)	C1–C4	1.519(4)
C5–C6	1.317(3)	C1–C2	1.510(5)
C7–C10	1.505(4)	C6–C6$^{\text{i}}$	1.260(3)
C5–S1–C1	105.7(1)	C9–C7–S2	111.4(2)
C5–S2–C7	108.9(1)	C4–C1–C3	108.7(2)
C6–C5–S1	118.7(2)	C4–C1–C2	110.0(3)
C6–C5–S2	127.9(2)	C4–C1–S1	111.6(2)
S1–C5–S2	113.3(1)	C3–C1–C2	112.0(2)
C6–C6$^{\text{i}}$–C5	175.6(2)	C3–C1–S1	110.6(2)
C10–C7–S2	110.7(2)	C2–C1–S1	103.9(2)
C8–C7–C9	109.7(2)		
C8–C7–S2	102.5(2)		

(i) $+1+x$, $1/2+1-y$, $1/2-1+z$.

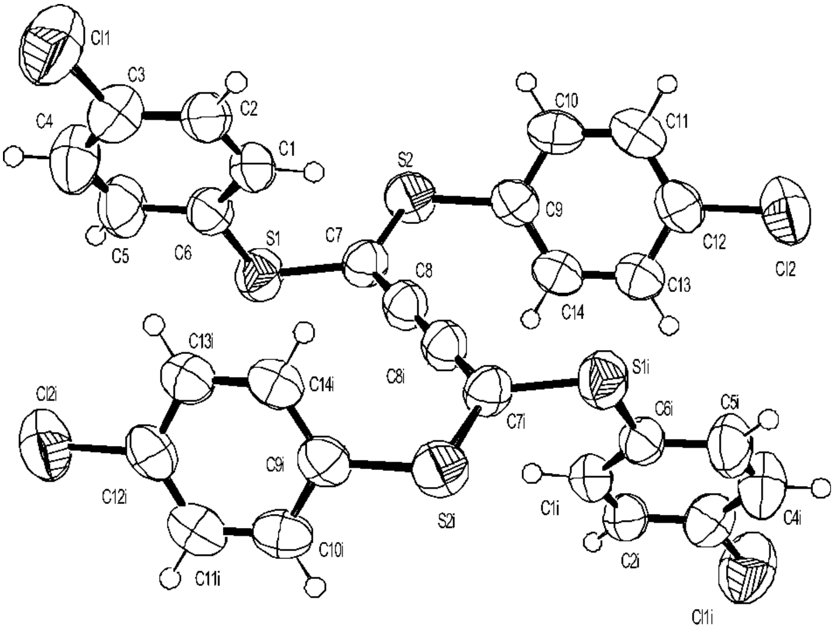


Figure 3. The molecular structure of compound **3a**. Displacement ellipsoids are plotted at the 50% probability level (symmetry transformations used to generate equivalent atoms: (i) x, $0.5-y$, $z+0.5$).

