Synthesis and Characterization Tricyanovinyl-Capped Oligothiophenes as Low Band-Gap Organic Materials

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Supporting Information

General Considerations. Synthetic procedures were carried out under an inert atmosphere of Argon unless stated otherwise. Tetrahydrofuran and dichloromethane were distilled from Na/benzophenone and phosphorous pentoxide respectively under a nitrogen atmosphere. Solvents for the solvatochromic studies were not dried and were used as received. 3′,4′-Dibutyl-2,2′:5′,2″-terthiophene **1** was synthesized similar to a previously reported method[1] with the exception that Ni(dppp)Cl_2 (Strem Chemicals Inc.) was used as the catalyst. The synthesis of 3',4',3"",4""-tetrabutyl-2,2':5',2":5",2"':5"',2"":5"",2""'-sexithiophene **2** has been described previously.[2] Fe(acac)$_3$ (Strem Chemicals Inc.) and tetracyanoethylene (Aldrich) were purchased and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR-300 or VXR-500 MHz instrument. The chemical shifts are reported in ppm and referenced to the residual chloroform peak (7.26 ppm) or dichloromethane peak (5.32 ppm). Mass spectra were obtained on a VG 7070E-HF or Finnigan MAT 95 mass spectrometer. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ.

3',4'-Dibutyl-2,2':5',2''-terthiophene (1). To a dried 250 mL 3 neck flask equipped with a condenser, addition funnel, and Ar inlet was added freshly ground Mg turnings (4.53 g, 0.186 mol) and 50 mL diethyl ether. To the addition funnel was added 10 mL diethyl ether and 2-bromothiophene (24.3 g, 0.149 mol). The 2-bromothiophene solution was slowly added to the magnesium/diethyl ether suspension over 40 minutes while maintaining a gentle reflux. The Grignard was refluxed for an additional hour. Meanwhile, a dry 500 mL 3 neck flask (equipped with a condenser, Ar inlet, and addition funnel) was charged with Ni(dppp)Cl_2 (0.25 g, 0.461 mmol), 2,5-dibromo-3,4-dibutylthiophene, and 100 mL diethyl ether. After cooling the Grignard

to room temperature, it was cannulated into the addition funnel of the second setup. The Grignard was added dropwise slowly at room temperature, allowed to stabilize, and heated to reflux for 3.5 days. The resulting black suspension was cooled to 0 °C and 60 mL of 2M HCl was added slowly with caution. The layers were separated and the aqueous layer was extracted with diethyl ether (4 x 25 mL). The organic fractions were combined, washed with $NaHCO_3$ solution, dried with $MgSO_4$, and concentrated. The crude product was purified by silica gel flash chromatography (100 % hexanes) to yield 12.5 g (93%) of **2** as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): 7.32 (dd, 2H, $J_{5,3}$=1.5 Hz, $J_{5,4}$=5.3Hz), 7.17 (dd, 2H, $J_{3,5}$=1.5 Hz, $J_{3,4}$=3.8 Hz), 7.09 (dd, 2H, $J_{4,3}$=3.8 Hz, $J_{4,5}$=5.3Hz), 2.75 (t, 4H), 1.59 (m, 4H), 1.47 (m, 4H), 0.99 (t, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): 139.97, 136.18, 129.80, 127.29, 125.79, 125.22, 32.90, 27.79, 22.98, 13.85.

Oligomer 3. To a dry 100 mL Schlenk flask containing 1 (0.923 g, 2.56 mmol) and 15 mL of THF was added *n*-butyllithium (2.15 mL, 5.38 mmol) at -78 °C over 30 min. The reaction mixture was warmed to 0 °C and allowed to stir for 0.5 h, resulting in the formation of a yellow precipitate. The suspension was then cooled back to -78 °C, and tetracyanoethylene (0.803 g, 6.27 mmol) was added in one portion, resulting in an immediate color change (yellow to dark green). After 20 min, the reaction mixture was allowed to warm to room temperature and the THF was subsequently removed by rotary evaporation. The crude solid was dissolved in dichloromethane (10 mL) followed by the addition of 10 mL of water. The dichloromethane was removed by rotary evaporation and the crude solid was filtered and washed with water (3 x 5 mL). The crude solid was dissolved in acetone (100 mL) and neutral alumina was added to the solution. The suspension was filtered over diatoms and the acetone filtrates were concentrated. The resulting solid was dissolved in dichloromethane (50 mL) and filtered over diatoms. The dichloromethane soluble filtrates were concentrated and the solid was suspended in hexanes and washed with hexanes (3 x 5 mL) to provide 0.602 g (41.8 %) of **3** as a dark olive-green solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.07 (d, 2H, J = 4.5 Hz), 7.47 (d, 2H, J = 4.5 Hz), 2.87 (t, 4H), 1.55

