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Synthesis and transformations of a few 9-(pent-4-yn-1-yl)anthracene-type systems

Eason M. Mathew, Tomson Devassia, Sreedharan Prathapan, and Perupparampil A. Unnikrishnan*

Department of Applied Chemistry, CUSAT, Kochi-22, India
Email: paunni@gmail.com

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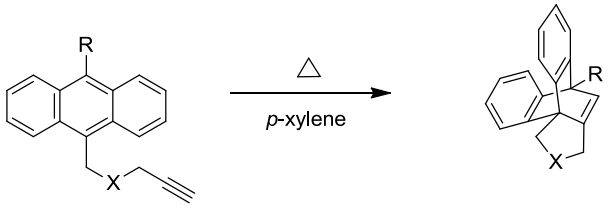
Abstract

9-(Pent-4-yn-1-yl)anthracene-type compounds can potentially undergo intramolecular Diels-Alder (IMDA) reaction to form 9,11-annulated dibenzobarrelenes. Herein we report the synthesis and IMDA reactions of several heteroatom incorporated 9-(pent-4-yn-1-yl)anthracene-type compounds.

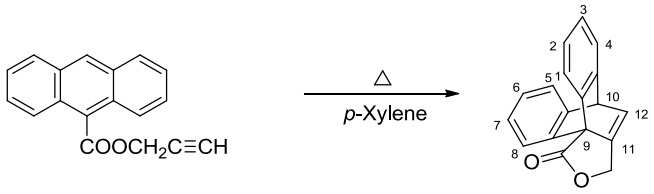


a) R = H b) R = CH_3 c) R = OCH_3 d) R = Ph
b) X= S, SO_2, O

Keywords: Dibenzobarrelenes, Intramolecular Diels-Alder (IMDA) reaction, tethered barrelenes, fused-ether, ester, sulfide and sulfone, ^{1}H and ^{13}C NMR

Introduction

Synthesis of bicyclo[2,2,2]octa-2,5,7-triene (barrelene) was first reported by Zimmerman[1] *et al* in 1960. Its barrel-shaped array of molecular orbitals and three ethylene units that are like staves attached to the two methine units attracted the attention of chemists. Synthesis of several barrelene derivatives, especially dibenzobarrelenes, exploited Diels-Alder reaction.[2-7] Intramolecular Diels-Alder (IMDA) reaction of suitably substituted anthracenes to give tricyclic systems that may be regarded as annulated barrelenes was first reported by Meek and Dann.[8,9] In 1980, Ciganek[5] reported a systematic investigation on the synthesis of 9,11-bridged dibenzobarrelene via IMDA reaction (Scheme **1**). Entropically favoured IMDA reaction generally proceeded with increased reaction rates under mild reaction conditions and the products were obtained in good yield.

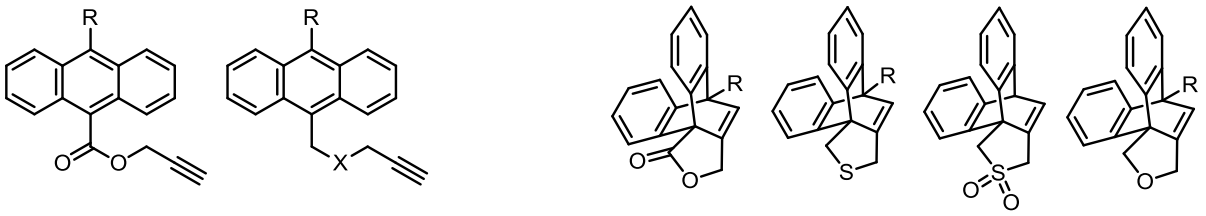


Scheme 1

Barrelene undergoes singlet mediated rearrangement to give cyclooctatetraene and triplet mediated di-π methane rearrangement[10-12] to afford semibullvalene. Initially, diverse photochemistry of dibenzobarrelenes occupied center stage and most attempts on dibenzobarrelene synthesis were directed towards deciphering the effect of substituents on controlling the photochemistry of barrelenes.[13] However chemistry of barrelenes has now transcended to encompass several fields including recently found applications in OLEDs[14] and photoluminescent materials.[15,16] Dibenzobarrelene based azaacenes found enhanced device performance than corresponding appended iptycene motifs.[14] Dibenzobarrelenes have been exploited in the biological field also; dibenzobarrelene fused with thiazole and thiophene entities showbiological activities[17] and are employed in drug discovery. In this context, we explored the possibility of synthesizing different types of 9,11-annulated barrelenes with ester, ether, sulfide and sulfone tethers constructed between 9- and 11-positions in the newly synthesized barrelenes.

Result and Discussion

We employed IMDA strategy to generate several 9,11-bridged dibenzobarrelenes where ester, sulfide, sulfone and ether linkages constituted the putative 9,11-bridges. As expected, IMDA reactions proceeded under mild conditions with high reaction rates. Structure of IMDA adducts were arrived at on the basis of spectral and analytical data and single crystal X-ray diffraction studies on a few representative examples. Structure of 9-(pent-4-yn-1-yl)anthracene-type compounds (**3**,**4**) and their IMDA products (**5**,**6**,**7**,**8**) are listed in Figure **1**. Steps involved in the synthesis of 9-(pent-4-yn-1-yl)anthracene-type compounds and their respective IMDA products are depicted in Scheme **2**.



3 **4** X= O, S **5** **6** **7** **8**

a) R=H **b**) R=CH_3 **c**) R=OCH_3 **d**) R=Ph

Figure 1

Aldehydes **9** acted as common precursors for our targets. They could be oxidized with *t*-butylhydroperoxide (TBHP) in *t*-butanol to give the corresponding acids **10** in high yields. Acids **10** were quantitatively converted to the corresponding acid chlorides **12** by treating with cyanuric chloride **11**. Reaction of **12** with propargyl alcohol gave the corresponding propargyl esters **13**. IMDA reactions of **13** was successfully performed in refluxing in *p*-xylene to giver ester bridged dibenzobarrelenes **5a-d** (Scheme **2**). Structures of all synthesized bridged esters were confirmed by spectral and analytical data. Compound **5a**,[5] exhibited in ^{1}H NMR a signal at δ 6.75, assigned to vinylic proton, whereas the bridgehead proton appeared as a doublet at δ 5.21. The eight aromatic protons appeared as a multiplet in the δ 6.95-7.45 region and the doublet due to two protons at δ 4.98 was assigned to methylene protons. The ^{1}H NMR spectrum of **5b** and **5c** showed a singlet due to three protons at δ 2.23 and δ 3.94 respectively, assigned to methyl and methoxy protons. Single Crystal XRD (ORTEP diagrams) obtained for compounds **5c** and **5d** are given in the Figure 2.

Sulfide bridged barrelenes **6** were also synthesized from aldehydes **9,** which after reduction with sodium borohydride/methanol gave corresponding alcohols **14.** Reaction between alcohol **14** and two equivalents of thiourea in acetone in the presence of 5N HCl followed by treatment sodium hydroxide gave thiol **16**. Anthracenethiols **16** dissolved in chloroform and KOH dissolved in methanol were mixed and stirred overnight followed by addition of propargyl bromide to generate propargyl sulfide **17** that underwent IMDA reaction in *p*-xylene to give bridged sulfides **6** (Scheme **2**). Structure of bridged sulfides **6** were confirmed by analytical results and spectral data.

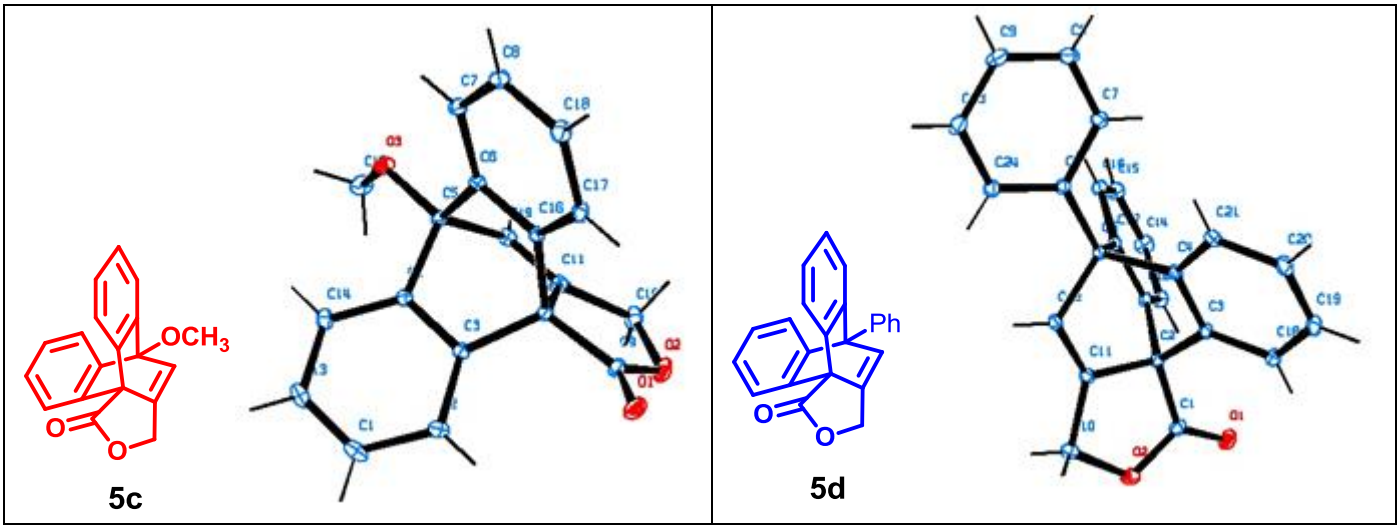
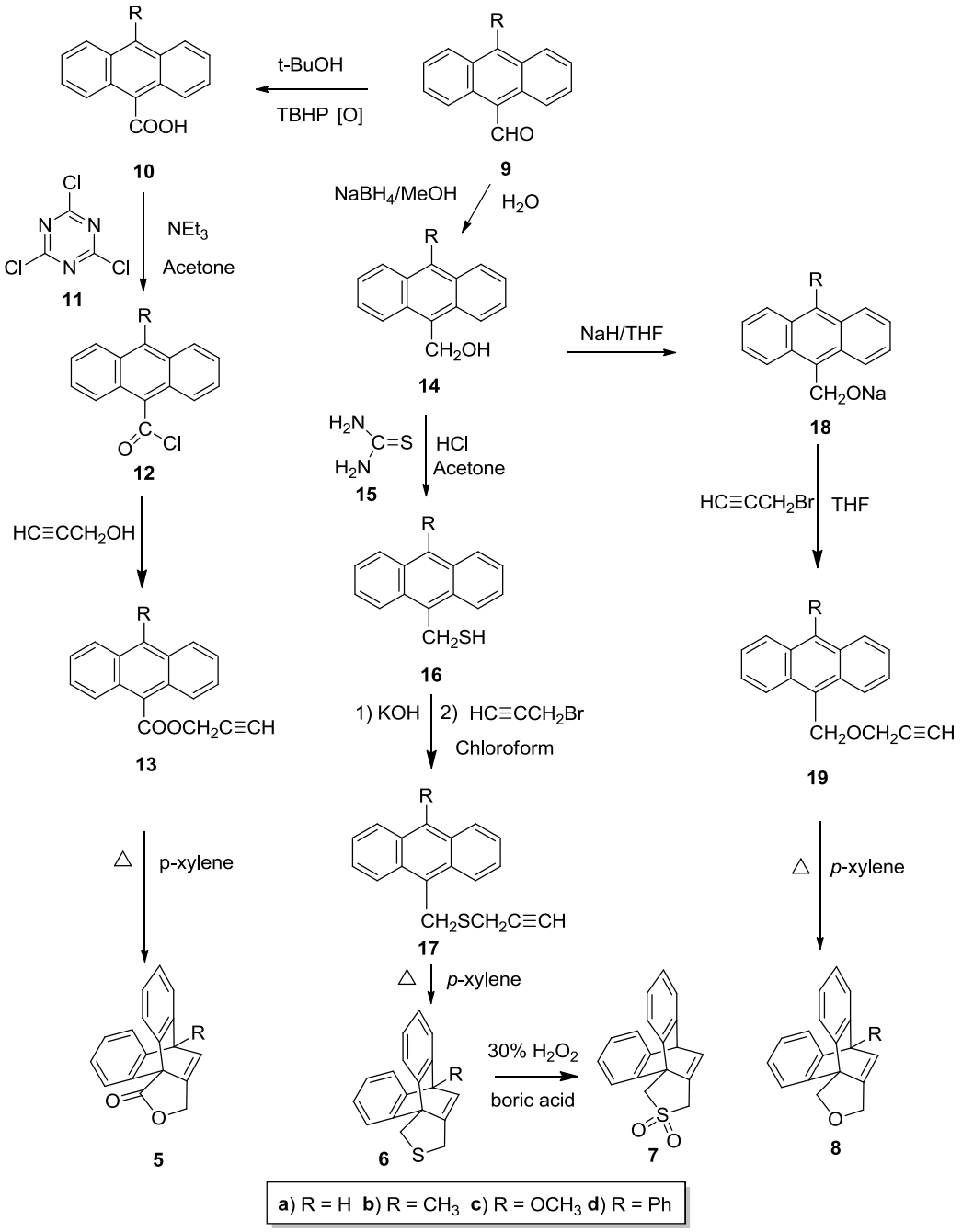


Figure 2

Boric acid catalyzed reaction of bridged sulfide **6a** with 30% hydrogen peroxide (Scheme **2**) resulted in the formation of corresponding bridged sulfone **7**. Structure of bridged sulfone **7** was elucidated on the basis of analytical results and spectral data. In the IR spectrum, sulfones generally show strong absorption bands at 1350-1300 cm^{-1} region due to asymmetric SO_2 stretching. The asymmetric SO_2 stretching of **7** occurred at 1318 cm^{-1}.

