

(Anthracen-9-yl)methyl sulfides as a mechanistic probe for chemical as well as photochemical electron-transfer reactions

Reshma Gopalakrishnan, Jomon P. Jacob, Sa ada Farhana T. Moideen, Ligi M. Lalu, Perupparampil A. Unnikrishnan, and Sreedharan Prathapan*

*Department of Applied Chemistry, Cochin University of Science and Technology,
Cochin-682 022, Kerala, India.
E-mail: prathapans@gmail.com*

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Abstract

We have examined the intermediacy of sulfur-centred radical cations in the one-electron oxidation of (anthracen-9-yl)methyl sulfides. Reaction of (anthracen-9-yl)methyl sulfides with ceric ammonium nitrate (CAN) gave predominantly nitration and oxidation products along with products arising through sulfur-centred radical cations in minor amounts. Upon irradiation, (anthracen-9-yl)methyl sulfides underwent efficient intramolecular single electron transfer leading to a variety of products arising through the intermediacy of sulfur-centred radical cations.

Keywords: Single electron transfer, (anthracen-9-yl)methyl sulfides, ceric ammonium nitrate, oxidation, nitration

Introduction

Electron-transfer reactions in solution have been thoroughly investigated in chemical reaction dynamics and major progress has been made in the field of the dependence of electron-transfer rates on the free energy of reaction, on donor-acceptor distances as well as on the static properties of the solvents.^{1,2} Organic sulfides undergo fast one-electron oxidation reactions, owing to their relatively low ionization potentials. It is reported that organic sulfides are ideal precursors for sulfur-centred radical cations that can be used for probing mechanisms of electron-transfer quenching of excited states as well as for monitoring the fate of sulfur radicals.³⁻¹¹ One of the most frequently used reagents for the oxidative generation of radicals is the strong one-electron oxidant cerium(IV) ammonium nitrate (CAN). CAN has been widely used in organic reactions which include oxidation,¹²⁻¹⁶ oxidative addition,¹⁷⁻²¹ photooxidation,²² nitration,²³⁻²⁵ deprotection,^{26,27} graft polymerization,^{28,29} etc. Intermediates formed in these reactions may undergo oxidative fragmentation,^{30,31} rearrangement,³²⁻³⁴ or C-H, C-C and C-S

bond³⁵⁻³⁸ cleavages. Organic sulfides can be oxidized with catalytic amounts of Ce(IV) salts rapidly and selectively to sulfoxides.^{39,40}

Anthracene undergoes oxidation with cerium(IV) ammonium nitrate to form the anthracene radical cation which undergoes nitration followed by O-N fragmentation and dimerization to give 9,10-anthraquinone, bianthrone etc.⁴¹ There are also reports on the radical oxidation and addition reactions of some anthracene derivatives with dimethyl malonate in the presence of CAN.^{42,43} In the presence of acetic acid and polyethylene glycol, anthracene reacted with CAN and sodium bromate to give 1-nitro-9,10-anthracenedione.⁴⁴

Several reports discuss photooxidation of organic sulfides under a variety of reaction conditions: (i) autooxidation⁴⁵⁻⁴⁷ (ii) electron-transfer sensitization⁴⁸⁻⁵⁰ and (iii) singlet oxygen oxidation.⁵¹⁻⁵⁴ Organic sulfides undergo fast one-electron oxidation reactions because of their relatively low ionization potentials. These sulfide radical cations decay through competitive pathways involving deprotonation at C α -H bond, C-S fragmentation, oxidation, aromatic substitution and dimerization by photoinduced electron-transfer reaction.^{55,56} (Anthracen-9-yl)methyl sulfides with in-built sulfide and arene units are potent candidates for intramolecular electron-transfer reactions leading to intramolecular radical anion/radical cation pairs. In the present study, we examined the reaction of several (anthracen-9-yl)methyl sulfides with CAN in acetonitrile-water and compared these results with photochemical reactions of (anthracen-9-yl)methyl sulfides.

Results and Discussion

Anthracenemethyl sulfides are conveniently synthesized via a one-pot reaction of 9-anthracenemethanol, thiourea and the corresponding alkyl halide and also by base promoted one-pot reductive coupling of tosylhydrazones with thiols.^{57,58} For the present investigation, we selected six (anthracen-9-yl)methyl sulfides **1a-f** (Chart 1) having different steric and electronic environments around the sulfur atom.

