

# $^1\text{H}$ and $^{13}\text{C}$ NMR assignments for a series of Diels–Alder adducts of anthracene and 9-substituted anthracenes

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## Introduction

One of the characteristic features of anthracene behaving as a diene is its ability to easily undergo Diels–Alder reaction with various dienophiles across the 9 and 10 positions, under both thermal and photochemical conditions, to produce bridged adducts.<sup>[1–4]</sup> This enables the access to large diversity of compounds with a wide range of applications. In fact, Diels–Alder adducts of anthracene have been used as photoactivated chiral auxiliaries,<sup>[2,4]</sup> as a key component in the synthesis of carbosiloxane dendrimers,<sup>[5–7]</sup> as well as potential anxiolytic drug candidates.<sup>[8–10]</sup> They also found application as tetrapodal molecular switches and motors,<sup>[11]</sup> fluorescent sensors,<sup>[12]</sup> and in ‘click’ chemistry,<sup>[13–15]</sup> to name just a few. Because many of these applications involve the incorporation of anthracene into a much larger macromolecule mainly through a Diels–Alder reaction, monitoring such transformations using NMR techniques requires an accurate appreciation of the chemical shifts of protons and carbons in these materials. Thus, the total assignment of protons and carbons in a series of Diels–Alder adducts of anthracene and 9-substituted anthracene derivatives, with either 1-octylmaleimide or maleic anhydride as a dienophile, assisted by their crystal structures could serve as a reference for such an endeavor.

An octylmaleimide Diels–Alder adducts of anthracene (**1**) and a 9-substituted derivative (**2**) were obtained by reacting the corresponding anthracene derivative with 1-octylmaleimide as described in Scheme 1.

The two other compounds (**3** and **4**) are Diels–Alder adducts of 9-substituted anthracene, obtained by reacting the corresponding anthracene derivative with maleic anhydride (Scheme 2). The total assignment of protons and carbons for all these compounds was achieved through a combination of  $^1\text{H}$ , DEPTQ135, COSY60SW, HSQCEDET, and HMBCLPND, assisted by single crystal X-ray diffraction (Fig. 1), which are reported here for the very first time.

## Experimental methods

### Synthesis

All these compounds were prepared by refluxing one equivalent of the corresponding anthracene derivatives with one equivalent of either 1-octylmaleimide (Scheme 1) or maleic anhydride (Scheme 2)

in tetrahydrofuran for 6 h to produce the expected adducts in good yields after purification on a silica gel column using a mixture of hexanes and dichloromethane: **1** (86%, mp 134.5–135.7 °C), **2** (89%, mp 80.0–81.2 °C), **3** (85%, mp 164.1–164.5 °C), and **4** (91%, mp 131.4–131.6 °C). Melting points were measured on a Barnstead digital capillary melting point apparatus (Electrothermal 9100, Bibby Scientific, Burlington, New Jersey, US), calibrated with benzoic acid ( $\geq 99.5\%$ ) [mp 122.38 °C (lit), obtained 122.2–122.4 °C].

All the starting materials were from Sigma-Aldrich, Milwaukee, Wisconsin, USA and were used without any further purification.

### Crystal structure

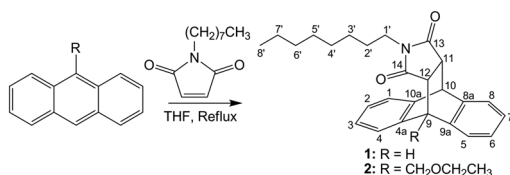
Single crystals of various samples (**1** and **2**) suitable for X-ray structure determination were mounted on the tip of a glass fiber using silicon grease, and intensity data were recorded at 293 K on a STOE IPDS-2T diffractometer using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Intensity data for all crystals were readily indexed, and the structures were solved by direct method and refined by full-matrix least-squares techniques in the SHELXTL<sup>[16]</sup> package of programs. The structure solutions revealed the positions of all non-hydrogen atoms within the crystal with some of the hydrogen positions. In subsequent refinement steps, the positions of the remaining hydrogen atoms were deduced from difference Fourier syntheses. The software Diamond<sup>[17]</sup> was utilized to create the graphic representations of the crystal structures with ellipsoid representations (50% probability level) for all non-hydrogen atoms.