Sodium salt of anthracenemethanols **14** on reaction with propargyl bromide afforded the corresponding propargyl ethers **19**. IMDA reaction of **19** in refluxing *p*-xylene gave ether bridged dibenzobarrelenes **8** (Scheme **2**). Structures of bridged ethers **8** were also established on the basis of analytical results and spectral data.



Scheme 2

Conclusions

Several 9-(pent-4-yn-1-yl)anthracene-type compounds were successfully synthesized in high yields and were converted to the corresponding 9,11-bridged dibenzobarrelene derivatives in high yields via an entropically favored IMDA reaction. These bridged dibenzobarrelenes are potential candidates to examine regiochemical preferences in barrelene to semibullvalene rearrangement.

Experimental Section

General. Melting points are uncorrected and recorded on a Neolab melting point apparatus. Infrared spectra were recorded on Jasco 4100 and ABB Bomem (MB Series) FT-IR spectrometers. ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz Bruker Avance III FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using Elementar Systeme (Vario EL III). Molecular mass was determined by electron impact (EI) method using GC-MS (Agilent GC-7890A, Mass-5975C).

General procedure for the synthesis of bridged esters 5. Aldehydes **9** were synthesized via formylation[18,19] of anthracene by a known procedure. Aldehydes **9** (16 mmol) were oxidized with *t*-butyl hydroperoxide (1.92 mL, 20 mmol) and Se(IV) oxide (0.14 g, 1.25 mmol) (48-70h) in *t*-butanol at 75 ^{o}C. Undissolved materials were filtered off and filtrate was evaporated. The residue thus obtained was dissolved in dichloromethane (120 mL) and stirred with 5N HCl (200 mL) at room temperature for 4h. The aqueous and organic layers were separated and from the aqueous layer, the acids were extracted with dichloromethane. The organic solutions were collected and dried over anhydrous sodium sulfate and solvents were evaporated to obtain corresponding acids **10** (76-80 % yield, Table 1). Triethylamine (1.40 mL, 10 mmol) was added to a solution of **10** (10 mmol) and cyanuric chloride (1.84 g, 10 mmol) in acetone and stirred at room temperature for 1h to get the corresponding acid chloride **12**. Propargyl alcohol (0.60 mL, 10 mmol) was added into it (one pot reaction) and the mixture was stirred for 4h. The products obtained were washed with sodium bicarbonate and extracted with dichloromethane. Esters **13** were purified by silica gel column chromatography using a mixture of hexane and dichloromethane as eluents. Pure products were obtained in 82-90 % yield. Anthracene derivatives appended with acetylinic substituents **13** (5 mmol) were refluxed in *p*-xylene (10 mL) (48-64h) to generate corresponding barrelenes **5** that were purified by silica gel column chromatography using a mixture of hexane and dichloromethane as eluents (80-90% yield).

Table 1. Amount of reactants taken in each step of the reactions and yields of intermediates **10** and **13**

Aldehydes **9**, 16 mmol (g)	Acids **10**, 10 mmol (g)	Yield %	Targets **13**, 5 mmol (g)	Yield %
9a) 3.30	**10a**) 2.20	78	**13a**) 1.30	90
9b) 3.52	**10b**) 2.36	76	**13b**) 1.37	82
9c) 3.77	**10c**) 2.52	79	**13c**) 1.45	85
9d) 4.51	**10d**) 2.98	80	**13d**) 1.68	83

General procedure for the synthesis of bridged sulfides 6. Aldehydes **9** (16 mmol) dissolved in methanol, were reduced to corresponding alcohols **14** using sodium borohydride (1.1 g, 30 mmol) in methanol. Alcohols

14 (10 mmol) and two equivalents of thiourea (1.5 g, 20 mmol) were dissolved in acetone (25 mL) and 5N HCl (5 mL) was added to it and stirred overnight. The precipitate formed was filtered and treated with sodium hydroxide (10 %, 30 mL) solution and stirred at room temperature for 2h. Acidification with 5N HCl (25 mL) yielded **16** in 87-95 % yield as shown in Table 2. To a solution of anthracenethiols **16** (5 mmol) dissolved in chloroform (20 ml), KOH (0.20 g, 5 mmol) dissolved in methanol was added at 0 ^{o}C followed by propargyl bromide (0.38 mL, 5 mmol) and stirred overnight. Reaction mixture was concentrated, washed with water and extracted with dichloromethane to obtain thioethers **17** in 75-85 % yields. Thioethers **17** were purified by silica gel column chromatography using a mixture of hexane and dichloromethane as eluents. IMDA reaction of **17** (5 mmol) was effected by refluxing in *p*-xylene (10 mL) (5-10h) to obtain corresponding barrelenes **6** in 70-80 % yields after recrystallization from suitable solvents.

Table 2. Amounts and yields of formation of intermediates **14**, **16** and **17**

Alcohols **14**, 10 mmol (g)	Yield %	Thiols **16**, 5 mmol (g)	Yield %	Thioethers **17**, 5 mmol (g)	Yield %
14a) 2.08	92	**16a**) 1.12	95	**17a**) 1.38	83
14b) 2.22	88	**16b**) 1.19	92	**17b**) 1.45	85
14c) 2.38	86	**16c**) 1.27	87	**17c**) 1.53	75
14d) 2.84	90	**16d**) 1.50	90	**17d**) 1.76	78

Synthesis of tethered sulfone 7. Tethered barrelene **6a** (200 mg, 0.76 mmol) was dissolved in DMF (5 mL) and stirred with hydrogen peroxide (30 %, 2 mL) and boric acid (0.006 g, 0.1 mmol) for 12h to obtain the corresponding sulfone **7** (78 %).

General procedure for the synthesis of tethered ethers 8. Aldehydes **9** (16 mmol) were reduced to anthracene methanols **14** using sodium borohydride (1.1 g, 30 mmol) dissolved in methanol. Anthracenemethanols **14** (10 mmol) were converted to the corresponding sodium salts **18** by treating with sodium hydride (0.48 g, 20 mmol) in THF. Propargyl bromide was added to it and stirred at room temperature for 2h followed by refluxing in THF for 4h to obtain **19** (75-85 % yield, Table 3). Propargyl ethers **19** (5 mmol) were refluxed in *p*-xylene (10 mL) (12 h to 20 h) to obtain the corresponding barrelenes **8** (80-90 %). The products were purified by silica gel column chromatography using a mixture of hexane and dichloromethane as eluents followed by recrystallization from suitable solvents and structures were confirmed by spectral and analytical data.

Table 3. Amounts and yields of formation of intermediate **19**

Ethers **19**, 5 mmol (g)	Yield %
19a) 1.30	85
19b) 1.37	78
19c) 1.45	75
19d) 1.68	81

Compound 5a[5]. Yield 87 %, mp 232-235 °C; IR (ν_{max}, cm^{-1}): 1764, 1350, 750; ^{1}H NMR ($CDCl_3$): δ 7.45-6.95 (m, 8H), 6.75 (dt, 1H, J_1 6 Hz, J_2 2.4 Hz), 5.21 (d, 1H, *J* 5.6 Hz). 4.98 (d, 2H, *J* 2.4 Hz); ^{13}C NMR ($CDCl_3$): δ 173.1,

147.0, 144.6, 142.5, 129.8, 125.5, 124.9, 123.5, 121.2, 68.2, 59.6, 52.2; MS: *m/z* 260 (M^+); Anal. Calcd. for $C_{18}H_{12}O_2$: C: 83.06, H: 4.65. Found: C: 83.01, H: 4.62.

Compound 5b. Yield 82 %, mp 175-178 °C; IR (ν_{max}, cm^{-1}): 1778, 1350, 750; ^{1}H NMR ($CDCl_3$): δ 7.52-7.01 (m, 8H), 6.43 (t, 1H, *J* 2.4 Hz), 5.03 (d, 2H, *J* 2.4 Hz), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 173.2, 147.5, 146.9, 143.5, 134.0, 125.2, 124.5, 120.8, 120.6, 68.0, 59.1, 51.3, 15.4; MS: m/z 274 (M^+). Anal. Calcd. for $C_{19}H_{14}O_2$: C: 83.19, H: 5.14. Found: C: 83.10, H: 5.12.

Compound 5c. Yield 88 %, mp 200-202 °C; IR (ν_{max}, cm^{-1}): 1769, 1330, 750; ^{1}H NMR ($CDCl_3$): δ 7.44-6.93 (m, 9H), 4.99 (d, 2H, *J* 2 Hz), 3.94 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 172.6, 145.8, 144.8, 140.8, 127.9, 125.4, 124.9, 120.8, 120.7, 88.5, 67.9, 57.9, 55.2; MS: *m/z* 290 (M^+); Anal. Calcd. for $C_{19}H_{14}O_3$: C: 78.61, H: 4.86. Found: C: 78.52, H: 4.78.

Compound 5d. Yield 85 %, mp 274-276 °C; IR (ν_{max}, cm^{-1}): 1778, 1320, 750; ^{1}H NMR ($CDCl_3$): δ 7.70-6.94 (m, 14H), 5.11 (d, 2H, *J* 2.4 Hz); ^{13}C NMR ($CDCl_3$): δ 173.1, 149.1, 147.2, 142.9, 134.5, 130.0, 129.5, 128.7, 127.9, 124.9, 124.9, 123.8, 121.0, 68.1, 61.3, 59.8; MS: *m/z* 336 (M^+); Anal. Calcd. for $C_{24}H_{16}O_2$: C: 85.69, H: 4.79.Found: C: 85.61, H: 4.70.

Compound 6a[5]. Yield 80 %, mp 129-132 °C; IR (ν_{max}, cm^{-1}): 1350, 750; ^{1}H NMR ($CDCl_3$): δ 7.30-6.95 (m, 8H), 6.66 (dt, 1H, J_1 6 Hz, J_2 1.6 Hz), 5.09 (d, 1H, *J* 6 Hz), 3.98 (s, 2H), 3.57 (d, 2H, *J* 1.6 Hz); ^{13}C NMR ($CDCl_3$): δ 155.3, 147.6, 145.8, 128.9, 124.6, 124.2, 122.9, 120.0, 64.2, 51.6, 33.4, 30.7; MS: *m/z* 262(M^+); Anal. Calcd. for $C_{18}H_{14}S$: C: 82.40, H: 5.38, S: 12.22. Found: C: 82.34, H: 5.37, S: 12.29.