(m, 8H), 0.99 (t, 6H). HREIMS cald 562.1068, found 562.1053 (M^+). Anal. Calcd for $C_{30}H_{22}N_6S_3$: C, 64.03; H, 3.94. Found: C, 63.82; H, 3.75.

Oligomer 4. Compound **4** was prepared from 0.302 g (0.420 mmol) of **2**, *n*-butyllithium (0.35 mL, 0.88 mmol), and tetracyanoethylene (0.132 g, 1.03 mmol) using the general procedure described for the synthesis of 3. After addition of the TCNE, the solution was allowed to warm to room temperature and 10 mL of water was added. The THF was removed by rotary evaporation and the crude solid was filtered and washed with water (3 x 5 mL). The crude solid was purified as follows: 127 mg of the solid was placed in a 250 mL rbf and stirred in 100 mL of dichloromethane for 50 min. The suspension was filtered over diatoms and the dichloromethane soluble filtrates were concentrated to dryness. The resulting solid was suspended in acetone and washed with acetone (3 x 5 mL) to provide 70 mg of a dark purple solid (39.5% yield based on initial purified crude solid). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.03 (d, 2H, J = 4.5 Hz), 7.41 (d, 2H, J = 4.2 Hz), 7.26 (d, 2H, J = 3.6 Hz), 7.23 (d, 2H, J = 3.9 Hz), 2.84 (m, 8H), 1.54 (m, 16H), 1.00 (m, 12H). FABMS cald 921.2, found 921.1 ($M+H^+$). Anal. Calcd for $C_{50}H_{44}N_6S_6$: C, 65.18; H, 4.81. Found: C, 64.94; H, 4.57.

Absorption Measurements. The UV-Vis-NIR solution spectra (230-1000 nm) were recorded with a computer controlled Cary 17 spectrometer. Solid films in the Vis-NIR region were collected by the attenuated total reflectance (ATR) method on a cubic zirconia crystal connected to an Ocean Optics spectrometer.

Electrochemical Measurements. Room temperature electrochemical measurements were performed with a BAS 100B electrochemical analyzer using methods previously described.[3] Potentials are reported vs aqueous Ag/AgCl and are not corrected for the junction potential. The $E^{\circ\prime}$ values for the ferrocenium/ferrocene couple for concentrations similar to those used in this study were 0.46 V for dichloromethane solutions at a glassy carbon electrode.

Single-Crystal X-ray Study of 3. A crystal (approximate dimensions 0.4 x 0.15 x 0.1 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens SMART Platform CCD diffractometer for a data collection at 173(2) K. A preliminary set of

cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 85 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 45 seconds and a detector distance of 4.848 cm. A randomly oriented region of reciprocal space was surveyed to the extent of 1.5 hemispheres and to a resolution of 0.84 Å. Three major sections of frames were collected with 0.30º steps in ω at 3 different ϕ settings and a detector position of -28º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[4] Final cell constants were calculated from the xyz centroids of 3146 strong reflections from the actual data collection after integration (SAINT).[5] Please refer to Table S1 for additional crystal and refinement information.

The structure was solved using SHELXS-97 (Sheldrick, 1990)[6] and refined using SHELXL-97 (Sheldrick, 1997).[3] The space group P 2(1)/n was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.1419$ and $wR2 = 0.3151$ (F^2, all data).