Compound **1** crystallizes in the orthorhombic crystal system with  $a = 11.197(2) \text{ \AA}$ ,  $b = 8.3999(17) \text{ \AA}$ , and  $c = 44.997(9) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$  space group *Pbca*, while compound **2** crystallizes in the triclinic crystal system with  $a = 11.137(2) \text{ \AA}$ ,  $b = 11.184(2) \text{ \AA}$ ,  $c = 11.502(2) \text{ \AA}$ ,

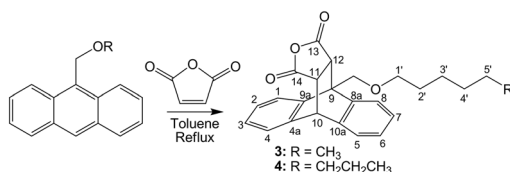
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**Scheme 1.** Synthesis of *N*-octylmaleimide Diels–Alder adducts of anthracene and a derivative.



**Scheme 2.** Synthesis of maleic anhydride Diels–Alder adducts of anthracene.

$\alpha = 93.16(3)^\circ$ ,  $\beta = 100.04(3)^\circ$ , and  $\gamma = 115.20(3)^\circ$ , space group *P*-1. Cambridge Crystallographic Data Centre (CCDC) 1052506 and CCDC 1052505 contain the supplementary crystallographic data for compounds **1** and **2**, and copies of these materials can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, <http://www.ccdc.am.ac.uk>.

### NMR measurements

Nuclear magnetic resonance data were collected on a Bruker Ascend<sup>TM</sup>-400 spectrometer operating at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C. The concentration of all samples was 20 mg/0.5 ml of CDCl<sub>3</sub>, and the chemical shifts were referenced to the TMS, used as the internal standard. The NMR data were recorded at 300 K, with chemical shifts ( $\delta$ ) reported in parts per million and coupling constants (*J*) in hertz. The <sup>1</sup>H NMR spectra were recorded with a spectral width of 8.012 kHz, 64 K data points, relaxation delay of 6.50  $\mu$ s, and a 30° excitation pulse width of 4.6  $\mu$ s. Whereas the <sup>13</sup>C NMR (DEPTQ135) spectra were recorded with a spectral width of 24.038 kHz, 64 K data points, relaxation delay of 6.50  $\mu$ s, and a pulse width of 10.0  $\mu$ s. The gradient-selected COSY60SW were recorded with a spectral width of 8.012 kHz, 2 K data points, relaxation delay of 6.50  $\mu$ s, and a 30° excitation pulse width of 4.6  $\mu$ s, with a qsine multiplication applied in both dimensions. The gradient-selected HSQC (HSQCEDET) spectra were recorded in mode echo–antiecho, with 80 transients over 256 increments (zero-filled to 1 K) and 1 K data points with spectral widths of 8.012 kHz in F2 and 24.038 kHz in F1, and the one-bond heteronuclear coupling value was set to 145 Hz. The recycle delay was 1.5 s, with a qsine multiplication applied in both dimensions. The gradient-selected HMBC (HMBCLPND) spectra were also

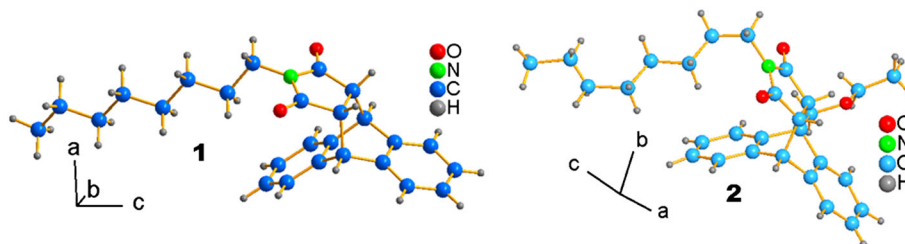
recorded in mode echo–antiecho, with 256 transients over 160 increments (zero-filled to 1 K) and 4 K data points with spectral widths of 8.012 kHz in F2 and 24.038 kHz in F1. The recycle delay was 1.5 s, with a sine multiplication applied in F2 and a qsine multiplication applied in F1.

## Results and discussion

The structures of compounds **1** and **2** as well as the numbering used for protons and carbons assignment are shown in Scheme 1, while that of compounds **3** and **4** are shown in Scheme 2. The structures of compounds **1** and **2** were also unambiguously elucidated by single crystal X-ray diffraction. The molecular structures are shown in Fig. 1, with displacement ellipsoids drawn at a 50% probability level and H atoms as small spheres.