Compound 6b. Yield 74 %, mp 112-114 °C; IR (ν_{max}, cm^{-1}): 2965, 1350, 750; ^{1}H NMR ($CDCl_3$): δ 7.29-7.00 (m, 8H), 6.29 (t, 1H, *J* 2 Hz), 3.98 (s, 2H), 3.58 (d, 2H, *J* 2 Hz), 2.16 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 156.0, 149.9, 146.8, 133.3, 124.3, 124.0, 120.0, 119.6, 63.6, 49.9, 33.5, 31.0, 15.7; MS: *m/z* 276(M^+); Anal. Calcd. for $C_{19}H_{16}S$: C: 82.56, H: 5.83, S: 11.61. Found: C: 82.51, H: 5.87, S: 11.62.

Compound 6c. Yield 78 %, mp 153-156 °C; IR (ν_{max}, cm^{-1}): 2936, 1350, 750; ^{1}H NMR ($CDCl_3$): δ 7.39-6.91 (m, 8H), 6.79 (t, 1H, *J* 2 Hz), 3.90 (s, 3H), 3.88 (s, 2H), 3.54 (d, 2H, *J* 2 Hz); ^{13}C NMR ($CDCl_3$): δ 153.1, 146.6, 143.2, 125.9, 123.5, 123.3, 118.9, 118.5, 86.2, 61.8, 53.9, 32.6, 29.8; MS: *m/z* 292(M^+); Anal. Calcd. for $C_{19}H_{16}OS$: C: 78.05, H: 5.52, S: 10.97. Found: C: 78.01, H: 5.44, S: 10.88.

Compound 6d. Yield 75 %, mp 218-221 °C; IR (ν_{max}, cm^{-1}): 1350, 750; ^{1}H NMR ($CDCl_3$): δ 7.71-6.89 (m, 14H), 4.06 (s, 2H), 3.66 (d, 2H, *J* 1.6 Hz); ^{13}C NMR ($CDCl_3$):- δ 157.4, 150.1, 146.1, 135.5, 130.2, 128.6, 128.5, 127.5, 124.3, 124.0, 123.1, 119.9, 63.8, 60.0, 33.9, 31.2; MS: *m/z* 338(M^+); Anal. Calcd. for $C_{24}H_{18}S$: C: 85.17, H: 5.36, S: 9.47. Found: C: 85.08, H: 5.38, S: 9.54.

Compound 7. Yield 78 %, mp 129-132 °C; IR (ν_{max}, cm^{-1}): 1318, 1300, 750; ^{1}H NMR ($CDCl_3$): δ 7.26 -6.87 (m, 9H), 5.09 (d, 1H, *J* 6 Hz), 4.10 (s, 2H), 3.80 -3.73 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 148.3, 145.6, 144.3, 134.4, 133.3, 119.4, 119.0, 118.7, 58.48, 53.9, 50.5, 50.2; MS: *m/z* 294(M^+); Anal. Calcd. for $C_{18}H_{14}O_2S$: C: 73.44, H: 4.79, S: 10.89. Found: C: 73.41, H: 4.78, S: 10.91.

Compound 8a[5]. Yield 90 %, mp 198-200 °C; IR (ν_{max}, cm^{-1}): 2880, 1350, 750; ^{1}H NMR ($CDCl_3$): δ 7.29-6.97 (m, 8H), 6.61 (dt, 1H, J_1 6 Hz, J_2 2 Hz), 5.16 (d, 1H, *J* 6 Hz), 4.99 (s, 2H), 4.41 (d, 2H, *J* 2 Hz); ^{13}C NMR ($CDCl_3$): δ 154.9, 147.2, 145.1, 125.7, 124.6, 124.3, 123.0, 120.0, 67.5, 66.4, 62.1, 52.0; MS: *m/z* 246(M^+); Anal. Calcd. for $C_{18}H_{14}O$: C: 87.78, H: 5.73. Found: C: 87.76, H: 5.7.

Compound 8b. Yield 81 %, mp 139-142 °C; IR (ν_{max}, cm^{-1}): 2925, 1350, 750; ^{1}H NMR ($CDCl_3$): δ 7.32 -6.99 (m, 8H), 6.25 (t, 1H, *J* 2 Hz), 5.00 (s, 2H), 4.42 (d, 2H, *J* 2 Hz), 2.19 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 154.5, 148.5, 145.1, 128.9, 123.4, 123.0, 119.0, 118.6, 66.53, 65.5, 60.5, 49.4, 14.7; MS: *m/z* 260(M^+); Anal. Calcd. for $C_{19}H_{16}O$: C: 87.66, H: 6.19. Found: C: 87.62, H: 6.17.

Compound 8c. Yield 85 %, mp 155-158 °C; IR (ν_{max}, cm^{-1}): 2940, 1350, 750; ^{1}H NMR ($CDCl_3$): δ 7.49-6.98 (m, 8H), 6.83 (t, 1H, *J* 3 Hz), 5.00 (s, 2H), 4.56 (d, 2H, *J* 3 Hz), 4.00 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 153.7, 147.3, 143.6,

124.6, 124.3, 123.7, 120.1, 119.6, 87.9, 67.6, 66.6, 60.6, 55.0; MS: *m/z* 276(M^+). Anal. Calcd. for $C_{19}H_{16}O_2$: C: 82.58, H: 5.84. Found: C: 82.49, H: 5.84.

Compound 8d. Yield 87 %, mp 233-236 °C; IR (ν_{max}, cm^{-1}): 2863, 1350, 750; ^{1}H NMR ($CDCl_3$): δ 7.24-7.35 (m, 13H), 7.19 (t, 1H, *J* 2 Hz) 5.09 (s, 2H), 4.49 (d,2H, *J* 2 Hz); ^{13}C NMR ($CDCl_3$): δ 157.0, 149.8, 145.5, 135.5, 130.2, 128.5, 127.5, 125.4, 124.3, 124.0, 123.2, 119.8, 67.8, 66.7, 61.8, 60.5; MS: *m/z* 322(M^+); Anal. Calcd. for $C_{24}H_{18}O$: C: 89.41, H: 5.63. Found: C: 89.36, H: 5.61.

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Adv. Org. Chem. Lett. 2019, 6(1), 13-16 Article

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Single electron transfer vs Diels Alder reaction: A comparative study of the reaction of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine and (anthracen-9-ylmethyl)(methyl)sulfane with dibenzoylethylene

Tomson Devassia, Jomon P. Jacob, Perupparampil A. Unnikrishnan*

Department of Applied Chemistry, Cochin University of Science and Technology, Cochin-682 022, Kerala, India.

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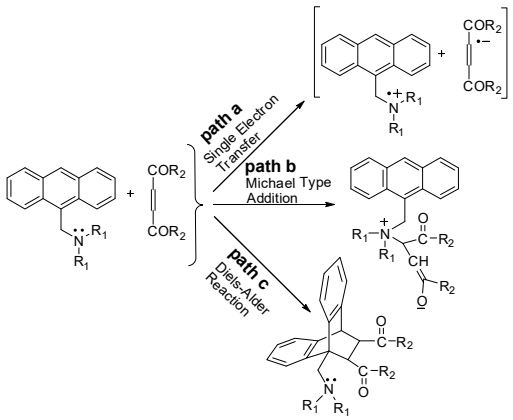
ABSTRACT



We have examined the reactions of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine and (anthracen-9-ylmethyl)(methyl)sulfane with dibenzoylethylene in different solvents. Single electron transfer mediated reactions predominated in the case of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine while the Diels-Alder pathway was important for (anthracen-9-ylmethyl)(methyl)sulfane.

Keywords: (anthracen-9-yl)methanamines, (anthracen-9-yl)methylsulfanes, dibenzoylethylene, cycloaddition, electron transfer reaction.

INTRODUCTION

Electron transfer reactions are ubiquitous in nature[1]. Thanks to the presence of lone pair electrons, amines and sulfanes are easy to oxidize[2] and hence are good single electron donors.[3-7] Both amines and sulfanes are active Michael donors as well.[8,9]

Corresponding Author: Perupparampil A. Unnikrishnan
Tel: 0484 286 2420
Email:paunni@gmail.com

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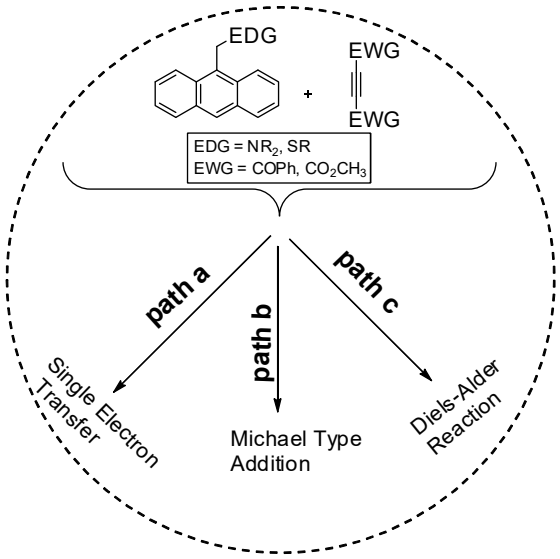
Competing one electron transfer, two electron transfer and Diels-Alder reaction possibilities exist for (anthracen-9-yl)methanamines[10] and (anthracen-9-yl)methylsulfanes.[11] We have successfully established dramatic solvent and concentration dependence of the reaction of (anthracen-9-yl)methanamines[12] and sulfanes[13] with suitable electron deficient acetylenes such as dimethyl acetylenedicarboxylate (DMAD) and dibenzoylacetylene (DBA). Reactions of (anthracen-9-yl)methanamines and (anthracen-9-yl)methylsulfanes with electron deficient acetylenes followed a similar pattern in different solvents at different concentrations.[12,13] Both amines and sulfanes gave products arising through single electron transfer, nucleophilic addition and cycloaddition. At concentrations <0.05 M, the cycloaddition pathway did not

operate for amines. But with sulfides, cycloaddition was predominant in all solvents at all concentrations.



Scheme 1. Competing reactions between anthracenemethanamines/anthracenemethylsulfanes with electron deficient acetylenes.

Both DMAD and DBA are highly reactive and hence less selective in their reactions. Moreover, extensive oligomerization of DBA and DMAD rendering product separation tedious was observed in their reactions with amines and sulfanes. We reasoned that selection of a dienophile of lower reactivity is more appropriate to unravel selectivity among the competing reaction pathways available for amine/sulfane reaction with dienophiles. Hence, we selected dibenzoylethylene (DBE) as the reactive dienophile for the present investigation. We observed that DBE exhibits differential reactivity towards amine and sulfanes: as single electron acceptor towards (anthracen-9-yl)methanamines and as a dienophile towards (anthracen-9-yl)methylsulfanes.

Results and Discussion

1-(Anthracen-9-yl)-*N*,*N*-dimethylmethanamine (**1**) and (anthracen-9-ylmethyl)(methyl)sulfane (**2**) were synthesised by modified procedures developed in our laboratory.[10,11] DBE (**3**) is commercially available (Chart 1).

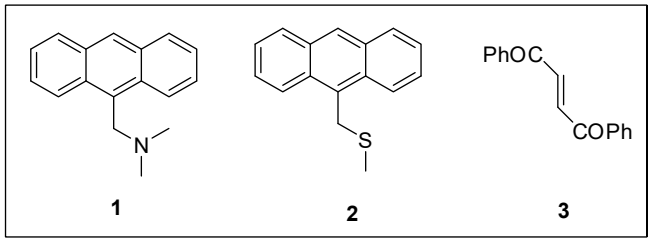


Chart 1. Starting materials for studying the diverse reactivity of anthracenemethanamines and anthracenemethylsulfanes with electron deficient alkene.

We examined the reaction of **1** and **2** with DBE (**3**) in different solvents at low concentration (0.05 M). As expected, reactions proceeded very slowly and even after 60 h, substantial quantities of starting materials remained unchanged (35-70%). In most cases, 9-methylanthracene (**4**), 9-anthraldehyde (**5**), lepidopterene (**6**), 1,2-bis(9-anthracenyl)ethane (**7**) and 9,10-anthraquinone (**8**) formed in variable amounts (Chart 2).

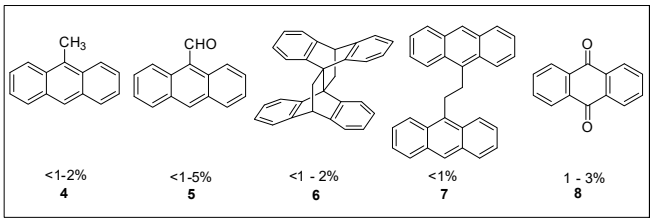


Chart 2. Products formed through one electron transfer and oxidation reactions.

