

Article

Synthesis and NMR Spectral Studies of the 7-C₆₀-Adduct of *N,N*-(Tetrachlorophthaloyl)dehydroabietylamine

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Abstract: The 7-C₆₀-adduct of *N,N*-(tetrachlorophthaloyl)dehydroabietylamine was synthesized for the first time and characterized by IR, UV-vis, mass and NMR spectral studies. The ¹H-NMR and ¹³C-NMR resonance signals of the new compound are unambiguously assigned by using homo- and heteronuclear 2D NMR spectroscopic techniques such as COSY, ROESY, HSQC and HMBC. The *C_i* symmetric structure with 6,6-junction of compound was determined.

Keywords: 7-C₆₀-adduct of *N,N*-(tetrachlorophthaloyl)dehydroabietylamine; ¹H-NMR; ¹³C-NMR; 2D NMR; *C_i* symmetric structure

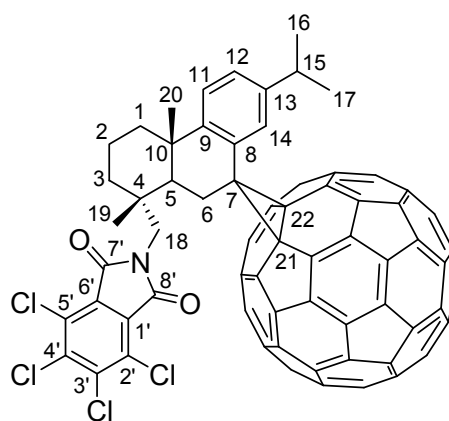
1. Introduction

Dehydroabietylamine, which possesses an aromatic diterpene structure with three rings and a reactive amino group and is the main component of disproportionated rosin amine, can be easily isolated from the latter. Dehydroabietylamine and its derivatives have attracted considerable interest due to their wide range of uses such as chiral resolution agents [1,2], antibacterial substances [3,4] and chiral surfactants [5,6].

Since the discovery of C₆₀, its peculiar cage structure has attracted great attention. Cycloaddition reactions of C₆₀, especially 1,3-dipolar addition reactions, have been the subject of a large variety of studies and shown to be a useful methods for the synthesis of functionalized fullerene derivatives [7–11]. These results prompted us to study new cycloadducts of dehydroabietylamine with C₆₀ as a part of an

on-going program for the development of new rosin amine derivatives with potential biological or material properties. So far, the majority of the studies on the chemical transformations of dehydroabietylamine have focused on the amine group and benzene ring, but the chemical transformation in other skeleton has seldom been reported. In this paper, we report the synthesis for the first time of the 7-C₆₀-adduct of *N,N*-(tetrachlorophthaloyl)dehydroabietylamine (**5**, Figure 1) and describe the structure determination of the new compound, along with its detailed ¹H- and ¹³C-NMR assignments.

Figure 1. Chemical structure of 7-C₆₀-adduct of *N,N*-(tetrachlorophthaloyl)dehydroabietylamine (**5**).



2. Results and Discussion

2.1. Synthesis Procedures

The general procedure for the synthesis of compound **5** is shown in Scheme 1. Dehydroabietylamine (**1**) was prepared as described in the literature [12]. Dehydroabietylamine reacted with tetrachlorophthalic anhydride (TCPA, an amino protecting group) to give compound **2**, which then was transformed into **3** by C-7 benzylic oxidation. Subsequently, the reaction of **3** with *p*-tosylhydrazide yielded *p*-tosylhydrazone **4**. Compound **5** was prepared according to the reported method [13]. According to the literature [13], heating a solution of the *p*-tosylhydrazone with C₆₀ at 70 °C afford the [5,6]-open isomer. However, in our experiment, no traces of this expected [5,6]-open isomer were found and the only isolated product was the [6,6]-closed isomer (methanofullerene), which is likely due to a rearrangement of the 5,6-open isomer into the thermodynamically more stable 6,6-closed isomer at 70 °C.