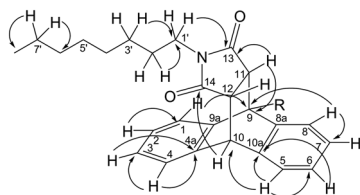
Obtained as transparent crystals, **1** is the only compound of this series to lack additional substituent at the 9 position. However, because the *N*-alkylmaleimide portion of the molecule is bent toward one of the aromatic rings of the anthracene core as shown by the crystal structure (Fig. 1), the protons and carbons of the aromatic rings, which otherwise would have been equivalent because of the symmetry plan across positions 9 and 10, appeared to display four different doublet of doublets of 2H each in the <sup>1</sup>H NMR of **1**. The first signal appears at 7.36 ppm (2H, dd, *J* = 8.4 and 2.0 Hz) attributable to the protons at positions 1 and 4 on the aromatic ring toward which *N*-alkylmaleimide portion of the molecule is bent (see the numbering in Scheme 1). These two protons are attached to C-1 and C-4 (both at 124.2 ppm) and appeared to couple with the two protons (H-2 and H-3) at 7.15 ppm (2H, dd, *J* = 8.4, and 7.6 Hz) as indicated by the coupling constants and the COSY spectrum. H-2 and H-3 attached to C-2 and C-3 both appearing at 126.7 ppm as indicated by the HSQC spectrum. The four protons from the other aromatic rings appear at 7.26 ppm (2H, dd, *J* = 8.8 and 1.7 Hz, H-5 and H-8) attached to the carbons at 125.0 ppm (C-5 and C-8) and at 7.01 ppm (2H, dd, *J* = 8.8 and 7.8 Hz, H-6 and H-7) attached to the carbons at 126.9 ppm (C-6 and C-7), respectively. The protons at positions 9 and 10 on the central ring of anthracene appear as a doublet of 2H at 4.77 ppm (2H, d, *J* = 6.6 Hz, H-9 and H-10) and are attached to the carbons at 45.6 ppm (C-9 and C-10), while the two protons of maleimide also appear as a doublet at 3.15 ppm (2H, *J* = 6.6 Hz, H-11 and H-12) and are attached on the carbons at 46.8 ppm (C-11 and C-12).

As for the *N*-alkyl side chain, H-1' appears as a triplet of 2H at 3.06 ppm (2H, t, *J* = 7.6 Hz, H-1') and is attached to the carbon at 38.5 ppm. One of the most intriguing observations of this study is the fact that H-2' (0.73 ppm, 2H, q\*, *J* = 7.6 Hz) and H-3' (0.86 ppm, 2H, q\*, *J* = 7.6 Hz) appeared to be more shielded than the terminal methyl protons H-8' (0.88 ppm, 3H, t, *J* = 7.4 Hz). The only obvious explanation for this unusual shielding comes from the crystal structure that indicates that, because of the geometry of that part of the



**Figure 1.** A representation of the molecular structure of **1** and **2**. Ellipsoids correspond to 50% probability level.

molecule, these protons appear to be bent toward the centroid of one of the aromatic rings and lie in the region where the anisotropy current of the aromatic system opposes the external magnetic field, resulting in an unusual shielding for these protons. These protons are attached to the carbons at 27.2 ppm (C-2') and 26.4 ppm (C-3'), respectively. The chemical shifts of H-4' (1.07 ppm, 2H, m), H-5' (1.17 ppm, 2H, m), H-6' (1.22 ppm, 2H, m), and H-7' (1.29 ppm, 2H, m) are consistent with the expectation. These protons are attached to the carbons at 29.2 ppm (C-4<sup>ab</sup>), 29.1 (C-5<sup>ab</sup>), 31.9 (C-6'), and 22.6 (C-7'), while the terminal methyl protons are attached to the carbon at 14.1 ppm. These assignments are based on a combination of



**Scheme 3.** Key long-range (HMBC) correlations in compounds **1** and **2**.

COSY, HSQC, and HMBC data. However, C-4' and C-5' could not be unambiguously assigned and thus are interchangeable.

Quaternary carbons were assigned using HMBC data. In fact, the carbons at 138.8 ppm display long-range correlations with the protons at 7.26 and 7.01 ppm and was assigned as C-8a and C-9a, while the carbons at 141.6 ppm display long-range correlations with the protons at 7.36 and 7.15 ppm and was assigned as C-4a and C-10a. The only carbonyl signal at 176.9 ppm was assigned to C-13 and C-14. Overall, **1** displays a well-balanced symmetry, despite the fact that the maleimide portion of the molecule is bent toward one of the aromatic rings.