Reactivity of dibenzoylethylene with (anthracen-9-yl)methanamines and (anthracene-9-ylmethyl)sulfanes in different solvents

Reactions in non-polar medium: xylene

A 0.050 M solution of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine (**1**) was refluxed with four equivalents of DBE (**3**) in xylene. Due to the lower reactivity of DBE, its reaction with **1** was very slow. After 60 h, in addition to unreacted starting materials (70%), 9-methylanthracene (**4**), 9-anthraldehyde (**5**), lepidopterene (**6**), 1,2-bis(9-anthracenyl)ethane (**7**), 9,10-anthraquinone (**8**), dibenzoylethane (**9**)[14] and 1,6-diphenyl-3,4-dibenzoyl-l,6-butanedione (**10**)[15] were obtained in low yields.

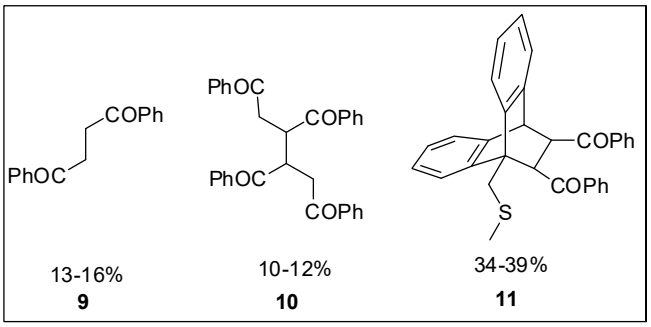


Chart 3. Diels-Alder adduct and radical mediated products formed from DBE.

In continuation, we examined the reaction of (anthracen-9-ylmethyl)(methyl)sulfane (**2**) with DBE (**3**) in refluxing xylene. Even after 60 h, substantial amount of **2** remain unchanged. Though products such as **4-8** were formed in trace amounts, DBE derived products such as **9** and **10** were not formed in detectable amounts. Anthraquinone (**8**) was generated in yields comparable with that obtained with **1**. The major product formed in this case was the Diels-Alder adduct **11** (Chart 3).

These results point towards different reactivity pattern for amines and sulfanes towards DBE.

Reactions in polar aprotic medium: dimethylformamide

To assess the role of solvent polarity in controlling selectivity in the reaction of dibenzoylethylene with (anthracen-9-yl)methanamines and anthracene-9-ylmethylsulfanes, we examined the reaction between **1**/**2** with DBE in polar aprotic medium: dimethylformamide (DMF) under reflux for 60 h. In the reaction between **1** and DBE, substantial quantities of **1** remained unchanged and products **4-10** were isolated in yields comparable with those obtained in xylene. On the other hand, in the reaction between **2** and DBE, cycloadduct **11** was obtained in major amounts along with unchanged **2** (48%) and **4-8** in trace amounts. It appears that even in polar aprotic solvents, the one electron transfer pathway predominates for (anthracen-9-yl)methanamines and the Diels-Alder pathway is more important for anthracenemethylsulfanes.

Reactions in polar protic medium: a) methanol

Compounds **1**, **2** and DBE (**3**) exhibited poor solubility in methanol and remained almost insoluble in other alcohols such as ethanol, propanols and butanols. In the reaction between **1** and **3** at low concentration in methanol, even after refluxing continuously for 150 h, unchanged starting material could be isolated in near quantitative amounts. Similar results were obtained with **2** and **3** in refluxing methanol. It appears that at low concentration and temperature below 65 °C, amine **1** and sulfane **2** remain unreactive towards DBE.

Reactions in polar protic medium: b) acetic acid

We refluxed a 0.050 M solution of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine (**1**) with four equivalents of DBE (**3**) in acetic acid. After, 60 h acetolysis product (anthracen-9-yl)methyl acetate (**12**)[16,17] and its Diels-Alder adduct **13** (Chart 4) along with electron transfer mediated products **4-7** and anthraquinone (**8**) were formed. Reaction of (anthracen-9-ylmethyl)(methyl)sulfane (**2**) with DBE (**3**) on the other hand gave cycloadduct **11** as the major product along with single electron transfer mediated products **4-7** and anthraquinone (**8**) in trace amounts. Acetolysis was not observed in this case, It appears that (anthracen-9-yl)methanamines in acetic acid follow single electron transfer and Michael type addition while anthracenemethylsulfanes follow usual cycloaddition pathway.

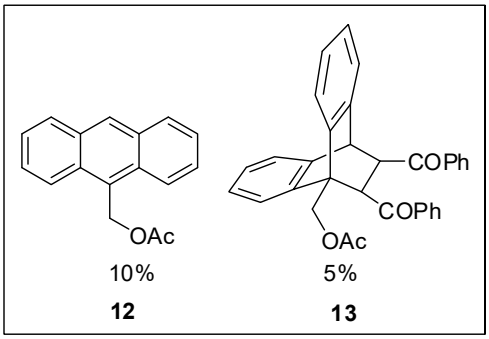


Chart 4. Acetolysis and Diels-Alder products formed by the reaction of **1** with **3**.

In our previous investigations on the reaction of anthracenmethanamines and sulfanes with reactive acetylenes such as DBA and DMAD, selectivity was not observed: both amines and sulfanes reacted in similar fashion under identical conditions.[12,13] We have now observed that DBE, thanks to its lower reactivity, exhibits selectivity in its reactions with anthracemnmethanamines and sulfanes. However, several common products are obtained in reactions of anthracenmethanamines and sulfanes with DBA, DMAD and DBE. Mechanisms for the formation of different products under different conditions are understood in terms of those proposed in our previous articles and are is included as supporting information.[12,13] Anthraquinone (**8**) is formed by the reaction with adventitious oxygen. We could isolate **8** in comparable quantities when 0.05 M solutions of **1** and **2** (in the absence of DBE) were refluxed for 60 h in solvents such as xylene, DMF and acetic acid.

CONCLUSION

Nucleophilic addition, single electron transfer and cycloaddition possibilities coexist in the reaction between anthracenemethanamines/sulfides and dibenzoylethylene. Both nature of substrate and solvent play important roles in deciding the major reaction pathway. With anthracenemethanamines, single electron transfer and nucleophilic addition possibilities are favoured, while for sulfanes, cycloaddition is favoured in all solvents. Thus it appears that anthracenemethanamines are better single and two electron donors in comparison with anthracenemethylsulfanes in their reaction with DBE.

EXPERIMENTAL

General methods

All reactions were carried out using oven dried glasswares. All experiments were done with distilled and dried solvents by using standard protocols. All starting materials were purchased from either *Sigma-Aldrich* or *Spectrochem* Chemicals and were used without further purification. Separation and purification of compounds were done by column chromatography using either silica gel (*Spectrochem Chemicals*, 60-120 mesh) or neutral alumina (*Spectrochem Chemicals*). The products were further purified by recrystallization from suitable solvent systems. Melting points are uncorrected and were determined on a *Neolab* melting point apparatus. Infra-red spectra were recorded using *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz on a *Bruker Avance III* FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario EL III)*. Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A*, *Mass-5975C*) and fast atom bombardment (FAB) using *JMS 600 JEOL* mass spectrometer. Here we are giving the spectral and analytical data only for novel compounds and the corresponding reference cited for known compounds. 1-(anthracen-9-yl)-*N*,*N*-

dimethylmethanamine (**1**), (anthracen-9-yl)methyl methyl sulfane (**2**) were synthesized using previously reported procedures and dibenzoylethylene (**3**) procured commercially was used as such.

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Solutions of **1** and **2** in solvents such as xylene, DMF and acetic acid (0.05 M) were refluxed for 60 h. Work up of the reaction mixture gave anthraquinone (<3%) along with unchanged starting materials (>95%).

General experimental procedure for the reactions of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine (1)/(anthracen-9-ylmethyl)(methyl)sulfane (2) with electron-deficient dienophile DBE (3)

To a solution (0.050 M) of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine (**1**, 700 mg, 3.0 mmol)/(anthracen-9-ylmethyl)(methyl)sulfane (**2**, 710 mg, 3.0 mmol) in corresponding solvent (60 mL), DBE (**3**, 4 equivalents) was added, and the mixture was refluxed for 60 h. Progress of the reaction was monitored by TLC. At the end of 60 h, the reaction mixture was cooled, and the solvent was removed under reduced pressure. The product mixture obtained was separated and purified by column chromatography on silica gel using hexane and dichloromethane.

CHARACTERIZATION DATA

Compound 11:- Off-white crystalline solid (34-39%); mp: 175-176 °C; IR ν_{max} (KBr): 3061, 3029, 2983, 2911, 2853, 1660, 1645, 1598, 1448, 1385, 1276, 1069, 690 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.88-6.92 (m, 18H), 4.89 (d, 1H, *J* = 6.0 Hz), 4.45 (d, 1H, *J* = 1.6 Hz), 3.84 (dd, 2H, *J* = 6.4 Hz and 2.0 Hz), 3.68 (d, 1H, *J* = 12.4 Hz), 2.03 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 201.7, 197.3, 142.4, 139.7, 136.3, 133.2, 133.1, 128.9, 128.4, 128.3, 126.4, 126.3, 126.0, 125.9, 124.8, 122.8, 122.6, 54.2, 48.8, 36.1, 18.0; MS: *m/z* 475 *(M+1)*; Anal. Calcd for $C_{32}H_{26}O_2S$: C: 80.98; H: 5.52; S: 6.76; Found: C: 80.91; H: 5.43; S: 6.69.

Compound 13: White solid (5%); mp: 209-211 °C; IR ν_{max} (KBr): 1736, 1670, 1594, 1245 cm^{-1}; ^1H NMR ($CDCl_3$): 7.00-7.38 (m, 18H), 5.17 (d, 1H, *J* = 11.6 Hz), 4.97 (d, 1H, *J* = 11.6 Hz), 4.84 (d, 1H, *J* = 6.0 Hz), 4.06 (dd, 1H, *J* = 6.0 and 2.0 Hz), 1.81 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 201.6, 197.9, 170.6, 142.8, 142.4, 139.9, 139.7, 138.1, 136.1, 133.3, 133.2, 128.9, 128.6, 128.5, 128.4, 126.6, 126.5, 126.4, 126.2, 125.0, 123.2, 123.1, 121.5, 62.9, 54.5, 49.1, 48.6, 46.7, 20.5; MS: *m/z* 486 (M^+), 105; Anal. Calcd for $C_{33}H_{26}O_4$: C: 81.47, H: 5.38; Found: C: 81.48, H: 5.38.

Supporting Information

Detailed mechanisms of the above reactions and ^1H and ^{13}C NMR data of novel compounds are included.

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Data Article

Synthesis, characterization, crystal structure and hirshfeld surface analysis of heteroatom substituted annulated dibenzobarrelenes

Tomson Devassia, Eason M. Mathew, Lincy Tom, M.R. Prathapachandra Kurup, Perupparampil A. Unnikrishnan*

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, 682 022 Kerala, India

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ABSTRACT

Dibenzobarrelenes, white or colorless solids, prone to give single crystals in suitable solvents are important bicyclic compounds exhibiting remarkable photophysical properties. Herein we discuss the synthesis, characterization and Hirshfeld surface analysis of 10-methoxy- derivatives of 9,11-ether annulated dibenzobarrelene and 9,11-thioether annulated dibenzobarrelene.

Specifications table

Subject area	*Organic Chemistry, Spectroscopy, Computational Chemistry, Crystallography*
Compounds	*10-Methoxy-9,11-ether annulated dibenzobarrelene and 10-methox-9,11-thioether annulated dibenzobarrelene.*
Data category	*Spectral, synthesis, crystallographic studies, computational simulations.*
Data acquisition format	*^{1}H NMR, ^{13}C NMR, IR, Mass spectra, SCXRD*
Data type	*Process, Analysis, Simulation*
Procedure	*Intramolecular Diels-Alder (IMDA) reaction of suitably substituted (acetylene-appended) anthracene yielded corresponding 9,11-annulated dibenzobarrelene.*
Data accessibility	*Data is provided with the article.*

1. Rationale

Dibenzobarrelene derivatives generally are white or colorless crystalline solids and good single crystals can be obtained for compounds with appropriate substitution pattern. Ever since Zimmerman and Grunewald reported the photoisomerization of barrelene into semibullvalene [1], synthesis and exploration of photochemistry of these compounds with varied structural features have attracted wide attention. Apart from their widely explored photochemistry [1–3], recent reports have illustrated the applications of dibenzobarrelenes in OLEDs [4] and photoluminescent materials [5]. Dibenzobarrelenes

* Corresponding author.
E-mail address: paunni@cusat.ac.in (P.A. Unnikrishnan).