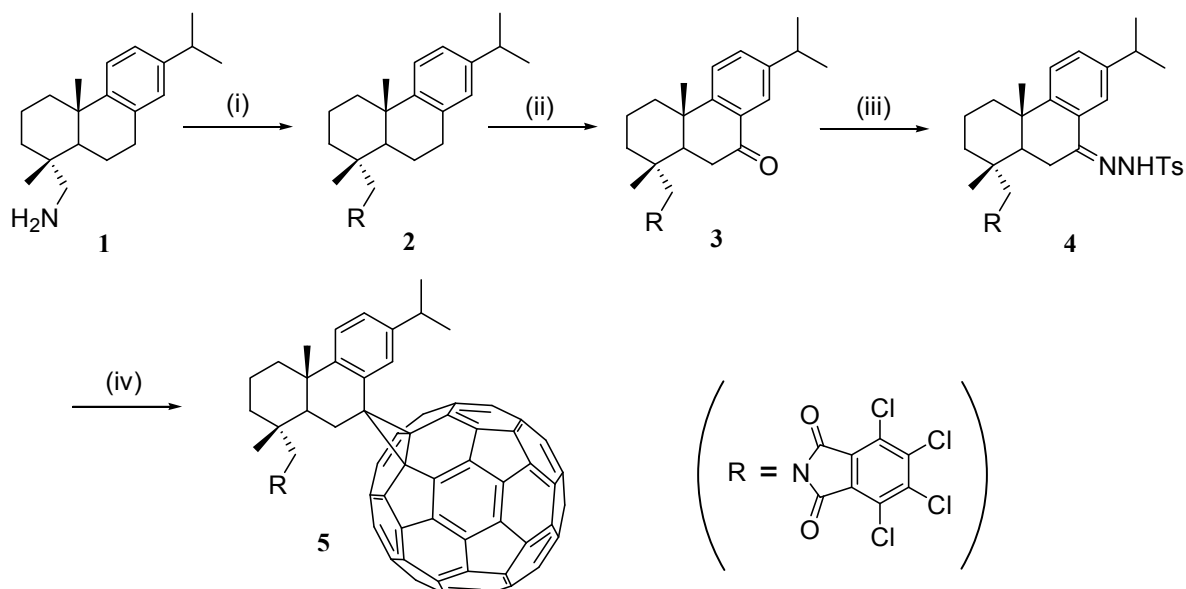
2.2. Analysis of Compound **5**

2.2.1. IR, UV-Vis and Mass Spectrum Analysis of Compound **5**

The IR spectrum of compound **5** showed bands indicating the presence of the different expected functional groups: Characteristic asymmetric and symmetric stretching bands of the imide carbonyl (C=O) at 1,776 and 1,721 cm^{−1} and at 526 cm^{−1} for the C₆₀ skeleton. In the UV-vis spectrum, the characteristic absorptions for the methanofullerenes was also observed at 436.50, 697.00 nm [13]. Meanwhile, the structure of compound **5** as a monoadduct was supported by the matrix-assisted laser

desorption/ionization time of flight mass spectrum (MALDI-TOF MS) which display the expected peak at m/z 1,271.4.

Scheme 1. Preparation of compound **5**.



Reagents and conditions: (i) TCPA, acetic acid, N_2 , 135 °C, 2.5 h; (ii) 65% *t*-BuOOH, CrO_3 (cat.), pyridine, CH_2Cl_2 , rt, 24 h; (iii) TsNHNH_2 , PTSA (cat.), benzene-EtOH (4:1), reflux, 8 h; (iv) NaOMe, pyridine, 15 min, rt; then C_{60} in chlorobenzene, N_2 , 70 °C, 24 h.

2.2.2. ^1H -NMR Spectrum Analysis of Compound **5**

The ^1H -, ^{13}C -NMR and 2D NMR spectra for compound **5** are summarized in Table 1.

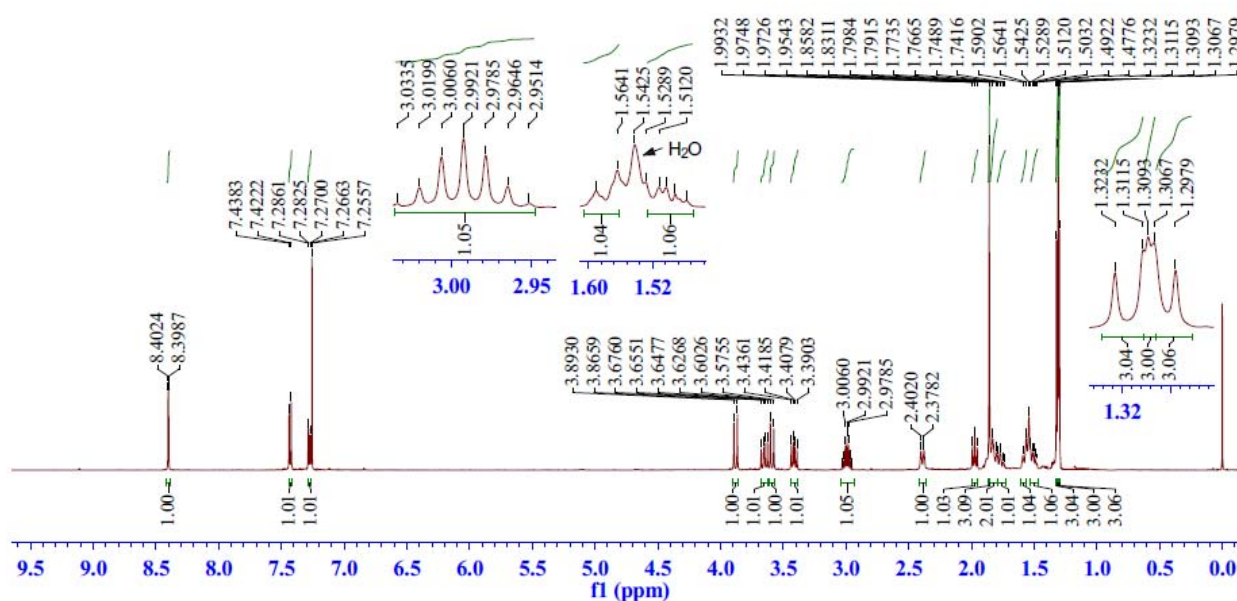
Table 1. ^1H - and ^{13}C -NMR data, ^1H - ^1H correlations in COSY, ROESY spectra and ^1H - ^{13}C correlations in HSQC, HMBC spectra for compound **5**.