The structure was also found to contain disordered heptane molecules. Using the program SQUEEZE,[7] it was determined that the structure contained a total solvent accessible volume of 770.2 $Å^3$ per unit cell with a total electron count of 86 electrons per unit cell that was not accounted for by atoms refined in the structure. This is roughly 1.5 heptane molecules per unit cell. Some residual electron density was located in the obvious solvent channels shown in the packing diagram which agrees with a tentative assignment as heptane solvate molecules. The packing diagram shows solvent accessible channels. Due to the treatment of this structure using

SQUEEZE, the calculated values of F(000) and density as well as the empirical formula and formula weight are inaccurate.

References

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Table S1. Crystal Data and Structure Refinement for 3.

Identification code	03005x	
Empirical formula	C63 H50 N12 O S6	
Formula weight	1183.57	
Temperature	173(2) K	
Wavelength	0.71073	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	*a*= 7.7157(9)	α= 90¡
	b= 19.226(2)	β= 90.028(2)¡
	c= 43.385(5)	γ = 90¡
Volume	6436.0(13) ^{3}	
Z	4	
Density (calculated)	1.221 Mg/m^{3}	
Absorption coefficient	0.262 mm^{-1}	
F(000)	2464	
Crystal color, morphology	metallic green, plate	
Crystal size	0.4 x 0.15 x 0.1 mm^{3}	
Theta range for data collection	1.16 to 25.06¡.	
Index ranges	$-8 \le h \le 9$, $-22 \le k \le 22$, $-51 \le l \le 50$	
Reflections collected	42659	
Independent reflections	11393 [*R*(int) = 0.0606]	
Observed reflections	8924	
Completeness to theta = 25.06¡	99.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7720	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11393 / 0 / 739	
Goodness-of-fit on F^2	1.203	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.1419, *wR*2 = 0.3062	
R indices (all data)	*R*1 = 0.1638, *wR*2 = 0.3151	
Largest diff. peak and hole	1.091 and -0.620 e. $^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (^{2} x 10^3) for **3**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
S5	-2519(3)	2656(1)	3358(1)	39(1)
S4	2059(3)	1359(1)	3480(1)	42(1)
S2	-7299(3)	-2876(1)	3289(1)	42(1)
S6	-7049(3)	3063(1)	3928(1)	45(1)
S1	-2731(3)	-1626(1)	3453(1)	44(1)
S3	-11794(3)	-3425(1)	3833(1)	50(1)
C20	-8271(10)	-2383(4)	3813(2)	39(2)
C11	-6656(10)	-2044(4)	3740(2)	38(2)
C22	-10367(10)	-3237(4)	3539(2)	39(2)
C21	-8795(10)	-2842(4)	3584(2)	37(2)
C36	3285(11)	1493(4)	3148(2)	48(2)
C10	-5956(11)	-2270(4)	3470(2)	41(2)
C6	-1556(10)	-1677(4)	3118(2)	43(2)
C56	-10051(10)	3858(4)	3804(2)	44(2)
C50	-3482(10)	2070(4)	3867(2)	40(2)
C51	-3989(10)	2554(4)	3658(2)	39(2)
C2	498(10)	-770(4)	3536(2)	39(2)
C52	-5572(11)	2980(4)	3629(2)	43(2)
C32	5332(10)	533(4)	3554(2)	38(2)
C12	-5869(11)	-1481(5)	3939(2)	50(2)
C19	-9268(11)	-2226(5)	4104(2)	48(2)
C4	1066(12)	-1004(5)	3248(2)	51(2)
C40	-1164(9)	2029(4)	3516(2)	36(2)
C54	-7734(12)	3655(4)	3416(2)	56(2)
C35	4968(11)	1203(4)	3089(2)	44(2)
C9	-4429(10)	-2091(4)	3291(2)	42(2)
C38	796(11)	2116(4)	3055(2)	51(2)
C55	-8388(11)	3568(4)	3699(2)	43(2)
C42	-1021(10)	1166(4)	3963(2)	40(2)
C39	417(10)	1876(4)	3344(2)	39(2)
C3	966(11)	-1590(5)	2758(2)	51(2)