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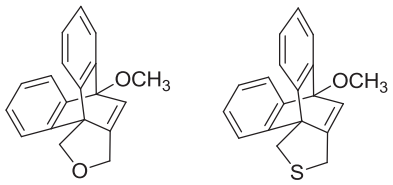


1 2

are also known to exhibit antibacterial activity [6]. General strategy of synthesis of 9,11-annulated dibenzobarrelenes with varying substitutions on the bridgehead positions involve an intramolecular Diels-Alder (IMDA) reaction [7]. Recently we have demonstrated the IMDA reactions of hetero atom incorporated 9-(pent-4-yn-1-yl)anthracene-type compounds leading to several dibenzobarrelenes [8]. 10-Methoxy-9,11-ether annulated dibenzobarrelene (**1**) and 10-methoxy-9,11-thioether annulated dibenzobarrelene (**2**) showed excellent crystal characteristics and we now report characterization, crystal structure and Hirshfeld surface analysis of these compounds.

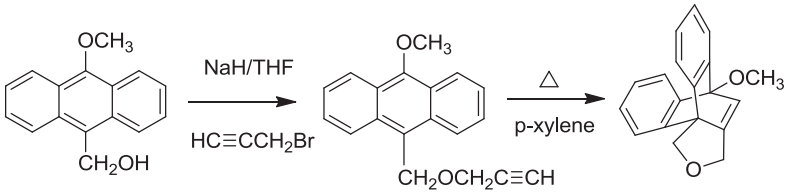
2. Procedure

2.1. General techniques

Reactions were performed with dried glassware and chemicals and reagents were bought from *Sigma Aldrich* or *Spectrochem Chemicals*. Reactions were monitored by thin layer chromatography (Aluminium sheets coated with silica gel, *E. Merck*) and visualisation of TLC plates was achieved by exposure to UV lamp or iodine vapours. Compounds were purified by column chromatography over silica gel (*Spectrochem Chemicals*, 60–120 mesh). Products were recovered from eluent by distillation under reduced pressure using *Heidolph, IKA or Buchi* rotary evaporators and were further purified by recrystallization from suitable solvents. Melting points were determined on a *Neolab* melting point apparatus and are uncorrected. Infrared spectra were recorded on *Jasco 4100* FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz *Bruker Avance III* FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Molecular mass was determined by electron impact (EI) method using GC–MS (*Agilent GC-7890A, Mass-5975C*). Crystallographic data were collected with a Bruker SMART APEX diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) X-ray source.

2.2. Synthesis of ether annulated dibenzobarrelene 1 (Scheme 1)

A mixture of the alcohol **3** (1.19 g,5 mmol), sodium hydride (0.25 g, 10 mmol) and propargyl bromide (0.38 mL, 5 mmol) in THF (5 mL) was stirred in an RB flask for 2 h. The reaction mixture was washed with water and extracted with dichloromethane (DCM). Removal of solvent, followed by purification by column chromatography over silica gel using a 5:95 mixture of DCM-hexane as eluent gave **4** (1.09 g, 91% yield). The ether **4** (1 g, 3.36 mmol) was refluxed in *p*-xylene (10 mL) for 12 h and the IMDA reaction product isolated by removal of solvent was further purified by column chromatography over silica gel using 5:95 mixture of ethyl acetate-hexane to get the 10-methoxy-9,11-annulated dibenzobarrelene (**1**) (0.80 g, 80% yield). Single crystals of **1** were prepared by slow evaporation of a solution in acetonitrile [8].



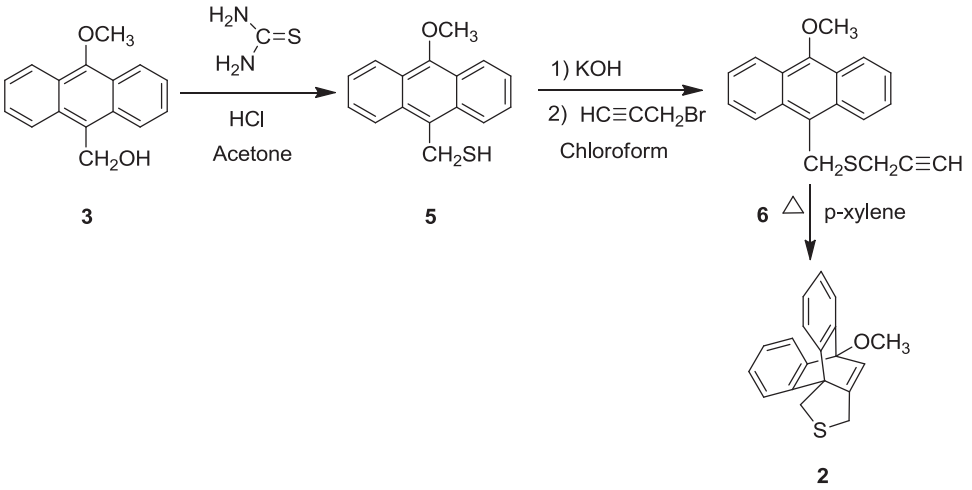
3 4 1

Scheme 1. Synthesis of ether annulated dibenzobarrelene **1**.

2.3. Synthesis of thioether annulated dibenzobarrelene 2 (Scheme 2)

The alcohol **3** (4.76 g, 20 mmol) was treated with two equivalents of thiourea (3 g, 40 mmol) in acetone (50 mL) in a 250 mL RB flask and 5 N HCl (5 mL) was added to it and stirred overnight. The precipitate formed was filtered and treated with sodium hydroxide solution (10%, 30 mL) and stirred at room temperature for 2 h and then acidified with 5 N HCl to get the anthracenethiol derivative **5** (4.29 g, 90% yield). Upon stirring the thiol **5** (1.27 g, 5 mmol) with propargyl bromide

(0.38 mL, 5 mmol) in presence of KOH (0.2 0 g, 5 mmol) in chloroform at ice cold temperature for 12 h, the thioether **6** was formed. The reaction mixture was washed with water and extracted with DCM. The product was purified by silica column chromatography using a mixture of DCM and hexane (5:95) as eluent to get **6** (1.15 g, 90% yield). The thioether **6** (1 g, 3.25 mmol) on refluxing in *p*-xylene (10 mL) for 12 h gave the IMDA product which was isolated by evaporation of solvent and further purified by column chromatography over silica gel using 5:95 mixture of ethyl acetate-hexane to get the 10–methoxy-9,11-annulated dibenzobarrelene **2** (0.83 g, 83% yield). Single crystals of **2** were obtained by slow evaporation from acetonitrile [8].



Scheme 2. Synthesis of thioether annulated dibenzobarrelene **2**.

3. Data, value and validation

3.1. Characterization of ether annulated dibenzobarrelene 1

White crystalline solid; (0.80 g, 80%); mp: 155–158 °C; IR (KBr), ν_{max} (cm^{-1}): 2940 (aromatic C–H stretch), 1350–1000 (C–C stretch) and 750–690 (aromatic out of plane bending); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): δ 7.49–6.98 (m, 8H, aromatic), 6.83 (s, 1H, vinylic proton), 5.00 (s, 2H, methylene protons α to bridgehead position), 4.56 (s, 2H, methylene protons at allylic position), 4.00 (s, 3H, methyl protons); ^{13}C NMR ($CDCl_3$): δ (ppm): δ 153.78, 147.35, 143.66, 124.63, 124.38, 123.75, 120.14, 119.66 (aromatic), 87.95 (C-bridgehead annulated), 67.66 (C-bridgehead), 66.61 (CH_2 α to bridgehead), 60.60 (CH_2-allylic), 55.08 (OCH_3); MS: *m/z* 276 (M^+) [8].

3.2. Characterization of thioether annulated dibenzobarrelene 2

White crystalline solid; (0.83 g, 83%); mp: 153–156 °C., IR (KBr), ν_{max} (cm^{-1}): 2936 (-C–H stretch), 1350–1000 (C–C stretch) and 750–690 cm^{-1} (aromatic out of plane bending); ^{1}H NMR ($CDCl_3$): δ 7.39–6.91 (m, 8H, aromatic), 6.79 (t, J 2 Hz, 1H, vinylic proton), 3.90 (s, 3H, methyl protons), 3.88 (s, 2H, methylene protons α to bridgehead position), 3.54 (d, J 2 Hz 2H, allylic protons); ^{13}C NMR ($CDCl_3$): δ 153.14, 146.64, 143.27, 125.90, 123.54, 123.35, 118.99, 118.59 (aromatic), 86.28 (C-bridgehead annulated), 61.84 (C-bridgehead), 53.93 (OCH_3), 32.67 (CH_2 α to bridgehead), 29.83 (CH_2-allylic); MS: *m/z* 292 (M^+) [8].

4. Single crystal X-ray diffraction

Bruker SMART software was used for data acquisition and Bruker SAINT Software for data integration [9]. Absorption corrections were carried out using SADABS based on Laue symmetry using equivalent reflections [10]. The structure was solved by direct methods and refined by full-matrix least-squares calculations with the SHELXL-2018 software package [11]. All non-hydrogen atoms were refined with anisotropic displacement parameters and positions of hydrogen atoms were located in the difference Fourier maps and were placed in calculated positions and refined as riding atoms: C–H = 0.93 Å (heteroaromatic), 0.96 Å (CH_3) and N–H = 0.86–0.87 Å with U_{iso}(H) = 1.2 U_{eq}(C,N). All the drawings of complexes were made using DIAMOND 3.2 k programs [12].

X-ray diffraction analysis revealed that both the compounds **1** and **2** were crystallized in the monoclinic crystal system with space group P21/n and P21/c respectively. For compound **1** unit cell parameters are; a = 9.3290(5) Å, b = 12.4556(6) Å, c = 12.0304(6) Å, β = 94.451(2)°, V = 1393.70(12) Å^3 and Z = 4. In compound **2** cell parameters are; a = 7.9988(5) Å,

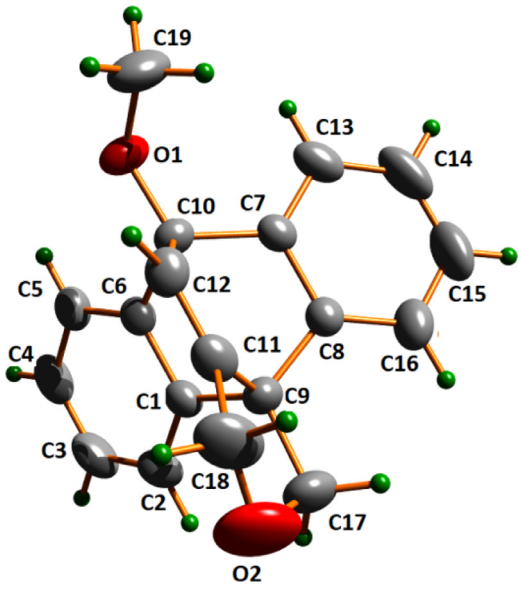


Fig. 1. Molecular structure and atom numbering scheme of compound **1** drawn with 50% probability ellipsoid.

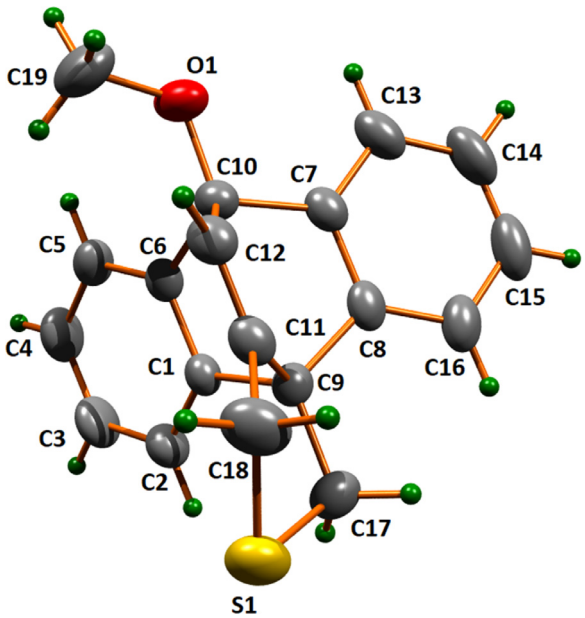


Fig. 2. Molecular structure and atom numbering scheme of compound **2** drawn with 50% probability ellipsoid.