C	δ_{C} (ppm)	H	δ_{H} (ppm)	HSQC	HMBC	COSY	ROESY
1	39.48	1 β	2.39 (br d, $J = 11.9$ Hz)	H-1 β , 1 α	H-20, 2, 3 α	H-1 α , 2	H-20, 11, 2, 1 α
		1 α	1.79–1.74 (m)			H-1 β , 2	H-5, 11, 1 β
2	18.18	2	1.85–1.79 (m, 2H)	H-2	H-19, 18 α , 18 β	H-3 β , 3 α , 1 β , 1 α	H-19, 3 β , 3 α , 1 β
		3 β	1.58 (br d, $J = 13.0$ Hz)			H-3 α , 2	H-19, 3 α , 2
3	37.52	3 α	1.53–1.47 (m)	—	H-19, 5, 18 α , 18 β , 6 β	H-3 β , 2	H-5, 18 α , 3 β , 2
		—	—			—	—
4	40.89	—	—	—	H-19, 20, 18 α , 18 β , 6 α , 6 β	H-6 β , 6 α	H-3 α , 1 α , 6 α , 18 α , 2
		5	1.97 (dd, $J = 10.3, 9.2$ Hz)			—	—
5	48.67	6 β	3.65 (dd, $J = 14.1, 10.5$ Hz)	H-6 β , 6 α	C-6/H-5	H-5, 6 α	H-19, 20, 6 α
		6 α	3.41 (dd, $J = 14.1, 8.8$ Hz)			H-5, 6 β	H-5, 6 β , 18 α
6	28.35	—	—	—	H-6 α , 6 β , 14, 11	—	—
7	44.61	—	—	—	H-6 β , 11,	—	—
8	132.15	—	—	—	H-14, 12, 20, 5	—	—
9	150.35	—	—	—	—	—	—

Table 1. Cont.

C	δ_c (ppm)	H	δ_H (ppm)	HSQC	HMBC	COSY	ROESY
10	38.83	—	—	—	H-20, 5, 6 α , 2, 11	—	—
11	123.40	11	7.43 (d, $J = 8.1$ Hz)	H-11	H-12	H-12	H-1 β , 1 α , 12
12	126.09	12	7.28 (dd, $J = 8.1, 1.8$ Hz)	H-12	H-15, 11, 14	H-11	H-15, 11, 16
13	145.43	—	—	—	H-16, 17, 15, 11	—	—
14	126.42	14	8.40 (d, $J = 1.8$ Hz)	H-14	H-12, 15	—	—
15	33.92	15	2.99 (septet, $J = 6.7$ Hz)	H-15	H-16, 17, 12, 14	H-16, 17	H-16, 17, 12
16	23.70	16	1.30 (d, $J = 6.8$ Hz, 3H)	H-16	H-15, 17,	H-15	H-15, 12
17	24.49	17	1.32 (d, $J = 7.0$ Hz, 3H)	H-17	H-15, 16	H-15	H-15
18	50.45	18 β	3.88 (d, $J = 13.6$ Hz)	H-18 β , 18 α	H-19, 5	H-18 α	H-18 α , 19
		18 α	3.59 (d, $J = 13.6$ Hz)			H-18 β	H-18 β , 5, 3 α , 6 α
19	18.89	19	1.31 (s, 3H)	H-19	H-5, 18 α , 18 β	—	H-20, 6 β , 18 β , 3 β , 2
20	22.50	20	1.86 (s, 3H)	H-20	H-1 α , 5	—	H-19, 6 β , 1 β
21,22	84.80	—	—	—	H-6 α , 6 β	—	—
	77.66	—	—	—	H-6 α	—	—
1',6'	127.52	—	—	—	—	—	—
2',5'	129.76	—	—	—	—	—	—
3',4'	140.35	—	—	—	—	—	—
7',8'	164.51	—	—	—	H-18 α , 18 β	—	—
C ₆₀	150.74–137.82	—	—	—	—	—	—

First, the assignment of some protons is easily accomplished by analysis of the ^1H -NMR chemical shifts, signal multiplicity and coupling constants. The signals of the aromatic protons (7.26–8.40 ppm) can be readily identified by their chemical environment (Figure 2).

Figure 2. ^1H -NMR spectrum of compound 5.