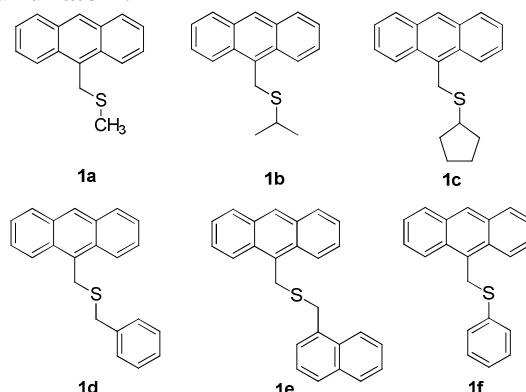
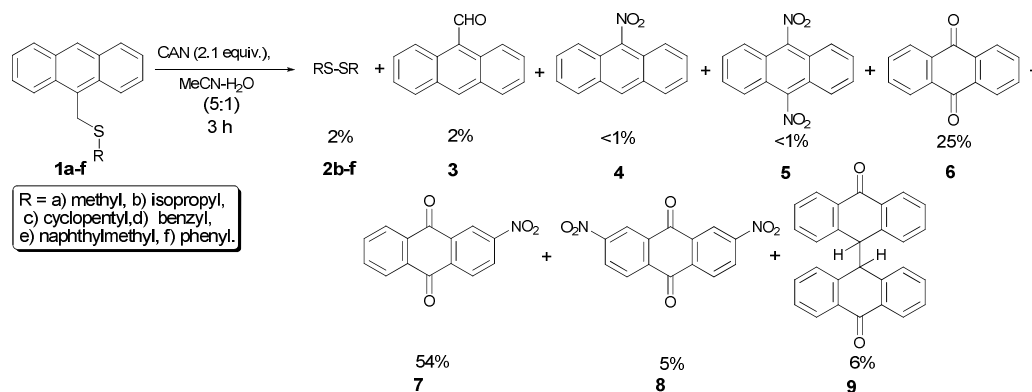


Chart 1. Structures of the (anthracen-9-yl)methyl sulfides.

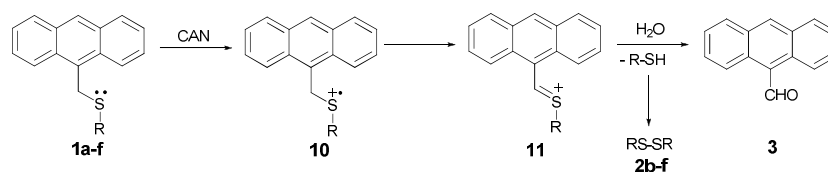
CAN-mediated transformations

When a 1:1 mixture of CAN and (anthracen-9-yl)methyl sulfides **1a-f** in 5:1 acetonitrile-water mixture was refluxed for three hours, a variety of products were formed (Scheme 1). Compounds **6** and **7** were formed in major amounts whereas compounds **2-5**, **8** and **9** were obtained in low yields.



Scheme 1. Products of (anthracen-9-yl)methyl sulfides **1a-f** with CAN in acetonitrile-water.

Generation of products **2-9** is explicable on the basis of two distinct reaction pathways. Disulfides **2** and 9-anthracenecarboxaldehyde (**3**) are generated by sulfur-to-CAN single electron transfer followed by further transformations as detailed in Scheme 2. On the other hand, nitration and oxidation products such as **4-9** are formed by the reaction of CAN with the anthracene component in **1a-f**. Among these, formation of **4**, **5**, **6** and **9** has already been reported in the reaction of anthracenes with CAN.⁴¹⁻⁴⁴ Mechanistic details of CAN-mediated nitration of several polynuclear arenes are available in literature.^{23,41-44,59-61} Interestingly, formation of **7** and **8** in the CAN-mediated transformation of anthracene and its derivatives has not been reported earlier. A logical conclusion here is that the 9-(2-alkylthiomethyl) substituent plays a persuasive role in the generation of **7** and **8**. In order to test this hypothesis, we reexamined the reaction of 9-methylanthracene with CAN under identical conditions. Products such as **4-8** were generated in comparable yields in these reactions ruling out any significant role for the 9-(2-alkylthiomethyl) substituent in the generation of **7** and **8**. In order to verify the involvement of the 9-substituent in the formation of **7** and **8**, we repeated the reaction of anthracene with CAN under identical conditions. In contrast to previous reports, products such as **7** and **8** were formed in substantial amounts in this reaction as well. These results indicated that reactivity of (anthracen-9-yl)methyl sulfides is similar to that of other anthracenes under the conditions employed by us. A major difference here is the concomitant sulfur-to-CAN single electron transfer that takes place as a minor competing pathway for (anthracen-9-yl)methyl sulfides. The nature of the *S*-substituent does not play a significant role in the reaction of (anthracen-9-yl)methyl sulfides with CAN.



Scheme 2. One electron oxidation of (anthracen-9-yl)methyl sulfides with CAN.