$b = 9.8093(6)$ Å, $c = 36.891(3)$ Å, $\beta = 93.247(2)°$, $V = 2889.9(3)$ Å^3 and $Z = 8$. The molecular structure of compound **1** and **2** are shown in Figs. 1 and 2. The details of the crystal data and structure refinement are given in Table 1. The compound **2** crystallizes with two independent molecules in the asymmetric unit.

The resulted bond lengths and bond angles are in good agreement with reported values, and are presented in Tables 2 and 3 [13,14]. The pentafuranose ring C9,C11,C17,C18/O1 (for **1**) and the five-membered heterocyclic ring C9,C11,C17,C18/S1 (for **2**) are in an envelope conformation on S1 [φ = 357.0(3)°] and O1φ = 8.3 (5)° [15]. The two fused six-membered rings are in a boat conformation.

The packing diagram of **1** and **2** along *a* axis is shown in Fig. 3. Even though, the compounds **1** and **2** are structurally similar they differ in stacking arrangements generating supramolecular isomers [16–19]. The hydrogen atom from the C4 in **1** has C–H···π interactions with the C7, C8, C16, C15, C14, ring, Cg(6) of a neighboring molecule with H···π distances of 2.97 Å. The interaction between C(4)–H4 and aromatic ring, Cg(21); C26,C27,C35,C34,C33,C32 in **2** is stronger than in **1** (Figs. 4 and 5) with an H···π distance of 2.88 Å (Table 4). The packing of molecules is dominated by these C–H···π and

Table 1
Crystallographic data and refinement parameters for **1** and **2**.

Parameters	Compound **1**	Compound **2**
Empirical formula	C_{19} H_{16} O_2	C_{19} H_{16} O S
Formula weight	276.32	292.38
Temperature	296(2) K	292.38 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P21/n	P21/c
Unit cell dimensions		
a (Å)	9.3290(5)	7.9988(5)(5)
b (Å)	12.4556(6)	9.8093(6)
c (Å)	12.0304(6)	36.891(3)
α (°)	90.00	90.00
β (°)	94.451(2)	93.247(2)
γ (°)	90.00	90.00
Volume	1393.70(12) A^3	2889.9(3) A^3
Z	4	8
Calculated density	1.317 Mg/m^3	1.344 Mg/m^3
Absorption coefficient	0.084 mm^{-1}	0.220 mm^{-1}
F(000)	584	1232
Crystal size	0.35 × 0.30 × 0.25 mm	0.50 × 0.45 × 0.40 mm
θ range for data collection	2.67–28.29°	1.11° to 28.30°
Limiting indices	$-12 \le h \le 10$ $-16 \le k \le 14$ $-15 \le l \le 15$	$-9 \le h \le 10$ $-11 \le k \le 13$ $-48 \le l \le 49$
Reflections collected	12,205	21,802
Unique reflections	3426 [R(int) = 0.0291]	7147 [R(int) = 0.0338]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.048	1.14
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0685, wR_2 = 0.1928	R_1 = 0.0690, wR_2 = 0.1625
R indices (all data)	R_1 = 0.0843, wR_2 = 0.2099	R_1 = 0.0813, wR_2 = 0.1697
Largest diff. peak and hole	1.421 and −0.393 $e.A^{-3}$	0.371 and −0.416 $e.A^{-3}$

Table 2
Bond lengths.

Compound **1**		Compound **2**	
C(1)–C(2)	1.381(3)	C(1)–C(2)	1.386(3)
C(1)–C(6)	1.394(3)	C(1)–C(6)	1.394(3)
C(1)–C(9)	1.533(3)	C(1)–C(9)	1.532(3)
C(6)–C(10)	1.528(2)	C(6)–C(10)	1.537(3)
C(10)–O(2)	1.400(2)	C(10)–O(1)	1.409(3)
C(17)–O(1)	1.439(4)	C(17)–S(1)	1.811(3)
C(18)–O(1)	1.401(4)	C(18)–S(1)	1.810(3)
C(9)–C(11)	1.527(3)	C(9)–C(11)	1.539(3)

Table 3
Bond angles.

Compound **1**		Compound **2**	
C(2)–C(1)–C(6)	119.84(19)	C(2)–C(1)–C(6)	120.0(2)
C(2)–C(1)–C(9)	128.13(19)	C(2)–C(1)–C(9)	126.8(2)
C(5)–C(6)–C(10)	125.83(17)	C(5)–C(6)–C(10)	126.3(2)
C(18)–C(11)–C(9)	107.8(2)	C(18)–C(11)–C(9)	113.4(2)
O(2)–C(10)–C(7)	114.41(15)	O(2)–C(10)–C(7)	110.0(2)
O(1)–C(17)–C(9)	105.4(2)	C(9)-C(17)-S(1)	106.09(19)
O(1)–C(18)–C(11)	105.2(2)	C(11)-C(18)-S(1)	105.17(19)

Table 4
C—H···π interactions in **1** and **2**.

	C-H···π	H···Cg	**X–H···Cg(°)**	**X···Cg(Å)**
Compound **1**	C(1)–H(1)···Cg(6)[a]	2.97	156	3.837(2)
Compound **2**	C(4)–H(4)···Cg(21)[b]	2.88	162	3.777(3)

Symmetry codes: $a = 2\text{-x},2\text{-y},\text{-z}$; $b = 1 + x,1 + y,z$.

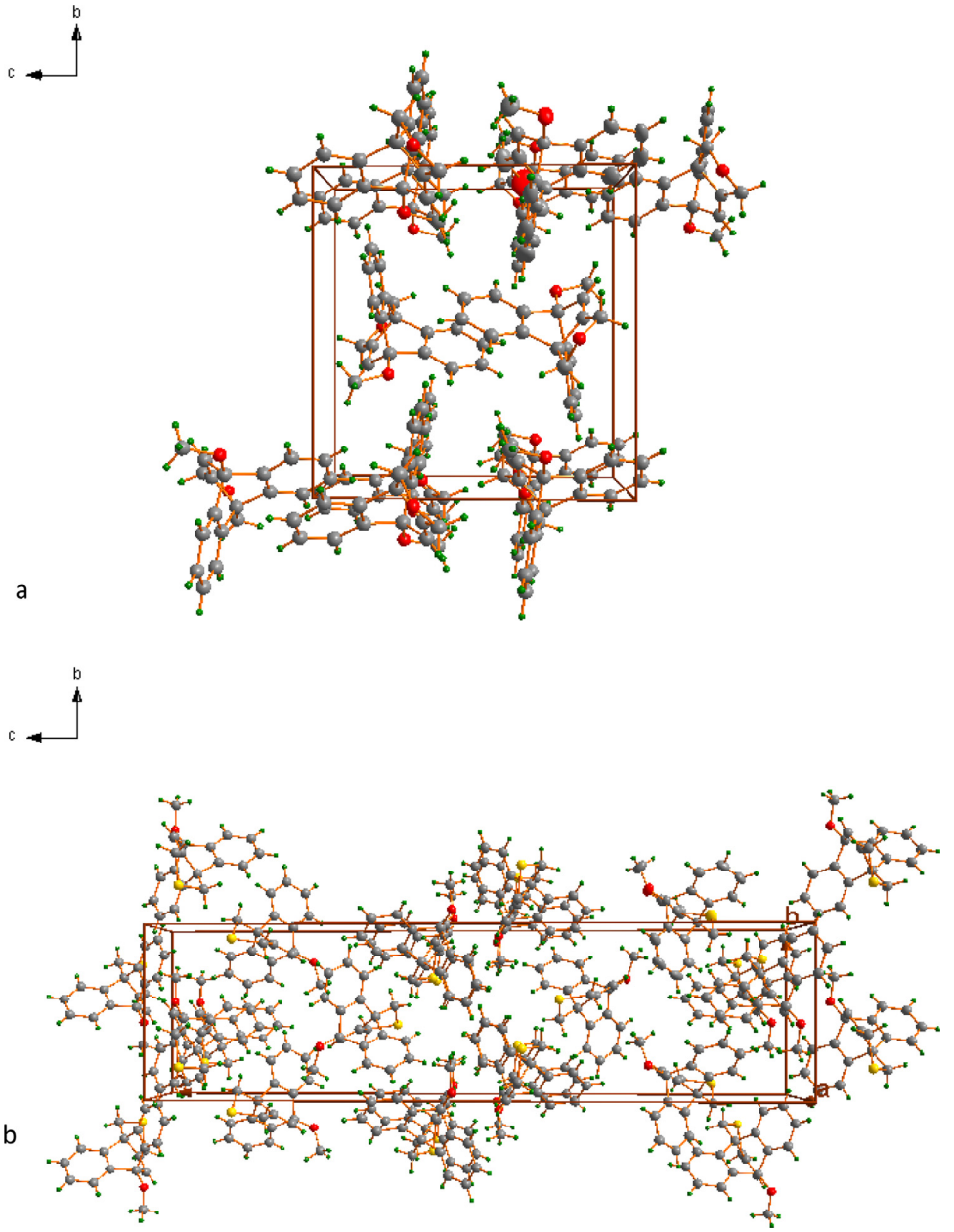


Fig. 3. Packing diagram of **1** (a) and **2** (b) viewed along 'a' axis.

van der Waals interactions. A weak $\pi\cdots\pi$ interaction with Cg···Cg distance 3.98 Å is observed in the crystal structure of **2** between two Cg(2) rings, Cg2 = C1–C6, and further corroborates the stable packing arrangement.

5. Hirshfeld surface analysis

Hirshfeld surfaces and their respective 2D fingerprint plots for all the compounds were calculated with the aid of the CRYSTALEXPLORER 3.1 [20] software. Hirshfeld surfaces [21] and 2D fingerprint plots [22] are useful to quantify the nature of the intermolecular interactions in the crystal lattice [23–25]. The d_{norm} is a function of distances to the surface from nuclei (atoms) inside (di) and outside (de) the Hirshfeld surface, compared with their respective van der Waals radii. The 3D d_{norm} surfaces are plotted over a fixed color scale of −0.65 au (red) – 1.27 au (blue) and curvedness −4.000 to +0.400 Å. The 2D fingerprint plots were displayed in the 0.6–2.4 Å range, and including reciprocal contacts.

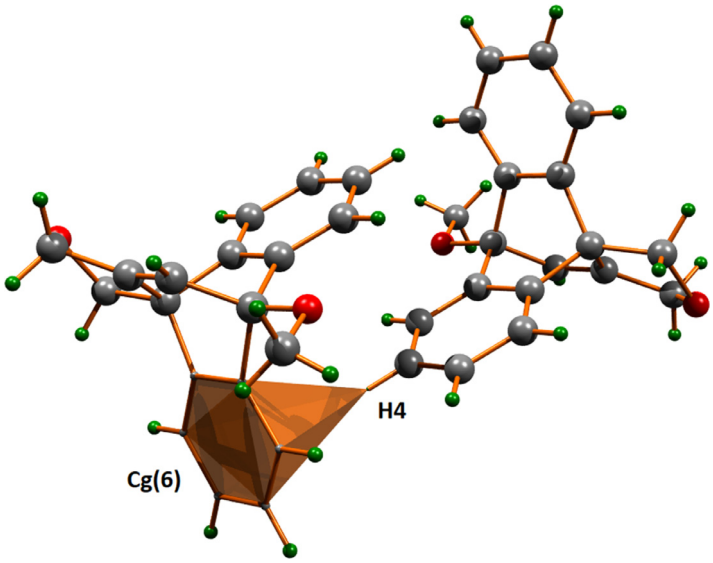


Fig. 4. C—H···π interactions in compound **1.**

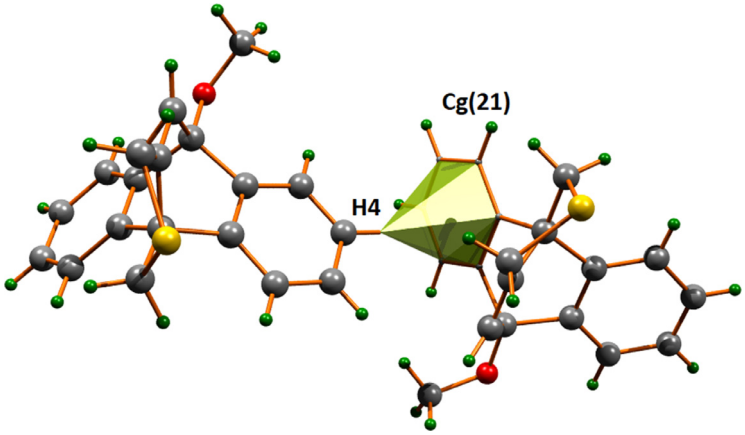


Fig. 5. C—H···π interactions in compound **2**.