The H-11 signal appeared as a doublet with coupling constants $J_{11,12} = 8.1$ Hz at 7.43 ppm, while the H-14 signal appeared at 8.40 ppm as a doublet with a lower coupling constant values $J_{14,12} = 1.8$ Hz because of the long distance between H-14 and H-12. H-12 signal appeared as a double doublet with $J_{12,11} = 8.1$ and $J_{12,14} = 1.8$ Hz at 7.28 ppm. The septet at 2.99 ppm ($J = 6.7$ Hz) was assigned to H-15 proton. In the higher frequency region there are three double doublets and two doublets at δ_H 3.65 (dd, $J = 14.1, 10.5$ Hz), 3.41 (dd, $J = 14.1, 8.8$ Hz) 1.97 (dd, $J = 10.3, 9.2$ Hz), 3.88 (d, $J = 13.6$ Hz) and 3.59 ppm (d, $J = 13.6$ Hz). Of the five signals, δ_H 3.88 and 3.59 ppm doublets were assigned to H-18 (H-18 β and H-18 α) on the basis of the correlations of δ_C 50.45 ppm/H-18 β , 18 α in the HSQC spectrum, while δ_H 3.65 and 3.41 ppm double doublets were assigned to the H-6 (H-6 β and H-6 α) on the basis of the correlations of δ_C 28.35 ppm/H-6 β , 6 α in the HSQC spectrum. The remaining double doublet at δ_H 1.97 ppm was assigned to H-5. To distinguish the non-equivalent H-18 and H-6 protons, we found that δ_H 3.59 and 3.41 ppm showed ROE correlations with H-5, but δ_H 3.88 and 3.65 ppm showed no ROE correlations with H-5 in the ROESY spectrum. Therefore, we assigned H-18 α at δ 3.59, H-6 α at δ 3.41, H-18 β at δ 3.88 and H-6 β at δ 3.65 ppm.

The signals of four-methyl group protons appeared as two singlets and two doublets. The two singlets, one at δ_H 1.86 ppm was assigned to H-20 methyl protons, and the other at δ_H 1.31 ppm was assigned to H-19 methyl protons based on the correlations of δ_H 1.86/H-19, 6 β and δ_H 1.31/H-20, 6 β , 18 β in the ROESY spectrum. The doublet at δ_H 1.30 ppm was readily assigned to H-16 methyl protons in the isopropyl moiety due to the δ_H 1.30/H-15 correlation in the COSY spectrum and δ_H 1.30/H-15, 12 correlations in the ROESY spectrum. The remaining doublet at δ_H 1.32 ppm was assigned to H-17 methyl protons.

Finally, the signals of the remaining three-methylene group protons (H-1, 2, 3) appeared as two broad doublets and three multiplets. The broad doublet at δ_H 2.39 ppm and the multiplet at δ_H 1.79–1.74 ppm were, respectively, assigned to H-1 β and H-1 α due to the correlations of δ_H 2.39/1.79–1.74/ δ_C 39.48 ppm in the HSQC spectrum and δ_H 2.39/H-20, 11, δ_H 1.79–1.74/H-5, 11 in the ROESY spectrum. Similarly, the broad doublet at δ_H 1.58 ppm and the multiplet at δ_H 1.53–1.47 ppm were, respectively, assigned to H-3 β and H-3 α based on the correlations of δ_H 1.58/1.53–1.47/ δ_C 37.52 ppm in the HSQC spectrum and δ_H 1.58/H-19, δ_H 1.53–1.47/H-5, 18 α in the ROESY spectrum. The remaining multiplet at δ_H 1.85–1.79 ppm was assigned to H-2, which also be demonstrated by the correlations of δ_H 1.85–1.79/H-3 β , 3 α , 1 β , 1 α in the COSY spectrum.

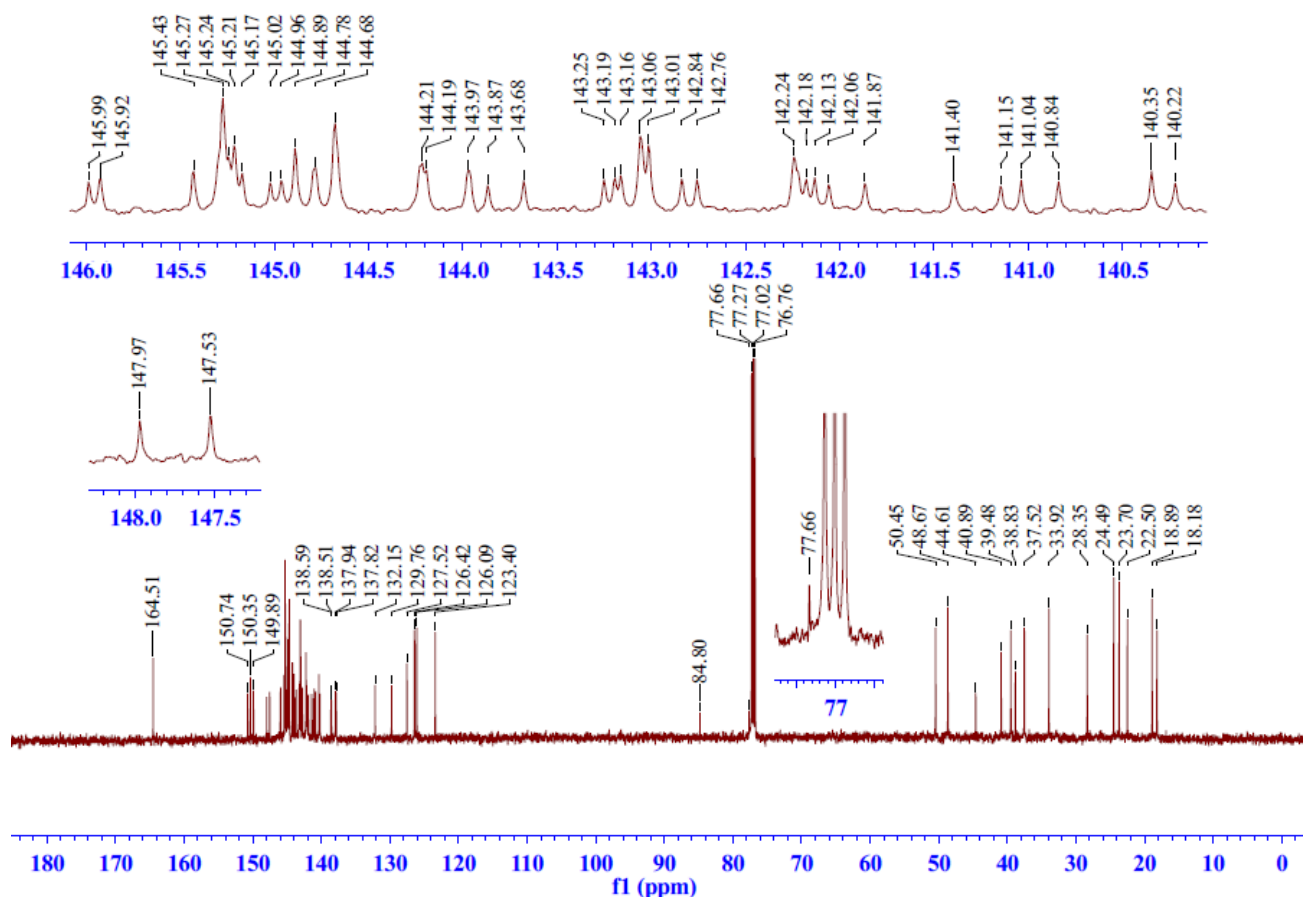
2.2.3. ^{13}C -NMR Spectrum Analysis of Compound 5