C25	-13187(11)	-3842(4)	3578(2)	49(2)
C41	-1837(10)	1755(4)	3786(2)	39(2)
C5	154(12)	-1393(5)	3062(2)	54(2)
C53	-6145(11)	3323(4)	3368(2)	52(2)
C57	-10820(11)	3796(5)	4078(2)	51(2)
C34	5890(12)	780(4)	3267(2)	50(2)
C49	-4465(11)	1874(4)	4152(2)	44(2)
C48	-4177(11)	2373(5)	4422(2)	54(2)
C26	-14786(12)	-4180(4)	3664(2)	53(2)
C33	5793(12)	1397(4)	2790(2)	50(2)
C31	7641(12)	544(4)	3161(2)	46(2)
C43	193(11)	1397(4)	4222(2)	47(2)
C58	-10942(12)	4253(4)	3574(2)	51(2)
C23	-10961(11)	-3499(4)	3269(2)	53(2)
C37	2424(12)	1914(4)	2947(2)	54(2)
C8	-4053(11)	-2257(5)	2992(2)	53(2)
C7	-2462(12)	-2038(4)	2892(2)	52(2)
C60	-12515(13)	4122(5)	4126(2)	60(3)
C44	1122(13)	794(5)	4377(3)	65(3)
C18	-8935(12)	-2753(5)	4364(2)	56(2)
C1	2780(13)	-747(4)	3145(2)	55(2)
C24	-12527(13)	-3843(5)	3292(2)	59(3)
C13	-4670(12)	-1741(5)	4190(2)	55(2)
C17	-10039(13)	-2633(6)	4646(2)	66(3)
C14	-3758(14)	-1145(6)	4361(2)	74(3)
C28	-15737(14)	-4537(5)	3417(3)	68(3)
C30	-17233(13)	-4515(5)	3983(3)	76(3)
C27	-15559(13)	-4177(5)	3935(3)	62(3)
C47	-5328(13)	2200(6)	4700(2)	66(3)
C29	-14852(14)	-3869(6)	4205(3)	71(3)
C59	-10111(12)	3435(5)	4331(2)	53(2)
C45	-88(18)	305(7)	4541(3)	94(4)
C16	-9666(17)	-1959(7)	4814(3)	89(4)
C46	-5184(18)	2708(8)	4945(3)	106(5)
C15	-4944(16)	-672(7)	4535(3)	89(4)
N1	4124(11)	-551(4)	3079(2)	56(2)

N7	8935(10)	322(4)	3092(2)	55(2)
N2	96(12)	-588(4)	3778(2)	66(2)
N8	4947(11)	306(4)	3789(2)	60(2)
N10	-11690(11)	4567(4)	3387(2)	63(2)
N9	6313(12)	1556(5)	2557(2)	74(3)
N11	-9563(13)	3137(5)	4539(2)	81(3)
N3	1505(11)	-1759(5)	2530(2)	73(3)
N4	-16389(13)	-4793(5)	3215(3)	98(4)
N12	-13823(12)	4392(5)	4157(3)	90(3)
N5	-14294(14)	-3589(6)	4416(2)	95(3)
N6	-18576(13)	-4756(5)	4024(3)	99(4)
O1	-4000(20)	-1418(5)	2251(3)	157(5)
C61	-3810(20)	-787(7)	2299(3)	93(4)
C62	-2040(20)	-478(8)	2354(3)	117(5)
C63	-5410(20)	-293(9)	2300(3)	126(6)

Table S3. Bond lengths [ ] and angles [¡] for **3** .