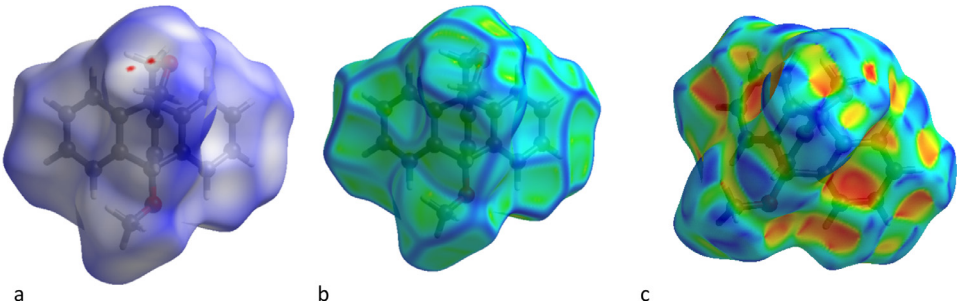


Fig. 6. d_{norm} Surface view (a), curvedness (b) and shape index (c) plot of compound **1**.

The intercontacts in the crystal packing of the compounds are quantized using Hirshfeld surface computational analyses (Figs. 6 and 7). The red colored spots over the Hirshfeld surface indicate the intercontacts involved in the intermolecular interactions. The dark red spots on the d_{norm} surface arise as a result of the short interatomic contacts. No significant red spots are observed corresponding to the strong hydrogen bonding interactions. For compound **2**, a dark red spot close to H18 atom in Fig. 7 depicts the non-classical interaction with C5 of adjacent molecule. The weak π interactions can be visualized

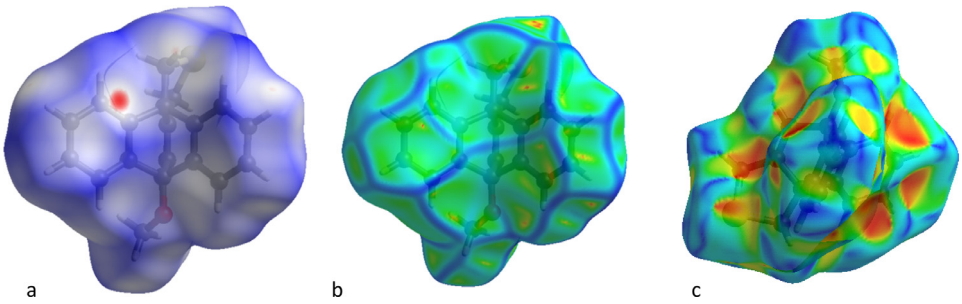
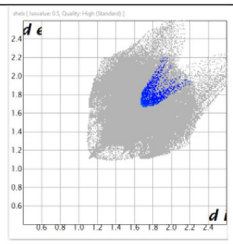
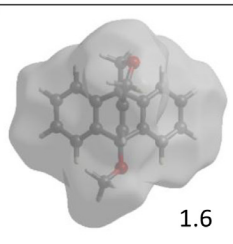
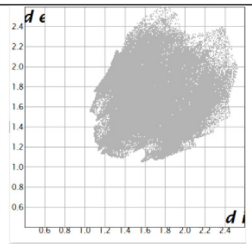
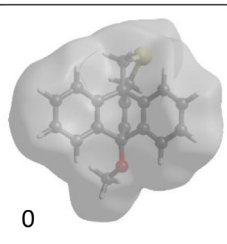
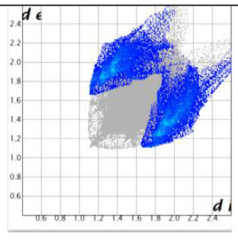
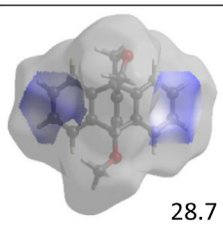
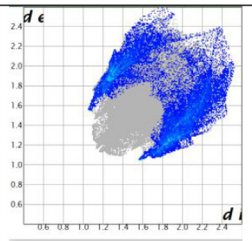
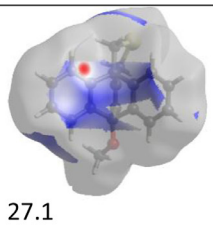
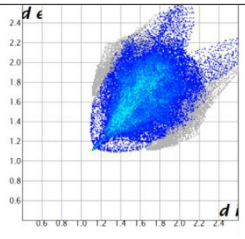
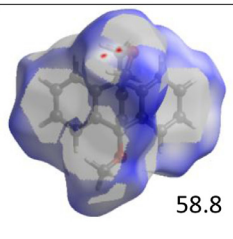
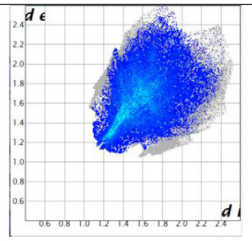
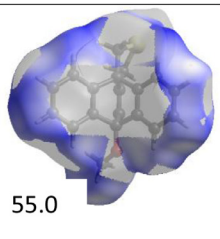
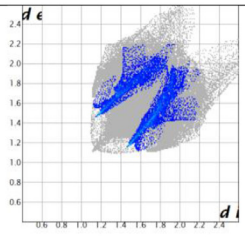
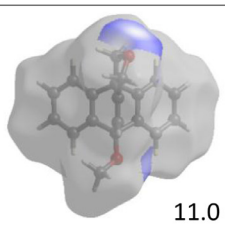
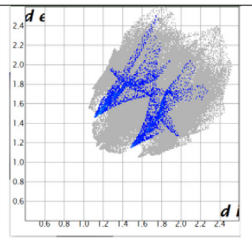
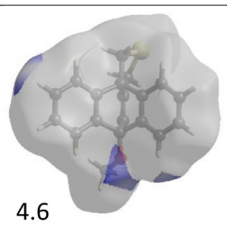


Fig. 7. d_{norm} Surface view (a), curvedness (b) and shape index plot (c) of compound **2**.

Table 5
2D Fingerprint plots for the compounds **1** and **2**.

	Compound **1**		Compound **2**	
C···C		 1.6		 0
C···H		 28.7		 27.1
H···H		 58.8		 55.0
O···H		 11.0		 4.6

in the compounds by curvedness and shape index plots (Figs. 6 and 7). This kind of interaction is evidenced by the presence of a high planarity zone and red/blue triangles on the same region of the curvedness and shape index surfaces respectively.

The 2D-fingerprint plots are used to plot intercontacts with respect to d_i and d_e. The intercontacts (quantification) were done using visualization of the Hirshfeld surfaces. The intercontacts were found to be similar as H···H (58.8%), C···H (28.7%), C···C (1.6%), O···H (11%) for compound **1** and H···H (55%), C···H (27.1%), C···C (0%), O···H (4.6%) for compound **2**. The 2D Finger print plots of these intercontacts are shown in Table 5. The major contributions are from H···H, C···H, and O···H when compared to other intercontacts. The distribution of intermolecular contacts in the two compounds is apparently similar.

6. Conclusion

Two 10-methoxy-9,11-annulated dibenzobarrelenes (**1** and **2**) were synthesized *via* IMDA reaction of suitably substituted acetylene-appended anthracenes and were characterized by IR, ^{1}H and ^{13}C NMR and mass spectroscopy and single crystal XRD techniques. Molecular structures of the compounds crystallizing with P21/n and P21/c space groups were further confirmed by single crystal XRD studies. Crystal structure and packing revealed that the compounds are supramolecular isomers. The packing is stabilized by different CH$\cdots\pi$ and $\pi\cdots\pi$ interactions. The analysis of intermolecular interactions through Hirshfeld surfaces and their fingerprints illustrate the contribution of such contacts. The HSA disclosed that H···H interactions has maximum contribution to the total Hirshfeld surface.

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Supplementary material

CCDC 1843614 and CCDC 1843615 contain the supplementary crystallographic data which can be accessed from the Cambridge Crystallographic Data Centre: deposit@ccdc.cam.ac.uk.

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Unusual reactivity of DMAD (dimethyl acetylenedicarboxylate) with *N*-alkyl-9-anthracenemethanamine

Tomson Devassia, Sreedharan Prathapan, Perupparampil A. Unnikrishnan*

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, Kerala 682 022, India

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ABSTRACT

This communication deals with the synthesis and characterization of a few *N*-alkyl-9-anthracenemethanamines and their reaction with dimethyl acetylenedicarboxylate (DMAD). Irrespective of reaction conditions, the corresponding dimethyl 2-((anthracen-9-ylmethyl)-amino)fumarates arising through a Michael-type addition reaction were exclusively formed in the reaction between these secondary amines and DMAD.

Specifications Table

Subject area	Organic chemistry, spectroscopy.
Compounds	Anthracene-9-yl-methanamines
Data category	Spectral, synthesized.
Data acquisition format	^{1}H NMR, ^{13}C NMR, IR, Mass spectra, m.p.
Data type	Process and analysis.
Procedure	Attempted Diels–Alder reaction of anthracenemethanamines with DMAD, resulted in 1,4 Michael adducts.
Data accessibility	Data is provided with this article

1. Rationale

Dimethyl acetylenedicarboxylate abbreviated as DMAD (**1**) is well known for its high reactivity towards cycloadditions, Michael type addition and single electron transfer reactions [1–12]. Anthracenemethanamines such as **2**, on the other hand, are potential dienes, Michael donors and single electron donors. Reaction between such complementary pair of substrates is of considerable interest (Chart 1).

* Corresponding author.
E-mail address: paunni@cusat.ac.in (P.A. Unnikrishnan).

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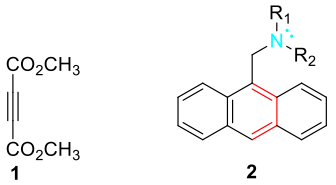


Chart 1

In recent reports from our group, we convincingly demonstrated solvent and concentration dependence on the reaction between anthracenemethanamines and DMAD [10–12]. We could successfully set conditions under which Diels-Alder reaction, Michael addition or single electron transfer mediated transformation manifested as the major reaction pathway for this complimentary substrate pair. In order to establish the generality of our observations, we carried out the reaction between **6a–c** and DMAD. In order to reduce the nucleophilicity of the secondary amines, bulky *N*-substituents such as isopropyl, *tert*–butyl and *sec*–butyl were introduced. In contrast to the reaction between tertiary amines **2** and DMAD, irrespective of the conditions applied, we observed that Michael addition is the only reaction observed between **6a–c** and DMAD leading to formation of the corresponding Michael adducts **8a–c** in near quantitative yields. Electron transfer mediated products and Diels-Alder adducts **7a–c** [10–12] were not formed in detectable amounts. Structure of **8a–c** was arrived at on the basis of spectral and analytical data. Thus our findings illustrate unusual difference in reactivity between secondary amines **6** and tertiary amines **2** towards a common reagent such as DMAD.