The proton noise decoupled ^{13}C -NMR spectrum (Figure 3) displayed 24 and 43 resonance signals respectively for (tetrachlorophthaloyl)dehydroabietylamine moiety and C_{60} moiety of compound 5. In the ^{13}C -NMR spectrum, the signal at δ_C 164.51 ppm could be assigned to C-7', 8', which was supported by the cross peaks of δ_C 164.51 ppm/H-18 α , 18 β in the HMBC spectrum.

In the HSQC spectrum, the signals at δ_C 23.70, 24.49, 18.89 and 22.50 ppm were attributed to C-16, 17, 19, 20 methyl carbon atoms due to the cross peaks of δ_C 23.70/H-16, δ_C 24.49/H-17, δ_C 18.89/H-19 and δ_C 22.50/H-20. In addition, the signals at δ_C 18.18, 39.48, 37.52, 28.35 and 50.45 ppm were attributed to C-2, 1, 3, 6, 18 methylene carbon atoms due to the cross peaks of δ_C 18.18/H-2, δ_C 39.48/H-1 α , 1 β , δ_C 37.52/H-3 α , 3 β , δ_C 28.35/H-6 α , 6 β and δ_C 50.45/H-18 α , 18 β . The resonance

signals at δ_C 48.67 and 33.92 ppm were assigned to methine carbon atoms C-5 and C-15 based on the cross peaks of δ_C 48.67/H-5 and δ_C 33.92/H-15. The HSQC spectrum also revealed the cross peaks between aromatic hydrogens H-11, 12, 14 and their corresponding carbon atoms. From the HSQC spectrum, we can clearly assign C-11 at δ_C 123.40, C-12 at δ_C 126.09 and C-14 at δ_C 126.42 ppm.

Figure 3. ^{13}C -NMR spectrum of compound 5.



The quaternary carbon atoms were assigned by using the long-range correlated HMBC experiment. The signals at δ_C 40.89, 132.15, 150.35, 38.83 and 145.43 ppm were assigned to C-4, 8, 9, 10, 13 quaternary carbon atoms because of the long-range cross peaks of δ_C 40.89 ppm/H-19, 5, 18 α , 18 β , 6 β , δ_C 132.15 ppm/H-6 β , 11, δ_C 150.35 ppm/H-14, 12, 20, 5, δ_C 38.83 ppm/H-20, 5, 6 α , 2, 11 and δ_C 145.43 ppm/H-16, 17, 15, 11. The signals at δ_C 44.61, 84.80, 77.66 ppm were assigned to C-7 and the sp^3 -hybridized bridgehead carbon atom C-21, 22 on the cyclopropyl moiety due to the long-range cross peaks of δ_C 44.61 ppm/H-6 α , 6 β , 14, 11, δ_C 84.80 ppm/H-6 α , 6 β and δ_C 77.66 ppm/H-6 α . This pattern is unambiguously diagnostic for C_I symmetric structure with 6,6-junction [14,15].

Only four signals were observed in the tetrachlorophthaloyl moiety due to the symmetry of C-7', 8', C-1', 6', C-2', 5' and C-3', 4'. The carbon signals at δ_C 127.52, 129.76, 140.35 ppm can be assigned to C-1', 6', C-2', 5' and C-3', 4' [16]. The remaining 41 resonance signals between δ_C 150.74–137.82 ppm were attributed to $\text{C}_{60}\text{-sp}^2$ carbon atoms (due to the overlapping, only 41 resonance signals for $\text{C}_{60}\text{-sp}^2$ carbon atoms were observed, maximum 58 sp^2 -carbon resonance signals).