S(5)-C(40)	1.737(7)	C(32)-N(8)	1.148(10)
S(5)-C(51)	1.738(8)	C(32)-C(34)	1.398(12)
S(4)-C(39)	1.714(8)	C(12)-C(13)	1.513(12)
S(4)-C(36)	1.742(9)	C(12)-H(12A)	0.9900
S(2)-C(21)	1.727(8)	C(12)-H(12B)	0.9900
S(2)-C(10)	1.747(9)	C(19)-C(18)	1.540(12)
S(6)-C(55)	1.730(9)	C(19)-H(19A)	0.9900
S(6)-C(52)	1.735(9)	C(19)-H(19B)	0.9900
S(1)-C(6)	1.719(8)	C(4)-C(5)	1.306(13)
S(1)-C(9)	1.736(9)	C(4)-C(1)	1.481(13)
S(3)-C(22)	1.726(8)	C(40)-C(41)	1.386(11)
S(3)-C(25)	1.738(9)	C(40)-C(39)	1.459(10)
C(20)-C(21)	1.389(11)	C(54)-C(55)	1.341(12)
C(20)-C(11)	1.441(10)	C(54)-C(53)	1.398(12)
C(20)-C(19)	1.507(11)	C(54)-H(54A)	0.9500
C(11)-C(10)	1.362(11)	C(35)-C(34)	1.329(12)
C(11)-C(12)	1.510(12)	C(35)-C(33)	1.492(12)
C(22)-C(23)	1.353(12)	C(9)-C(8)	1.365(12)
C(22)-C(21)	1.445(10)	C(38)-C(39)	1.370(12)
C(36)-C(37)	1.363(13)	C(38)-C(37)	1.395(12)
C(36)-C(35)	1.436(11)	C(38)-H(38A)	0.9500
C(10)-C(9)	1.454(11)	C(42)-C(41)	1.506(11)
C(6)-C(7)	1.388(13)	C(42)-C(43)	1.531(11)
C(6)-C(5)	1.447(12)	C(42)-H(42A)	0.9900
C(56)-C(57)	1.334(12)	C(42)-H(42B)	0.9900
C(56)-C(58)	1.428(12)	C(3)-N(3)	1.122(11)
C(56)-C(55)	1.471(11)	C(3)-C(5)	1.509(13)
C(50)-C(51)	1.359(11)	C(25)-C(24)	1.342(13)
C(50)-C(41)	1.450(10)	C(25)-C(26)	1.444(12)
C(50)-C(49)	1.498(11)	C(53)-H(53A)	0.9500
C(51)-C(52)	1.476(11)	C(57)-C(59)	1.409(13)
C(2)-N(2)	1.149(11)	C(57)-C(60)	1.465(12)
C(2)-C(4)	1.397(12)	C(34)-C(31)	1.499(13)
C(52)-C(53)	1.382(12)	C(49)-C(48)	1.530(12)

C(49)-H(49A)	0.9900	C(14)-C(15)	1.496(15)
C(49)-H(49B)	0.9900	C(14)-H(14A)	0.9900
C(48)-C(47)	1.536(12)	C(14)-H(14B)	0.9900
C(48)-H(48A)	0.9900	C(28)-N(4)	1.123(14)
C(48)-H(48B)	0.9900	C(30)-N(6)	1.149(12)
C(26)-C(27)	1.319(14)	C(30)-C(27)	1.460(13)
C(26)-C(28)	1.470(14)	C(27)-C(29)	1.421(16)
C(33)-N(9)	1.127(11)	C(47)-C(46)	1.449(15)
C(31)-N(7)	1.127(11)	C(47)-H(47A)	0.9900
C(43)-C(44)	1.519(12)	C(47)-H(47B)	0.9900
C(43)-H(43A)	0.9900	C(29)-N(5)	1.146(14)
C(43)-H(43B)	0.9900	C(59)-N(11)	1.151(12)
C(58)-N(10)	1.165(11)	C(45)-H(45A)	0.9800
C(23)-C(24)	1.381(13)	C(45)-H(45B)	0.9800
C(23)-H(23A)	0.9500	C(45)-H(45C)	0.9800
C(37)-H(37A)	0.9500	C(16)-H(16A)	0.9800
C(8)-C(7)	1.369(12)	C(16)-H(16B)	0.9800
C(8)-H(8A)	0.9500	C(16)-H(16C)	0.9800
C(7)-H(7A)	0.9500	C(46)-H(46A)	0.9800
C(60)-N(12)	1.143(12)	C(46)-H(46B)	0.9800
C(44)-C(45)	1.503(15)	C(46)-H(46C)	0.9800
C(44)-H(44A)	0.9900	C(15)-H(15A)	0.9800
C(44)-H(44B)	0.9900	C(15)-H(15B)	0.9800
C(18)-C(17)	1.508(12)	C(15)-H(15C)	0.9800
C(18)-H(18A)	0.9900	O(1)-C(61)	1.240(15)
C(18)-H(18B)	0.9900	C(61)-C(62)	1.505(19)
C(1)-N(1)	1.140(11)	C(61)-C(63)	1.56(2)
C(24)-H(24A)	0.9500	C(62)-H(62C)	0.9800
C(13)-C(14)	1.535(14)	C(62)-H(62D)	0.9800
C(13)-H(13A)	0.9900	C(62)-H(62E)	0.9800
C(13)-H(13B)	0.9900	C(63)-H(63F)	0.9800
C(17)-C(16)	1.513(16)	C(63)-H(63G)	0.9800
C(17)-H(17A)	0.9900	C(63)-H(63H)	0.9800
C(17)-H(17B)	0.9900		