When compared with **1**, compound **2** displays several similarities in chemical shifts despite the side chain at position 9. In fact, the major impact of 9-substitution is the disappearance of the plane of symmetry observed in **1**, resulting in all the aromatic protons in **2** been non-equivalent. Because the maleimide portion of the molecule is still bent toward one of the aromatic rings, the eight aromatic protons appear separated from each other, although some of them overlap. In fact, H-1 appears as a doublet of doublets at 7.56 ppm (1H,  $J = 7.2$  and 2.1 Hz), H-2 as a doublet of doublets at 7.16 ppm ( $J = 8.4$  and 7.2 Hz), and H-3 as a doublet of doublets at 7.20 ppm ( $J = 8.8$  and 7.2 Hz), while H-4 also appears as a doublet

**Table 1.**  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (100 MHz), HMBC, and COSY spectra data ( $\text{CDCl}_3$ ,  $\delta$  in ppm,  $J$  in Hz) of **1** and **2**

		<b>1</b>			<b>2</b>	
C No	$\delta_{\text{H}}$	$\delta_{\text{C}}$	HMBC	COSY	$\delta_{\text{H}}$	$\delta_{\text{C}}$
1	7.36 (dd, $J = 8.4, 2.0$ , H-1)	124.2 CH	C-2, C-3, C-10a, C-10	H-2	7.56 (dd, $J = 7.2, 2.1$ , H-1)	124.2 CH
2	7.15 (dd, $J = 8.4, 7.6$ , H-2)	126.7 CH	C-1, C-4, C-10a	H-1	7.16 (dd, $J = 8.4, 7.2$ , H-2)	126.7 CH
3	7.15 (dd, $J = 8.4, 7.6$ , H-3)	126.7 CH	C-1, C-4, C-4a	H-4	7.20 (dd, $J = 8.8, 7.2$ , H-3)	126.8 CH
4	7.36 (dd, $J = 8.4, 2.0$ , H-4)	124.2 CH	C-2, C-3, C-4a, C-9	H-3	7.33 (dd, $J = 8.8, 1.7$ , H-4)	123.6 CH
4a	—	141.6 C	—	—	—	139.0 C
5	7.26 (dd, $J = 8.8, 1.7$ , H-5)	125.0 CH	C-6, C-7, C-9a, C-9	H-6	7.13 (dd, $J = 8.4, 1.8$ , H-5)	122.2 CH
6	7.01 (dd, $J = 8.8, 7.8$ , H-6)	126.9 CH	C-5, C-8, C-9a	H-5	7.09–7.11 (m, H-6 or H-7)	126.4 <sup>a</sup> CH
7	7.01 (dd, $J = 8.8, 7.8$ , H-7)	126.9 CH	C-5, C-8, C-8a	H-8	7.09–7.11 (m, H-6 or H-7)	126.5 <sup>a</sup> CH
8	7.26 (dd, $J = 8.8, 1.7$ , H-8)	125.0 CH	C-6, C-7, C-8a, C-10	H-7	7.27 (dd, $J = 8.0, 1.2$ , H-8)	125.2 CH
8a	—	138.8 C	—	—	—	142.3 <sup>a</sup> C
9	4.77 (d, $J = 6.6$ , H-9)	45.6 CH	C-4a, C-9a, C-12	H-12	—	48.8 C
9a	—	138.8 C	—	—	—	142.3 <sup>a</sup> C
10	4.77 (d, $J = 6.6$ , H-10)	45.6 CH	C-8a, C-10a, C-11	H-11	3.31 (d, $J = 8.4$ , H-10)	45.9 CH
10a	—	141.6 C	—	—	—	139.0
11	3.15 (d, $J = 6.6$ , H-11)	46.8 CH	C-8a, C-10, C-10a, C-13	H-10	4.72 (d, $J = 6.8$ , H-11)	45.9 CH
12	3.15 (d, $J = 6.6$ , H-12)	46.8 CH	C-4a, C-9, C-9a, C-14	H-9	3.19 ( $J = 8.4, 6.8$ , H-11)	47.7 CH
13	—	176.9 C	—	—	—	177.0 C
14	—	176.9 C	—	—	—	176.2 C
1'	3.06 (t, $J = 7.6$ , H-1')	38.5 CH <sub>2</sub>	C-13/C-14, C-2', C-3'	H-2'	3.06 (t, $J = 7.6$ , H-1')	38.5 CH <sub>2</sub>
2'	0.73 (q*, $J = 7.6$ , H-2')	27.2 CH <sub>2</sub>	C-1', C-3'	H-1', H-3'	0.76 (q*, $J = 7.2$ , H-2')	27.2 CH <sub>2</sub>
3'	0.86 (q*, $J = 7.6$ , H-3')	26.4 CH <sub>2</sub>	C-1', C-2'	H-2', H-4'	0.80 (q*, $J = 7.4$ , H-3')	26.5 CH <sub>2</sub>
4'	1.07 (m, H-4')	29.1 <sup>a</sup> CH <sub>2</sub>	C-6', C-3'	H-3', H-5'	1.05 (m, H-4')	29.0 <sup>a</sup> CH <sub>2</sub>
5'	1.17 (m, H-5')	29.0 <sup>a</sup> CH <sub>2</sub>	C-6', C-3', C-7'	H-4', H-6'	1.16 (m, H-5')	28.9 <sup>a</sup> CH <sub>2</sub>
6'	1.22 (m, H-6')	31.9 CH <sub>2</sub>	C-4'/C-5', C-7', C-8'	H-5', H-7'	1.18 (m, H-6')	31.8 CH <sub>2</sub>
7'	1.29 (m, H-7')	22.6 CH <sub>2</sub>	C-4'/C-5', C-8'	H-6', H-8'	1.29 (m, H-7')	22.6 CH <sub>2</sub>
8'	0.88 (t, $J = 7.4$ , H-8')	14.1 CH <sub>3</sub>	C-6', C-7'	H-7'	0.88 (t, $J = 6.8$ , H-8')	14.1 CH <sub>3</sub>
CH <sub>2</sub> -O	—	—	—	—	4.76 (1H, $J = 1.2$ Hz) 4.80 (1H, $J = 1.2$ Hz)	67.5 CH <sub>2</sub>
OCH <sub>2</sub> CH <sub>3</sub>	—	—	—	—	3.91 (q, $J = 7.2$ , OCH <sub>2</sub> )	67.2 CH <sub>2</sub>
OCH <sub>2</sub> CH <sub>3</sub>	—	—	—	—	1.38 (t, $J = 7.2$ , OCH <sub>2</sub> CH <sub>3</sub> )	15.4 CH <sub>3</sub>