3. Experimental

3.1. General

1D (^1H and ^{13}C) and 2D NMR experiments were performed on a Bruker AVANCE AV-500 NMR spectrometer (500.13 MHz for ^1H and 125.77 MHz for ^{13}C). The samples were dissolved in 0.5 mL CDCl_3 , ^1H -NMR and ^{13}C -NMR spectra were recorded using TMS as an internal reference. Chemical shifts were reported in parts per million (ppm). FT infrared (IR) spectrum were recorded as KBr pellets on a Nicolet 360 FT-IR spectrometer and UV-vis spectra on a Shimadzu UV-2550 UV-VIS spectrometer. ESI mass spectrometric were obtained on Agilent 1100 Capillary LC/Micromass Q-ToF Micro mass spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra was performed on a Bruker Daltonics Autoflex III mass spectrometer using α -cyano-4-hydroxycinnamic acid (CHCA) as a matrix in a negative-ion reflector mode. All chemicals and solvents were obtained from commercial sources and used as received or dried according to standard procedures. Column chromatography was performed on silica gel (ZCX II, 100–200 mesh). Chemical reactions were monitored by thin layer chromatography using precoated silica gel GF254 plates.

3.2. Preparation of *N,N*-(Tetrachlorophthaloyl)dehydroabietylamine (2)

A mixture of tetrachlorophthalic anhydride (5 g, 17.5 mmol), dehydroabietylamine (5 g, 17.5 mmol), and glacial acetic acid (60 mL) was stirred under N_2 at 135 °C for 2.5 h. Then the mixture was cooled and poured into 250 mL of ice water. The solid was filtered, washed successively with distilled water and ethanol, dried in vacuo to give the crude product, which was purified by column chromatography on silica gel (petroleum ether-toluene, 2:1) to yield **2** as a white solid (7.11 g, 73.4%), m.p. 220–221 °C. IR $\nu_{\text{max}}/\text{cm}^{-1}$: 2934, 2860, 1776, 1714, 1630, 1498, 1430, 1392, 1369, 1338, 1297, 1200, 1091, 1069, 879, 820, 736, 556, 476; ^1H -NMR: δ 7.13 (d, $J = 7.9$ Hz, 1H), 6.96 (dd, $J = 8.2, 1.5$ Hz, 1H), 6.91 (s, 1H), 3.68 (d, $J = 13.7$ Hz, 1H), 3.55 (d, $J = 13.7$ Hz, 1H), 2.98–2.96 (m, 2H), 2.81 (septet, $J = 6.9$ Hz, 1H), 2.26 (br d, $J = 12.5$ Hz, 1H), 2.22–2.18 (m, 1H), 1.86–1.79 (m, 1H), 1.75–1.62 (m, 2H), 1.49 (dd, $J = 13.4, 1.2$ Hz, 1H), 1.44–1.28 (m, 3H, H-1 α), 1.23 (s, 3H), 1.21 (d, $J = 7.0$ Hz, 6H), 1.05 (s, 3H); ^{13}C -NMR: δ 164.50 (2C=O, imide), 147.09, 145.69, 140.07 (2C, -N(CO) $_2$ C $_6$ Cl $_4$), 134.86, 129.58 (2C, -N(CO) $_2$ C $_6$ Cl $_4$), 127.52 (2C, -N(CO) $_2$ C $_6$ Cl $_4$), 127.05, 123.82, 123.78, 49.89, 45.39, 39.53, 38.09, 37.61, 37.21, 33.44, 30.07, 25.81, 23.96, 23.94, 19.45, 19.06, 18.45; TOF MS (ES $^-$) m/z 524.3 ([M($^{35}\text{Cl}_4$)-C $_2\text{H}_3$] $^-$), 526.2 ([M($^{35}\text{Cl}_3^{37}\text{Cl}$)-C $_2\text{H}_3$] $^-$), 528.2 ([M($^{35}\text{Cl}_2^{37}\text{Cl}_2$)-C $_2\text{H}_3$] $^-$). Anal. Calcd for C $_{28}\text{H}_{29}\text{Cl}_4\text{NO}_2$ (553.3): C, 60.78; H, 5.28; N, 2.53. Found: C, 60.37; H, 5.35; N, 2.48.

3.3. Preparation of 7-oxo-*N,N*-(Tetrachlorophthaloyl)dehydroabietylamine (3)

To a mixture of CrO $_3$ (45 mg, 0.45 mmol) and CH $_2$ Cl $_2$ (90 mL), 65% *t*-BuOOH (11.6 mL, 72.3 mmol) and pyridine (0.073 mL, 0.904 mmol) were added. After stirring at room temperature for 3 min, compound **2** (5 g, 9.035 mmol) was added. Stirring continued at room temperature for 24 h, the mixture was concentrated to about 15 mL *in vacuo* at 30 °C, then poured into methanol (60 mL). The precipitate formed was filtered and washed with methanol to give a crude product, which was purified by column chromatography on silica gel (toluene-ethyl acetate, 20:0.5) to afford compound **3** as a