C(40)-S(5)-C(51)	91.1(4)	N(2)-C(2)-C(4)	177.1(9)
C(39)-S(4)-C(36)	91.9(4)	C(53)-C(52)-C(51)	126.7(8)
C(21)-S(2)-C(10)	92.1(4)	C(53)-C(52)-S(6)	111.0(6)
C(55)-S(6)-C(52)	90.9(4)	C(51)-C(52)-S(6)	122.1(6)
C(6)-S(1)-C(9)	91.4(4)	N(8)-C(32)-C(34)	176.3(9)
C(22)-S(3)-C(25)	91.1(4)	C(11)-C(12)-C(13)	114.8(8)
C(21)-C(20)-C(11)	112.5(7)	C(11)-C(12)-H(12A)	108.6
C(21)-C(20)-C(19)	125.2(7)	C(13)-C(12)-H(12A)	108.6
C(11)-C(20)-C(19)	122.3(7)	C(11)-C(12)-H(12B)	108.6
C(10)-C(11)-C(20)	112.7(7)	C(13)-C(12)-H(12B)	108.6
C(10)-C(11)-C(12)	124.1(7)	H(12A)-C(12)-H(12B)	107.6
C(20)-C(11)-C(12)	123.1(7)	C(20)-C(19)-C(18)	113.5(7)
C(23)-C(22)-C(21)	126.6(8)	C(20)-C(19)-H(19A)	108.9
C(23)-C(22)-S(3)	110.3(6)	C(18)-C(19)-H(19A)	108.9
C(21)-C(22)-S(3)	123.0(6)	C(20)-C(19)-H(19B)	108.9
C(20)-C(21)-C(22)	132.5(8)	C(18)-C(19)-H(19B)	108.9
C(20)-C(21)-S(2)	111.2(6)	H(19A)-C(19)-H(19B)	107.7
C(22)-C(21)-S(2)	116.1(6)	C(5)-C(4)-C(2)	124.5(9)
C(37)-C(36)-C(35)	123.8(8)	C(5)-C(4)-C(1)	119.0(9)
C(37)-C(36)-S(4)	110.6(6)	C(2)-C(4)-C(1)	116.3(8)
C(35)-C(36)-S(4)	125.6(7)	C(41)-C(40)-C(39)	131.9(7)
C(11)-C(10)-C(9)	135.0(8)	C(41)-C(40)-S(5)	111.9(5)
C(11)-C(10)-S(2)	111.5(6)	C(39)-C(40)-S(5)	116.2(6)
C(9)-C(10)-S(2)	113.4(6)	C(55)-C(54)-C(53)	114.2(8)
C(7)-C(6)-C(5)	122.0(8)	C(55)-C(54)-H(54A)	122.9
C(7)-C(6)-S(1)	111.1(6)	C(53)-C(54)-H(54A)	122.9
C(5)-C(6)-S(1)	126.9(7)	C(34)-C(35)-C(36)	128.0(9)
C(57)-C(56)-C(58)	117.0(8)	C(34)-C(35)-C(33)	115.6(8)
C(57)-C(56)-C(55)	129.0(8)	C(36)-C(35)-C(33)	116.4(8)
C(58)-C(56)-C(55)	114.0(8)	C(8)-C(9)-C(10)	128.8(8)
C(51)-C(50)-C(41)	112.0(7)	C(8)-C(9)-S(1)	110.2(6)
C(51)-C(50)-C(49)	125.3(7)	C(10)-C(9)-S(1)	121.0(6)
C(41)-C(50)-C(49)	122.7(7)	C(39)-C(38)-C(37)	114.0(8)
C(50)-C(51)-C(52)	132.4(7)	C(39)-C(38)-H(38A)	123.0
C(50)-C(51)-S(5)	113.0(6)	C(37)-C(38)-H(38A)	123.0
C(52)-C(51)-S(5)	114.5(6)	C(54)-C(55)-C(56)	124.3(8)