q\*, quintet.

<sup>a</sup>Chemical shifts are interchangeable.

of doublets of 1H at a higher chemical (7.33 ppm,  $J=8.8$  and 1.7 Hz). These protons are attached to the carbons at 124.2 (C-1), 126.7 (C-2), 126.8 (C-3), and 123.6 ppm (C-4). On the other hand, H-5 appears as a doublet of doublets of 1H at 7.13 ppm ( $J=8.4$  and 1.8 Hz), while H-6 and H-7 overlap around 7.09–7.11 ppm as a multiplet of 2H and H-8 as a doublet of doublets at 7.27 ppm ( $J=8.0$  and 1.2 Hz). These protons are attached to the carbons at 122.2 (C-5), 126.4 (C-6<sup>a</sup>), 126.5 (C-7<sup>a</sup>), and 125.2 ppm (C-8), with C-6 and C-7 that could not be unambiguously assigned and thus are interchangeable. H-10 appears as a doublet of 1H at 3.31 ppm ( $J=8.4$  Hz) and is attached to the carbon at 45.9 ppm, H-11 displays a doublet of 1H at 4.72 ppm ( $J=6.8$  Hz) and is attached to the carbon at 45.9 ppm, while H-12 appears as a doublet of doublets at 3.19 ppm ( $J=8.4$  and 6.8 Hz) and is attached to the carbon at 47.7 ppm. The *N*-alkyl side chain is also very similar to that of compound **1**, with H-1' appearing as a triplet of 2H at 3.06 ppm ( $J=7.6$  Hz) and attached to the carbon at 38.5 ppm. H-2' (0.76 ppm, 2H, q\*,  $J=7.2$  Hz) and H-3' (0.80 ppm, 2H, q\*,  $J=7.4$  Hz) are also more shielded than the proton of the terminal methyl of the side chain (0.88 ppm, 3H, t,  $J=6.8$  Hz, H-8') and are attached to the carbons at 27.2 ppm (C-2'), 26.5 ppm (C-3') and 14.1 ppm (C-8'). H-4' (1.05 ppm), H-5' (1.16 ppm), H-6' (1.18 ppm), and H-7' (1.29 ppm) all appear as multiplets and are attached to the carbons at 29.0 (C-4<sup>a</sup>), 28.9 (C-5<sup>a</sup>), 31.8 (C-6'), and 22.6 (C-7'). On the other