white solid (3.51 g, 68.5%), m.p. 224–226 °C. IR $\nu_{\max}/\text{cm}^{-1}$: 2961, 2930, 2865, 1777, 1716, 1684, 1608, 1561, 1515, 1489, 1456, 1430, 1377, 1342, 1297, 1248, 1197, 1093, 977, 912, 831, 797, 738, 613, 558, 500, 471; $^1\text{H-NMR}$: δ 7.89 (d, $J = 2.1$ Hz, 1H), 7.39 (dd, $J = 8.1, 2.0$ Hz, 1H), 7.27 (d, $J = 7.3$ Hz, 1H), 3.64 (d, $J = 13.7$ Hz, 1H), 3.51 (d, $J = 13.7$ Hz, 1H), 3.06 (dd, $J = 18.0, 3.7$ Hz, 1H), 2.93 (septet, $J = 6.9$ Hz, 1H), 2.76 (dd, $J = 18.0, 14.0$ Hz, 1H), 2.32 (br d, $J = 12.8$ Hz, 1H), 2.00 (dd, $J = 13.9, 3.5$ Hz, 1H), 1.75–1.70 (m, 2H), 1.60–1.48 (m, 2H), 1.45–1.34 (m, 1H), 1.28 (s, 3H), 1.25 (d, $J = 7.0$ Hz, 6H), 1.12 (s, 3H); $^{13}\text{C-NMR}$: δ 198.61 (C=O), 164.34 (2C=O, imide), 153.18, 146.89, 140.06 (2C, -N(CO)₂C₆Cl₄), 132.48, 130.66, 129.60 (2C, -N(CO)₂C₆Cl₄), 127.44 (2C, -N(CO)₂C₆Cl₄), 125.18, 123.34, 49.71, 45.36, 39.16, 37.86, 37.29, 36.82, 36.34, 33.58, 24.18, 23.81, 18.72, 18.00; TOF MS (ES⁺) m/z 565.9 [M(³⁵Cl₄)+H]⁺, 567.9 [M(³⁵Cl₃³⁷Cl)+H]⁺, 569.9 [M(³⁵Cl₂³⁷Cl₂)+H]⁺, 571.9 [M(³⁵Cl³⁷Cl₃)+H]⁺, 573.9 [M(³⁷Cl₄)+H]⁺; Anal. Calcd for C₂₈H₂₇Cl₄NO₃ (567.3): C, 59.28; H, 4.80; N, 2.47. Found: C, 57.66; H, 4.95; N, 2.31.

3.4. Preparation of *N,N*-(Tetrachlorophthaloyl)dehydroabietylamine *p*-Tosylhydrazone (**4**)

To a solution of compound **3** (3 g, 5.288 mmol) in benzene (120 mL) and ethanol (30 mL), *p*-toluenesulfonyl hydrazide (1.65 g, 8.86 mmol) and *p*-toluenesulfonic acid (82 mg, 0.476 mmol) were added. The reaction mixture was stirred and refluxed during 8 h under N₂. After cooling to room temperature, the mixture was concentrated under vacuum, cooled in an ice bath and the precipitate was collected by filtration, and washed with ethanol. The crude product was purified by column chromatography on silica gel (toluene-ethyl acetate, 20:0.4) to yield **4** as a white solid (3.41 g, 87.8%), m.p. 218–220 °C. IR $\nu_{\max}/\text{cm}^{-1}$: 3224, 3065, 2927, 2860, 1779, 1719, 1595, 1489, 1433, 1380, 1329, 1199, 1163, 1086, 1017, 978, 914, 810, 737, 708, 664, 631, 574, 541, 498, 468; $^1\text{H-NMR}$: δ 8.08 (s, 1H, NH), 8.02 (d, $J = 8.4$ Hz, 2H, *o*-HArSO₂-), 7.79 (d, $J = 1.8$ Hz, 1H), 7.33 (d, $J = 8.1$ Hz, 2H, *m*-HArSO₂-), 7.14 (dd, $J = 8.1, 1.9$ Hz, 1H), 7.10 (d, $J = 8.2$ Hz, 1H), 3.61 (d, $J = 14.1$ Hz, 1H), 3.50 (d, $J = 14.1$ Hz, 1H), 3.15 (dd, $J = 17.3, 4.1$ Hz, 1H), 2.87 (septet, $J = 6.9$ Hz, 1H), 2.43 (s, 3H, CH₃ArSO₂-), 2.40 (dd, $J = 17.2, 13.4$ Hz, 1H), 2.21 (br d, $J = 12.5$ Hz, 1H), 1.73–1.63 (m, 4H), 1.51 (dd, $J = 13.3, 3.9$ Hz, 1H), 1.44–1.35 (m, 1H), 1.24 (d, 3H, $J = 6.9$ Hz), 1.23 (d, 3H, $J = 6.9$ Hz), 1.14 (s, 3H), 1.08 (s, 3H); $^{13}\text{C-NMR}$: δ 164.46 (2C=O, imide), 153.38 (C=N), 148.89, 146.25, 143.90 (*p*-ArSO₂-), 140.15 (2C, -N(CO)₂C₆Cl₄), 135.69 (*p*-ArCH₃), 129.77, 129.64 (2C, -N(CO)₂C₆Cl₄), 129.42 (2C, *m*-ArSO₂-), 128.51, 128.42 (2C, *o*-ArSO₂-), 127.34 (2C, -N(CO)₂C₆Cl₄), 123.09, 122.61, 49.36, 42.78, 39.44, 37.28, 37.27, 37.11, 33.53, 23.90, 23.72, 23.63, 21.58 (CH₃ArSO₂-), 19.03, 18.02; TOF MS (ES⁺) m/z 733.9 ([M(³⁵Cl₄)+H]⁺), 735.9 ([M(³⁵Cl₃³⁷Cl)+H]⁺), 737.9 ([M(³⁵Cl₂³⁷Cl₂)+H]⁺), 739.9 ([M(³⁵Cl³⁷Cl₃)+H]⁺). Anal. Calcd for C₃₅H₃₅Cl₄N₃O₄S (735.5): C, 57.15; H, 4.80; N, 5.71. Found: C, 57.53; H, 4.71; N, 5.86.