C(54)-C(55)-S(6)	111.8(6)	C(49)-C(48)-C(47)	112.5(8)
C(56)-C(55)-S(6)	123.9(7)	C(49)-C(48)-H(48A)	109.1
C(41)-C(42)-C(43)	114.3(7)	C(47)-C(48)-H(48A)	109.1
C(41)-C(42)-H(42A)	108.7	C(49)-C(48)-H(48B)	109.1
C(43)-C(42)-H(42A)	108.7	C(47)-C(48)-H(48B)	109.1
C(41)-C(42)-H(42B)	108.7	H(48A)-C(48)-H(48B)	107.8
C(43)-C(42)-H(42B)	108.7	C(27)-C(26)-C(25)	128.0(9)
H(42A)-C(42)-H(42B)	107.6	C(27)-C(26)-C(28)	115.3(9)
C(38)-C(39)-C(40)	125.3(8)	C(25)-C(26)-C(28)	116.6(9)
C(38)-C(39)-S(4)	110.6(6)	N(9)-C(33)-C(35)	175.5(11)
C(40)-C(39)-S(4)	124.1(6)	N(7)-C(31)-C(34)	175.0(10)
N(3)-C(3)-C(5)	176.5(10)	C(44)-C(43)-C(42)	113.1(7)
C(24)-C(25)-C(26)	124.3(9)	C(44)-C(43)-H(43A)	109.0
C(24)-C(25)-S(3)	110.8(7)	C(42)-C(43)-H(43A)	109.0
C(26)-C(25)-S(3)	124.8(8)	C(44)-C(43)-H(43B)	109.0
C(40)-C(41)-C(50)	112.1(7)	C(42)-C(43)-H(43B)	109.0
C(40)-C(41)-C(42)	124.0(7)	H(43A)-C(43)-H(43B)	107.8
C(50)-C(41)-C(42)	123.7(7)	N(10)-C(58)-C(56)	178.9(10)
C(4)-C(5)-C(6)	127.2(9)	C(22)-C(23)-C(24)	114.3(9)
C(4)-C(5)-C(3)	117.4(8)	C(22)-C(23)-H(23A)	122.9
C(6)-C(5)-C(3)	115.4(8)	C(24)-C(23)-H(23A)	122.9
C(52)-C(53)-C(54)	112.1(9)	C(36)-C(37)-C(38)	112.9(8)
C(52)-C(53)-H(53A)	123.9	C(36)-C(37)-H(37A)	123.5
C(54)-C(53)-H(53A)	123.9	C(38)-C(37)-H(37A)	123.5
C(56)-C(57)-C(59)	124.4(8)	C(9)-C(8)-C(7)	114.8(9)
C(56)-C(57)-C(60)	119.1(9)	C(9)-C(8)-H(8A)	122.6
C(59)-C(57)-C(60)	116.4(8)	C(7)-C(8)-H(8A)	122.6
C(35)-C(34)-C(32)	124.1(9)	C(8)-C(7)-C(6)	112.5(8)
C(35)-C(34)-C(31)	119.2(8)	C(8)-C(7)-H(7A)	123.7
C(32)-C(34)-C(31)	116.7(8)	C(6)-C(7)-H(7A)	123.7
C(50)-C(49)-C(48)	113.6(7)	N(12)-C(60)-C(57)	177.7(12)
C(50)-C(49)-H(49A)	108.8	C(45)-C(44)-C(43)	113.1(9)
C(48)-C(49)-H(49A)	108.8	C(45)-C(44)-H(44A)	109.0
C(50)-C(49)-H(49B)	108.8	C(43)-C(44)-H(44A)	109.0
C(48)-C(49)-H(49B)	108.8	C(45)-C(44)-H(44B)	109.0
H(49A)-C(49)-H(49B)	107.7	C(43)-C(44)-H(44B)	109.0