hand, the 2H of the CH<sub>2</sub> of the side chain attached at C-9 is non-equivalent because of the substitution on C-9 and thus displays two doublets of 1H each at 4.76 ppm ( $J=1.2$  Hz) and 4.80 ppm ( $J=1.2$  Hz). Both protons are attached to the carbon at 67.5 ppm. Finally, the ethoxy group displays a quartet of 2H at 3.91 ppm ( $J=7.2$  Hz) and a triplet of 3H at 1.38 ppm ( $J=7.2$  Hz) and are linked to the carbons at 67.2 and 15.4 ppm, respectively.

Quaternary carbons were attributed based on the HMBC data. For example, the carbon at 48.8 ppm displays correlation with H-11 (4.72 ppm), two aromatic protons H-1 (7.56 ppm) and H-8 (7.26 ppm) as well as with the CH<sub>2</sub> of the side chain attached on position 9 and was thus assigned as C-9. The carbon at 139.0 ppm that displays correlation with H-5 and H-6 was attributed to C-10a, while the one at 139.4 ppm shows correlations with H-4 and H-3 and was attributed to C-4a. The carbons at 142.3 ppm that display correlations with the protons H-1, H-2 and H-8, H-7 from both aromatic rings could not be distinguished and were attributed to C-8a and C-9a. The carbonyl at 176.2 ppm that displays correlations with H-10 and H-12 was attributed to C-14, while the other one at 177.0 ppm that displays correlations only with C-11 and C-12 was attributed to C-13. Key long-range correlations in compounds **1** and **2** are shown in Scheme 3, while the NMR data are summarized in Table 1.

Although *N*-alkylmaleimide is replaced by maleic anhydride in the preparation of compounds **3** and **4**, they display many

**Table 2.** <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz), HMBC, and COSY spectra data (CDCl<sub>3</sub>, δ in ppm,  $J$  in Hz) of **3** and **4**