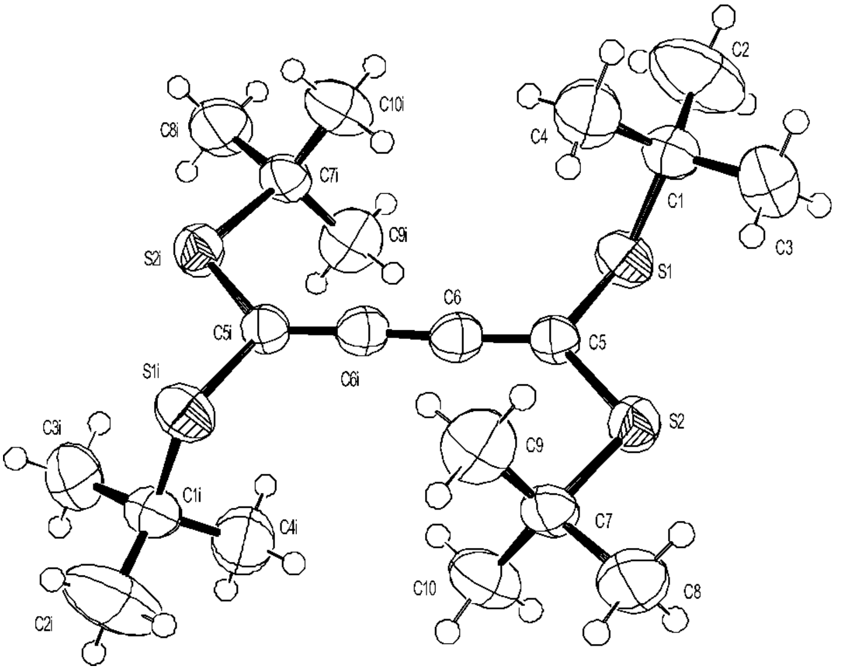


Figure 4. The molecular structure of compound **3b**. Displacement ellipsoids are plotted at the 50% probability level (symmetry transformations used to generate equivalent atoms: (i) $x + 0.5$, $0.5 - y$, $z + 0.5$).

cumulated butatriene with two sp^2 and two sp carbon atoms and substituted four chlorophenylthio rings. The phenylchloro rings are planar with a maximum deviation of 0.020(4) Å. The planar phenylchloro groups are inclined at an angle of 41.2(1)°. The cumulated double bonds lengths are C7–C8 [1.324(4) Å] and C8–C8^i [1.260(3) Å]. The third double bond C8^i–C7^i is equivalent to C7–C8 by crystallographic symmetry. The outer cumulated double bond length that indicated C_{sp2}–C_{sp} hybridization, C7–C8 is 1.324(4) Å, and this observed bond length is longer than the corresponding bond length 1.309 Å in butatriene compound that has been determined earlier.[20] Electronegative and resonance effect of p-Cl-C_6H_4-S groups lead to a longer double bond length. The shorter bond length of inner carbon atoms confirms the idea of sp hybridization. The shorter bond length, C8–C8^i, is attributed to the higher s-character for the central bond. The average C–S bond length is 1.757(3) Å, respectively. Spectroscopic analysis of **3a** supported this structure.

The compound **3b** also resides on an inversion center so that only half of the molecule is crystallographically unique. Compound **3b** is cumulated butatriene with two sp^2 and two sp carbon atoms and substituted four *tert*-butylthio groups. The most interesting conformational feature is the significant twist of A (C1, C2, C3, C4, S1) relative to B (C7, C8, C9,

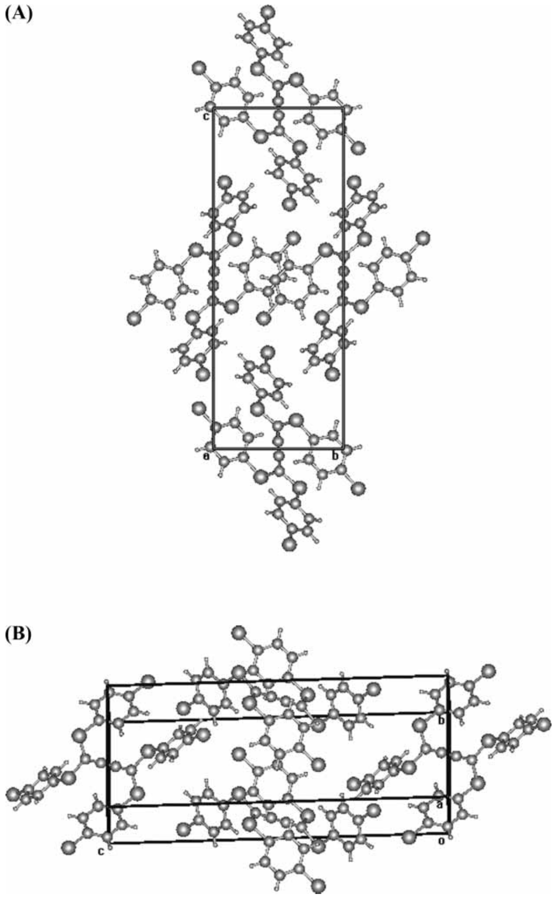


Figure 5. Unit cell packing diagram for compound **3a**; molecular overlap view from the a-axis (A) and from the LS plane (B).