H(44A)-C(44)-H(44B)	107.8	C(48)-C(47)-H(47A)	109.0
C(17)-C(18)-C(19)	113.6(8)	C(46)-C(47)-H(47B)	109.0
C(17)-C(18)-H(18A)	108.8	C(48)-C(47)-H(47B)	109.0
C(19)-C(18)-H(18A)	108.8	H(47A)-C(47)-H(47B)	107.8
C(17)-C(18)-H(18B)	108.8	N(5)-C(29)-C(27)	176.6(13)
C(19)-C(18)-H(18B)	108.8	N(11)-C(59)-C(57)	178.7(11)
H(18A)-C(18)-H(18B)	107.7	C(44)-C(45)-H(45A)	109.5
N(1)-C(1)-C(4)	176.9(11)	C(44)-C(45)-H(45B)	109.5
C(25)-C(24)-C(23)	113.5(9)	H(45A)-C(45)-H(45B)	109.5
C(25)-C(24)-H(24A)	123.3	C(44)-C(45)-H(45C)	109.5
C(23)-C(24)-H(24A)	123.3	H(45A)-C(45)-H(45C)	109.5
C(12)-C(13)-C(14)	112.4(8)	H(45B)-C(45)-H(45C)	109.5
C(12)-C(13)-H(13A)	109.1	C(17)-C(16)-H(16A)	109.5
C(14)-C(13)-H(13A)	109.1	C(17)-C(16)-H(16B)	109.5
C(12)-C(13)-H(13B)	109.1	H(16A)-C(16)-H(16B)	109.5
C(14)-C(13)-H(13B)	109.1	C(17)-C(16)-H(16C)	109.5
H(13A)-C(13)-H(13B)	107.9	H(16A)-C(16)-H(16C)	109.5
C(18)-C(17)-C(16)	114.5(9)	H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-H(17A)	108.6	C(47)-C(46)-H(46A)	109.5
C(16)-C(17)-H(17A)	108.6	C(47)-C(46)-H(46B)	109.5
C(18)-C(17)-H(17B)	108.6	H(46A)-C(46)-H(46B)	109.5
C(16)-C(17)-H(17B)	108.6	C(47)-C(46)-H(46C)	109.5
H(17A)-C(17)-H(17B)	107.6	H(46A)-C(46)-H(46C)	109.5
C(15)-C(14)-C(13)	114.7(9)	H(46B)-C(46)-H(46C)	109.5
C(15)-C(14)-H(14A)	108.6	C(14)-C(15)-H(15A)	109.5
C(13)-C(14)-H(14A)	108.6	C(14)-C(15)-H(15B)	109.5
C(15)-C(14)-H(14B)	108.6	H(15A)-C(15)-H(15B)	109.5
C(13)-C(14)-H(14B)	108.6	C(14)-C(15)-H(15C)	109.5
H(14A)-C(14)-H(14B)	107.6	H(15A)-C(15)-H(15C)	109.5
N(4)-C(28)-C(26)	175.6(13)	H(15B)-C(15)-H(15C)	109.5
N(6)-C(30)-C(27)	177.3(12)	O(1)-C(61)-C(62)	121.2(17)
C(26)-C(27)-C(29)	124.2(9)	O(1)-C(61)-C(63)	120.3(15)
C(26)-C(27)-C(30)	121.7(10)	C(62)-C(61)-C(63)	118.4(12)
C(29)-C(27)-C(30)	114.1(10)	C(61)-C(62)-H(62C)	109.5
C(46)-C(47)-C(48)	112.7(10)	C(61)-C(62)-H(62D)	109.5
C(46)-C(47)-H(47A)	109.0	H(62C)-C(62)-H(62D)	109.5

C(61)-C(62)-H(62E)	109.5
H(62C)-C(62)-H(62E)	109.5
H(62D)-C(62)-H(62E)	109.5
C(61)-C(63)-H(63F)	109.5
C(61)-C(63)-H(63G)	109.5
H(63F)-C(63)-H(63G)	109.5
C(61)-C(63)-H(63H)	109.5
H(63F)-C(63)-H(63H)	109.5
H(63G)-C(63)-H(63H)	109