2. Procedure

2.1. Materials and method

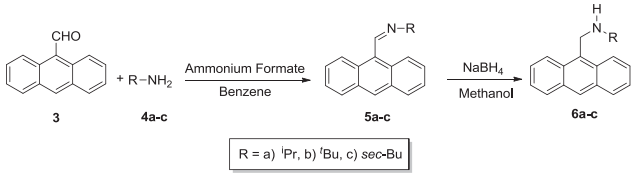
All reactions were carried out utilizing oven dried glassware. All the reagents were purchased from *Sigma-Aldrich* and used without further purification. Progress of the reaction and chromatographic separations were monitored by dried silica gel TLC plates (Aluminium sheets coated with silica gel, *E. Merck*). Visualisation of TLC plates was achieved by exposure to UV lamp or iodine vapours. Separation and purification of compounds were done by column chromatography using silica gel (*Spectrochem Chemicals*, 60–120 mesh), alumina (*Spectrochem Chemicals*). Melting points were determined on a *Neolab* melting point apparatus and are uncorrected. Infrared spectra were recorded on *Jasco 4100* FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz *Bruker Avance III* FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS.

2.2. General procedure for the synthesis of N-alkyl-9-anthracenemethanamine

Synthesis of *N*-alkylaminomethylanthracenes was achieved by modified Leuckart reaction [13–15] using 9-anthraldehyde and corresponding amine. In a 250 mL R. B. flask fitted with Dean-Stark trap, 9-anthraldehyde, primary amines **4a–c** and ammonium formate were taken in a 1:1:1 molar ratio in benzene as solvent. The mixture was refluxed for 3 h using an oil bath maintained at 95 °C. Imines **5a–c** obtained thereof were reduced with $NaBH_4$ (1 equivalent) in methanol. The reaction sequence is illustrated in Scheme. 1. The reaction mixture was poured into cold water and extracted with dichloromethane. Solvent was removed under reduced pressure and the product obtained was purified by column chromatography using alumina as the stationary phase. The product eluted with a mixture (1:19) of dichloromethane and hexane.

2.2.1. Synthesis of N-(anthracen-9-ylmethyl)propan-2-amine (6a)

9-Anthraldehyde (**3**, 3.30 g, 16 mmol) was refluxed with isopropylamine (**4a**, 1.40 mL, 16 mmol) and ammonium formate (1.00 g, 16 mmol) in benzene (25 mL) for 3 h in a round bottom flask. Water generated in the reaction was trapped by a Dean–Stark apparatus to drive the reaction to completion. $NaBH_4$ (0.74 g, 20 mmol) in methanol (5 mL) was added and the mixture was stirred at room temperature for 3 h. The resulting secondary amine was extracted with dichloromethane and crude product was isolated by removing the solvent under reduced pressure. The compound was further purified by column chromatography over alumina using a mixture (1:19) of dichloromethane and hexane. The structure of compound **6a** was confirmed on the basis of spectral and analytical data.



Scheme 1.

2.2.2. Synthesis of N-*(anthracen-9-ylmethyl)–2-methylpropan-2-amine (6b)*

9-Anthraldehyde (**3**, 3.30 g, 16 mmol), *tert*–butylamine (**4b**, 1.70 mL, 16 mmol) and ammonium formate (1.00 g, 16 mmol) were taken in a round bottom flask and refluxed in benzene for 3 h. Water formed during the reaction was collected in a Dean-Stark apparatus and resultant imine was reduced by stirring (3 h) with sodium borohydride (0.74 g, 16 mmol) dissolved in methanol (5 mL). The reaction mixture was washed with distilled water in a separating funnel and the crude product was extracted with dichloromethane. Solvent was removed and the product was purified by column chromatography over alumina, using a mixture (1:19) of dichloromethane and hexane as the eluent. Structure of **6b** was arrived at on the basis of spectral and analytical data.

2.2.3. Synthesis of N-*(anthracen-9-ylmethyl)butan-2-amine (6c)*

A mixture of 9-anthraldehyde (**3**, 3.30 g, 16 mmol), *sec*–butylamine (**4c**, 1.38 mL, 16 mmol) and ammonium formate (1.00 g, 16 mmol) in benzene was refluxed in a round bottom flask fitted with Dean-Stark trap for 3 h and the imine formed was reduced by stirring (3 h) with sodium borohydride (0.74 g, 16 mmol) in methanol (5 mL). The crude product was extracted using dichloromethane and compound was purified by column chromatography over alumina using a mixture (1:19) of dichloromethane and hexane as the eluent. Structure of the compound was confirmed by spectral and analytical data.

2.3. Reaction of anthracenemethanamines 6a–c with DMAD (1)

2.3.1. General procedure

When anthracenemethanamines **6a–c** (3 mmol) were refluxed with DMAD (**1**, 3 mmol) in solvents such as acetonitrile, dioxane, toluene, xylene and DMF (20 mL of solvent, substrate concentration, 0.15 M), the corresponding 1,4-adducts **8a–c** arising through nucleophilic addition were obtained in high yields (Scheme. 2). The crude products obtained after solvent evaporation were purified by column chromatography passed over silica using 1:19 ethyl acetate-hexane mixture. Products were isolated by removing the solvent under reduced pressure. Diels–Alder adducts **7a–c** and single electron transfer mediated products were not formed in detectable amounts [10–12]. Similar results were obtained when the experiment was repeated at 0.015 M substrate concentration in acetonitrile, dioxane, xylene and DMF. These experiments clearly illustrated that, in contrast to the reaction between DMAD (**1**) and tertiary amine **2** [10–12], the reaction between secondary amines **6** and **1** is not influenced by reaction temperature, solvent polarity and substrate concentration.

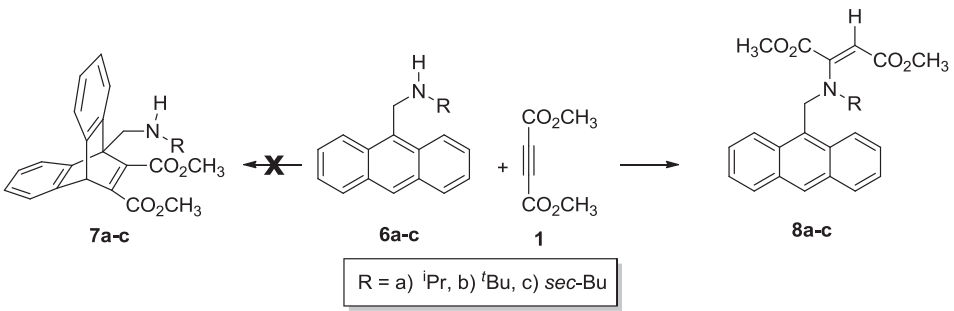
In a repeat run, we examined the reaction between **6a–c** and DMAD in the absence of solvents. Direct addition of amines **6a–c** to DMAD resulted in a highly exothermic reaction leading to instantaneous generation of adducts **8a–c** in excellent yields. Solvent-free reaction between **1** and **6** is scalable to multi gram level without loss of reaction yield and product selectivity. Yields for **8a–c** reported herein correspond to those obtained under solvent-free conditions. The structure of Michael adducts **8a–c** were confirmed on the basis of spectral and analytical data.

2.3.2. Reaction of anthracenemethanamine 6a with DMAD (1)

Anthracenemethanamine **6a** (0.75 g, 3 mmol) was refluxed with DMAD (0.27 mL, 3 mmol) in xylene (20 mL) for 3 h. The product formation was monitored by TLC and the crude product isolated by removal of xylene was purified by column chromatography over silica gel using ethyl acetate: hexane (1:19) as the eluent and the resulting **8a** was characterized by ^{1}H and ^{13}C NMR spectroscopy and other spectral data.

2.3.3. Reaction of anthracenemethanamine 6b with DMAD (1)

The secondary amine **6b** (0.78 g, 3 mmol) and DMAD (0.27 mL, 3 mmol) were refluxed in xylene (20 mL) for 3 h and completion of reaction was as confirmed by TLC. Removal of xylene under reduced pressure followed by further purification by column chromatography over silica gel with 1:19 ethyl acetate-hexane mixture gave **8b**, which was characterized by spectral and analytical data.



Scheme 2.

2.3.4. Reaction of anthracenemethanamine 6c with DMAD (1)

Refluxing *N*-(*sec*–butyl)anthracenemethanamine **6c** (0.78 g, 3 mmol) and DMAD (0.27 mL, 3 mmol) in xylene (20 mL) for 3 h resulted in the formation of Michael adduct **8c**. Isolation of the crude by removal of solvent under reduced pressure followed by column chromatography over silica gel with 1:19 ethyl acetate-hexane mixture resulted in the tertiary amine **8c**, as confirmed by spectral and analytical data.

3. Data, value and validation

3.1. Dimethyl 2-((anthracen-9-ylmethyl)(isopropyl)amino)fumarate (8a)

White solid; (0.66 g, 88%); m.p. 155–158 °C; IR (KBr), ν_{max} (cm^{-1}): 2985 (Aromatic C–H stretch), 1765 (C=O stretch, ester), 1760 (C=O stretch, ester), 1450 (C–H stretch), 1320 (C–O stretch, ester); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47-8.47 (m, 9H, aromatic), 5.23 (s, 2H, CH_2 spacer-anthracene), 5.10 (s, 1 H, olefinic CH), 3.69 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 3.40 (septet, J 7.2 Hz, 1H, isopropyl CH), 0.92 (d, J 7.2 Hz, 6H, isopropyl CH_3's); ^{13}C NMR ($CDCl_3$): δ (ppm): 168.20 (C=O, β to amine moiety), 166.87 (C=O, γ to amine moiety), 154.11 (olefinic C), 131.34, 129.32, 129.00, 126.90, 126.06, 125.19, 123.82 (aromatic); 88.18 (olefinic CH), 52.94 (isopropyl CH), 51.20 (OCH_3), 50.90 (OCH_3), 46.64 (CH_2-spacer-anthracene), 19.57 (isopropyl CH3's); MS: *m/z* 391 (M^+), 191 (anthracenemethyl cation).

3.2. Dimethyl 2-((anthracen-9-ylmethyl)(tert–butyl)amino)fumarate (8b)

Pale yellow solids; (0.68 g, 90%); m.p. 162–165 °C; IR (KBr) ν_{max} (cm^{-1}): 2954 (Aromatic C–H stretch), 1736 (C=O stretch, ester), 1696 (C=O stretch, ester), 1577 (C–H stretch), 1149 (C–O stretch, ester); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.44-7.43 (m, 9H, aromatic), 5.33 (s, 2H, CH_2 spacer-anthracene), 5.28 (s, 1H, olefinic CH), 3.50 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 1.36 (s, 9H, *tert*–butyl CH_3's); ^{13}C NMR ($CDCl_3$): δ (ppm): 167.02 (C=O, β to amine moiety), 166.95 (C=O, γ to amine moiety), 152.48 (olefinic C), 131.39, 130.71, 129.20, 128.47, 126.02, 124.85, 124.45 (aromatic), 109.47 (olefinic CH), 59.59 (*tert*–butyl C), 52.10 (OCH_3), 51.01 (OCH_3), 46.56 (CH_2-spacer-anthracene), 29.14 (*tert*–butyl CH_3's); MS: *m/z* 405 (M^+), 191 (anthracenemethyl cation).

3.3. Dimethyl 2-((anthracen-9-ylmethyl)(sec–butyl)amino)fumarate (8c)

Semisolid; (0.65 g, 86%); IR (KBr) ν_{max} (cm^{-1}): 2954 (Aromatic C–H stretch), 1739 (C=O stretch, ester), 1694 (C = O stretch, ester), 1375 (C–H stretch), 1149 (C–O stretch, ester); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31-7.30 (m, 9H, aromatic), 5.07 (m, 2H, spacer-anthracene), 4.98 (s, 1H, olefinic CH), 3.87 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 2.92 (q, J 6.8 Hz, 1H, 1.48 (m, 1H, CH), 1.04 (m, 1H), 0.63 (d, J 6.8 Hz, 3H, aliphatic CH_3), 0.40 (t, J 7.2 Hz, 3H, aliphatic CH_3); ^{13}C NMR ($CDCl_3$): δ (ppm): 167.18 (C=O, β to amine moiety), 165.80 (C=O, γ to amine moiety), 153.34 (olefinic C), 130.32, 130.22, 128.25, 127.94, 125.79, 125.01, 124.10, 122.84 (aromatic), 86.86 (olefinic CH), 56.50 (CH α to amine moiety), 51.85 (C=O β to amine moiety), 49.81 (C=O, γ to amine moiety), 46.07 (CH_2-spacer-anthracene), 25.60 (CH_2), 16.53 (CH_3), 10.43 (CH_3); MS: *m/z* 405 (M^+), 191 (anthracenemethyl cation).

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cdc.2018.07.004.

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