C10, S2). The orientation of A with respect to B is defined by the torsion angles between them [C1–S1–C5–S2 = 78.87(9)° and C7–S2–C5–S1 = −80.1(1)°]. The central C6–C6^{i} distance [1.260(3) Å] is slightly longer than the typical carbon–carbon triple bond length (1.20 Å), whereas the outer C6–C5 [1.317(3) Å] and C6^{i}–C5^{i} [1.307(3) Å] are slightly shorter than double-bond length (1.34 Å), respectively. Owing to inductive and hyperconjugation effect of *tert*-butylthio groups, the average double-bond length C_{sp2}–C_{sp} [1.312(3) Å] is slightly longer than the corresponding bond length 1.309 Å in butatriene.[20] The average C–S bond length is 1.763(3) Å, respectively. Both the observed C–S bonds in **3a** and **3b** are consistent with the corresponding value in the similar compound.[21] X-ray diffraction analysis of **3b** is found to be in good agreement with the spectroscopic

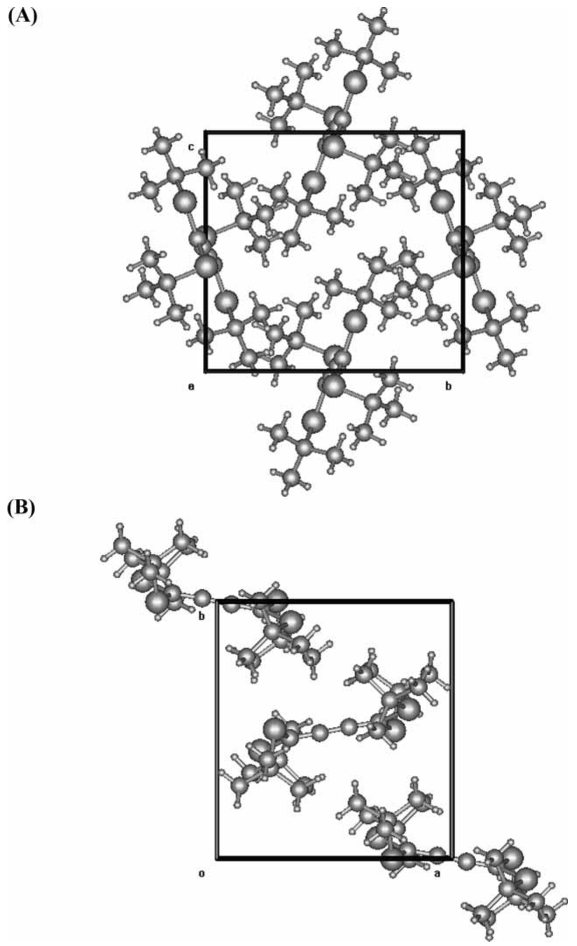


Figure 6. Unit cell packing diagram for compound **3b**; molecular overlap view from the a-axis (A) and from the c-axis (B).

analysis. In this study, the C7–C8–C8^{i} [symmetry code: (i) x, $0.5-y$, $z+0.5$] and C5–C6–C6^{i} [symmetry code: (i) $x+0.5$, $0.5-y$, $z+0.5$] angles that show the linearity in both structures, respectively, are 176.4(3)° in **3a** and 175.6(2)° in **3b**.

Experimental results have shown that outer cumulated bond lengths were affected by the substituents in both compounds.

The molecule packing diagrams for compounds **3a** and **3b** are shown in Figs. 5 and 6 as a projection along a-axis (A) and LC Plane (B) for **3a** and a-axis (A) and c-axis (B) for **3b**. The common motif is the typical herringbone arrangement in both compounds.[22] Compound **3a** displays a crystal packing similar to that of 1,1,4,4-tetrafluorobutatriene.[23] In compound **3a**, each **3a** molecule is held together in ways by Cl … Cl interactions. [Cl1 … Cl2$^{\mathrm{i}}$ 3.426(1) Å and Cl2 … Cl1$^{\mathrm{iii}}$ 3.426(1) Å, symmery code: (i) $+1+x$, $1/2+1-y$, $1/2-1+z$, (iii) $-1+x$, $1/2+1-y$, $1/2+z$].

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