		<b>3</b>			<b>4</b>	
C No	δ <sub>H</sub>	δ <sub>C</sub>	HMBC	COSY	δ <sub>H</sub>	δ <sub>C</sub>
1	7.53 (dd, $J=7.6, 1.8, H-1$ )	124.3 CH	C-2, C-3, C-9, C-9a	H-2, H-3	7.52 (dd, $J=7.2, 1.8, H-1$ )	124.3 CH
2	7.13–7.17 (m, H-2) <sup>a</sup>	126.7 <sup>a</sup> CH	C-1, C-3, C-4, C-9a	H-1, H-4	7.12–7.17 (m, H-2) <sup>a</sup>	126.7 <sup>a</sup> CH
3	7.13–7.17 (m, H-3) <sup>a</sup>	126.8 <sup>a</sup> CH	C-1, C-2, C-4, C-4a	H-1, H-4	7.12–7.17 (m, H-2) <sup>a</sup>	126.7 <sup>a</sup> CH
4	7.33 (dd, $J=8.4, 1.9, H-4$ )	123.8 CH	C-2, C-3, C-4a, C-9a, C-10	H-3, H-2	7.30 (dd, $J=8.2, 2.0, H-4$ )	123.7 CH
4a	—	138.8 C	—	—	—	138.8 C
5	7.31 (dd, $J=8.6, 2.4, H-5$ )	125.3 CH	C-6/C-7, C-8a, C-10, C-10a	H-6, H-7	7.28 (dd, $J=8.4, 1.8, H-5$ )	123.8 CH
6	7.11–7.14 (m, H-6) <sup>a</sup>	127.5 <sup>a</sup> CH	C-5, C-8, C-10a	H-5, H-8	7.12–7.15 (m, H-6) <sup>a</sup>	127.4 <sup>a</sup> C
7	7.11–7.14 (m, H-7) <sup>a</sup>	127.4 <sup>a</sup> CH	C-5, C-8, C-8a	H-5, H-8	7.12–7.15 (m, H-6) <sup>a</sup>	127.4 <sup>a</sup> C
8	7.22 (dd, $J=8.4, 2.3, H-8$ )	127.7 CH	C-6/C-7, C-8a, C-9	H-7, H-6	7.18 (dd, $J=7.8, 2.0, H-8$ )	127.1 CH
8a	—	141.1 C	—	—	—	141.4 C
9	—	48.7 C	—	—	—	48.6 C
9a	—	141.5 C	—	—	—	141.5 C
10	4.69 (d, $J=9.6, H-10$ )	45.6 CH	C-4, C-5, C-10a, C-11, C-12	H-11	4.67 (d, $J=9.6, H-10$ )	45.6 CH
10a	—	138.4 C	—	—	—	138.4 C
11	3.51 (dd, $J=9.2, 9.6, H-11$ )	48.6 CH	C-10, C-12, C-13, C-4a	H-10, H-12	3.43 (dd, $J=9.2, 9.6, H-11$ )	48.6 CH
12	3.68 (d, $J=9.2, H-12$ )	46.8 CH	C-9, C-9a, C-11, C-13/C-14	H-11	3.60 (d, $J=9.2, H-12$ )	46.7 CH
13	—	169.4 <sup>a</sup> C	—	—	—	169.4 <sup>a</sup> C
14	—	170.7 <sup>a</sup> C	—	—	—	170.7 <sup>a</sup> C
CH <sub>2</sub> -O	4.74 (d, $J=2.3$ ) 4.76 (d, $J=2.3$ )	66.9 CH <sub>2</sub>	C-1', C-9, C-12, C-8a, C-9a	—	4.72(d, $J=2.1$ ) 4.73 (d, $J=2.1$ )	66.9 CH <sub>2</sub>
1'	3.83 (t, $J=6.4, H-1'$ )	72.0 CH <sub>2</sub>	CH <sub>2</sub> , C-2', C-3'	H-2'	3.832 (t, $J=6.4, H-1'$ )	72.0 CH <sub>2</sub>
2'	1.73 (q*, $J=6.4, H-2'$ )	29.7 CH <sub>2</sub>	C-1', C-3', C-4'	H-1', H-3'	1.74 (q*, $J=6.4, H-2'$ )	29.7 CH <sub>2</sub>
3'	1.46 (m, H-3')	26.0 CH <sub>2</sub>	C-1', C-2', C-4', C-5'	H-2'	1.47 (m, H-3')	26.3 CH <sub>2</sub>
4'	1.32 (m, H-4')	22.7 CH <sub>2</sub>	C-2', C-3', C-5', C-6'	H-5'	1.44 (m, H-4')	29.4 CH <sub>2</sub>
5'	1.35 (m, H-5')	31.6 CH <sub>2</sub>	C-3', C-4', C-5'	H-4', H-6'	1.39 (m, H-5')	29.3 CH <sub>2</sub>
6'	0.91 (t, $J=6.8, H-6'$ )	14.0 CH <sub>3</sub>	C-4', C-5'	H-5'	1.38 (m, H-6')	22.6 CH <sub>2</sub>
7'	—	—	—	—	1.30 (m, H-7')	31.8 CH <sub>2</sub>
8'	—	—	—	—	0.89 (t, $J=6.4, H-6'$ )	14.13 CH <sub>3</sub>

q\*, quintet.

<sup>a</sup>Chemical shifts are interchangeable.