3.5. Preparation of 7-C₆₀-Adduct of *N,N*-(Tetrachlorophthaloyl)dehydroabietylamine (**5**)

Compound **4** (408.9 mg, 0.556 mmol) was dissolved in dry pyridine (7 mL) in a dried three-necked flask under N₂. Then, NaOMe (31.2 mg, 0.578 mmol) was added, and the mixture was stirred for 15 min at room temperature. A solution of C₆₀ (200 mg, 0.278 mmol) in chlorobenzene (55 mL) was added and the mixture was stirred at 70 °C for 24 h. After cooling to room temperature the solvent was evaporated *in vacuo*, the residue was column chromatographed on silica gel, pre-eluted with CS₂ to

remove unreacted C₆₀ (67.7 mg) and then with CS₂-CHCl₃ (10:1) to give **5** as a dark brown solid (145 mg, 41%). IR $\nu_{\max}/\text{cm}^{-1}$: 3430, 2923, 2858, 1776, 1721, 1628, 1559, 1514, 1459, 1427, 1372, 1334, 1163, 1059, 893, 825, 740, 555, 526, 472; UV-vis (CHCl₃) $\lambda_{\max}$ (nm): 697.00, 493.00, 436.50; ¹H-NMR: δ 8.40 (d, J = 1.8 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.28 (dd, J = 8.1, 1.8 Hz, 1H), 3.88 (d, J = 13.6 Hz, 1H), 3.65 (dd, J = 14.1, 10.5 Hz, 1H), 3.59 (d, J = 13.6 Hz, 1H), 2.99 (septet, J = 6.7 Hz, 1H), 2.39 (br d, J = 11.9 Hz, 1H), 1.97 (dd, J = 10.3, 9.2 Hz, 1H), 1.86 (s, 3H), 1.85–1.79 (m, 2H), 1.79–1.74 (m, 1H), 1.58 (br d, J = 13.0 Hz, 1H), 1.53–1.47 (m, 1H), 1.32 (d, J = 7.0 Hz, 3H), 1.31 (s, 3H), 1.30 (d, J = 6.8 Hz, 3H); ¹³C-NMR: δ 164.51 (2C=O, imide), 150.74, 150.35, 149.89, 147.97, 147.53, 145.99, 145.92, 145.43, 145.27, 145.24, 145.21, 145.17, 145.02, 144.96, 144.89, 144.78, 144.68, 144.21, 144.19, 143.97, 143.87, 143.68, 143.25, 143.19, 143.16, 143.06, 143.01, 142.84, 142.76, 142.24, 142.18, 142.13, 142.06, 141.87, 141.40, 141.15, 141.04, 140.84, 140.35 (2C, -N(CO)₂C₆Cl₄), 140.22, 138.59, 138.51, 137.94, 137.82, 132.15, 129.76 (2C, -N(CO)₂C₆Cl₄), 127.52 (2C, -N(CO)₂C₆Cl₄), 126.42, 126.09, 123.40, 84.80, 77.66, 50.45, 48.67, 44.61, 40.89, 39.48, 38.83, 37.52, 33.92, 28.35, 24.49, 23.70, 22.50, 18.89, 18.18; MALDI-TOF MS (matrix: CHCA, reflectron negative) m/z 1269.4 M[−](³⁵Cl₄), 1271.4 M[−](³⁵Cl₃³⁷Cl), 1273.4 M[−](³⁵Cl₂³⁷Cl₂), 1275.4 M[−](³⁵Cl³⁷Cl₃); Anal. Calcd for C₈₈H₂₇Cl₄NO₂ (1271.97): C, 83.09; H, 2.14; N, 1.10. Found: C, 82.48; H, 2.20; N, 1.04.

4. Conclusions

In conclusion, the new compound **5** was synthesized from dehydroabietylamine, the assignments of the proton and carbon signals for 7-C₆₀-adduct of *N,N*-(tetrachlorophthaloyl)dehydroabietylamine were made possible by using 1D and 2D NMR techniques including ¹H-, ¹³C-NMR, COSY, ROESY, HSQC and HMBC experiments. The two peaks at δ_{C} 84.80, 77.66 ppm in the ¹³C-NMR spectra correspond to the sp³-hybridized bridgehead carbons on the cyclopropyl moiety. This pattern is unambiguously diagnostic for *C_I* symmetric structure with 6,6-junction. All the spectral data support and confirm the proposed structure of the target compound.

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Sample Availability: Samples of the compounds **2–5** are available from the authors.

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