similarities with **1** and **2**. In fact, in both compounds, the protons on the aromatic ring of the anthracene core toward which the succinic moiety is bent appeared to be more deshielded than the counterparts, just like in **1** and **2**. On the other hand, it is not surprising that **3** and **4** display almost identical NMR data. For example, H-1 appears as doublet of doublets at 7.53 ppm (1H,  $J=7.6$ , and 1.8 Hz) and is attached to the carbon at 124.3 ppm (C-1) in **3**, while in **4**, it appears at 7.52 ppm (1H, dd,  $J=7.2$ , and 1.8 Hz) and is attached to the carbon at 124.3 ppm as well. H-2 and H-3 appear to overlap as a multiplet of 2H around 7.13–7.17 ppm and are attached to the carbons at 126.7 and 126.8 ppm (C-2<sup>a</sup> and C-3<sup>a</sup>) in **3**. As a result, the assignment of these two protons and the corresponding carbons are interchangeable. H-4 displays a doublet of doublets at 7.33 ppm (1H,  $J=8.4$ , and 1.9 Hz) and is attached to the carbon at 123.8 ppm (C-4). The protons from the other aromatic rings appear at 7.31 ppm (1H, dd,  $J=8.6$ , and 2.4 Hz) for H-5 and 7.22 ppm (1H, dd,  $J=8.4$ , and 2.3 Hz) for H-8, while H-6 and H-7 overlap as a multiplet between 7.11 and 7.14 ppm and could not be differentiated. These protons are attached to the carbons at 125.3 (C-5), 127.7 (C-8), 127.5 (C-6 or C-7), and 127.4 ppm (C-7 or C-6). H-10 displays a doublet at 4.69 ppm ( $J=9.6$  Hz) and is attached to the carbon at 45.6 (C-10); H-11 appears as a doublet of doublets at 3.51 ppm ( $J=9.2$  and 9.6 Hz) and is attached to the carbon at 48.6 ppm (C-11), while H-12 appears as a doublet at 3.68 ppm ( $J=9.2$  Hz) and is attached to the carbon at 46.8 ppm. As for the side chain attached at position 9, because of substitution on C-9, the 2H on the carbon linked to C-9 appears as two doublets at 4.74 ppm (1H,  $J=2.3$  Hz) and 4.76 ppm (1H,  $J=2.3$  Hz), with both protons attached to the same carbon at 66.9 ppm. The remaining of the side chain was assigned based on a combination of COSY, HSQC, and HMBC data similar to that used for **1** and **2**. Thus, H-1' displays a triplet of two protons at 3.83 ppm ( $J=6.4$  Hz) and is carried by the carbon at 72.0 ppm, H-2' at 1.73 ppm (2H, q\*,  $J=6.4$  Hz) attached to C-2' (29.7 ppm), H-3' at 1.46 ppm (2H, m) carried by C-3' (26.0 ppm), H-4' at 1.32 ppm (2H, m) attached to C-4' (22.7 ppm), H-5' as multiplet at 1.35 ppm (2H, m) carried by C-5' (31.6 ppm), and finally, H-6' as a triplet of 3H at 0.91 ppm ( $J=6.8$  Hz) attached to C-6' (14.0 ppm). Unlike the *N*-alkyl side chain in **1** and **2**, the chemical shifts here appeared to be consistent with the expectation, confirming that the side chain in this case is out of the way of the aromatic anisotropic current as suggested by the crystal structure from Fig. 1 (Compound **2**).

Based on long-range correlations observed in the HMBC spectrum of **3**, quaternary carbons were attributed as follows: 138.8 ppm (C-4a), 141.1 (C-8a), 48.7 ppm (C-9), 141.5 ppm (C-9a), and 138.4 ppm (C-10a), while C-13 (169.4 ppm) and C-14 (170.7 ppm) could not be indisputably assigned and thus are interchangeable. Needless to mention that the protons and carbons assignment in **4** are in many ways similar to that of **3**, and all the NMR data for both compounds are summarized in Table 2.

The results from this study indicate that the orientation of the maleimide or succinic anhydride moiety of the molecules discussed in this report has a significant impact on the chemical shift of the

aromatic protons of anthracene. Because during the Diels–Alder reaction, the two pi systems in presence approach each other face-to-face (endo-approach) to enable an easy overlap of orbitals required for the reaction to proceed, the maleimide or succinic anhydride portion of these compounds appears to be bent toward one of the aromatic rings. As a result, these aromatic protons are impacted by the anisotropic effect of the carbonyl and thus are more deshielded in comparison with the protons from other aromatic rings. Furthermore, in the case of maleimide derivatives, some protons of the *N*-alkyl side chain (H-2' and H-3'), due to the geometry of that part of the molecule, appear to lie in the region where the anisotropy current of the aromatic system opposes the external magnetic field, resulting in an unusual shielding for these protons that appear at a lower chemical shifts than the terminal methyl of the side chain.

### Acknowledgements

JF acknowledges support from the National Science Foundation under grant # MRI-1337372 and the Louisiana Board of Regent OPT-IN grant (LEQSF-EPS(2012)-OPT-IN-09). PFPP gratefully acknowledges financial support from the National Science Foundation Career Award DMR-1237550.

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### Supporting Information

Proton and carbon-13 (DEPT) spectra for each of these compounds are provided as supporting information, and may be found in the online version of this article at the publisher's website.