Photoinduced Electron-Transfer Reactions of (Anthracen-9-yl)methyl sulfides

In order to suppress dimerization via [4+4] addition, all irradiation experiments were conducted at low concentrations.⁶² In a typical run, degassed benzene solutions of (anthracen-9-yl)methyl sulfides **1a-f** (0.8 mM) were exhaustively irradiated at 350 nm. After completion of the reaction (45 to 90 minutes), solvent was removed under reduced pressure and the residue was separated by column chromatography. Various fractions were collected and analyzed using spectroscopic measurements. The products formed were identified as 9-anthraldehyde (**3**),⁶³ 9,10-anthraquinone (**6**),⁶⁴ 9-methylanthracene (**12**),⁶⁵ 1,2-bis(9-anthracenyl)ethane (**13**),⁶⁶⁻⁶⁹ lepidoptereⁿe (**14**),^{66,70-74} biplanene (**15**),⁷⁵⁻⁷⁷ anthrone (**16**)⁷⁸ along with products arising through the *S*-alkyl residues present in parent anthracenemethyl sulfides. Common products formed in the photoirradiation of (anthracen-9-yl)methyl sulfides **1a-f** are shown in Chart 2 and details of all the products isolated are presented in Scheme 3. In the case of **1a**, incipient sulfur-containing compounds are volatile and hence escaped detection/isolation. For reasons that are not fully understood, nature of sulfur containing products varies from substrate to substrate.

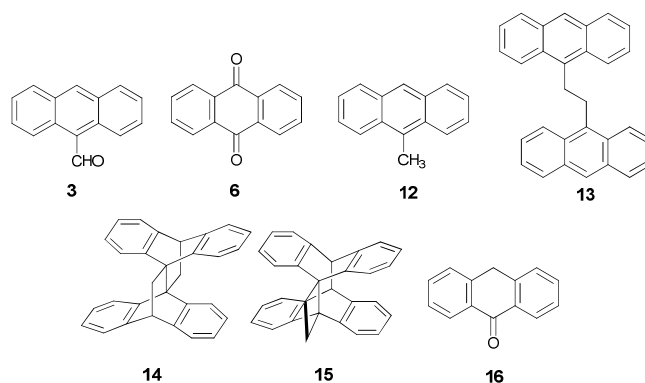
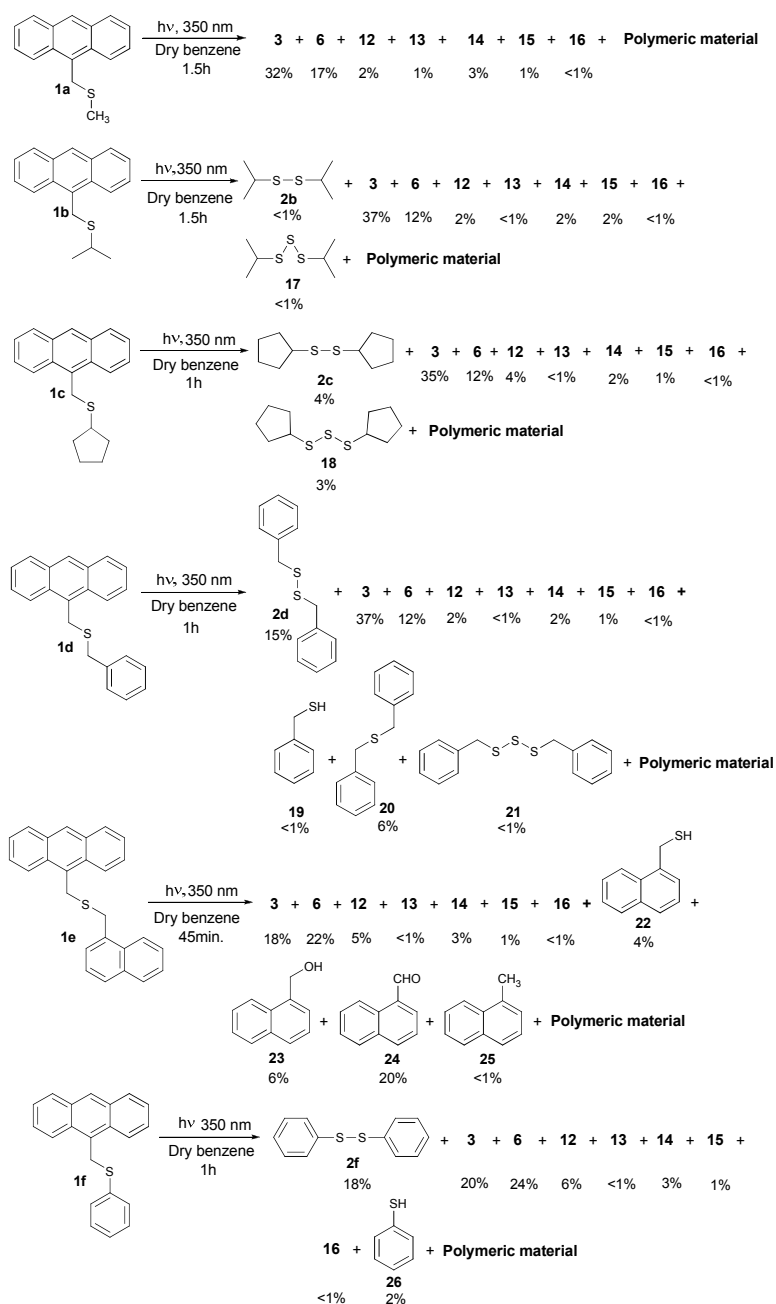


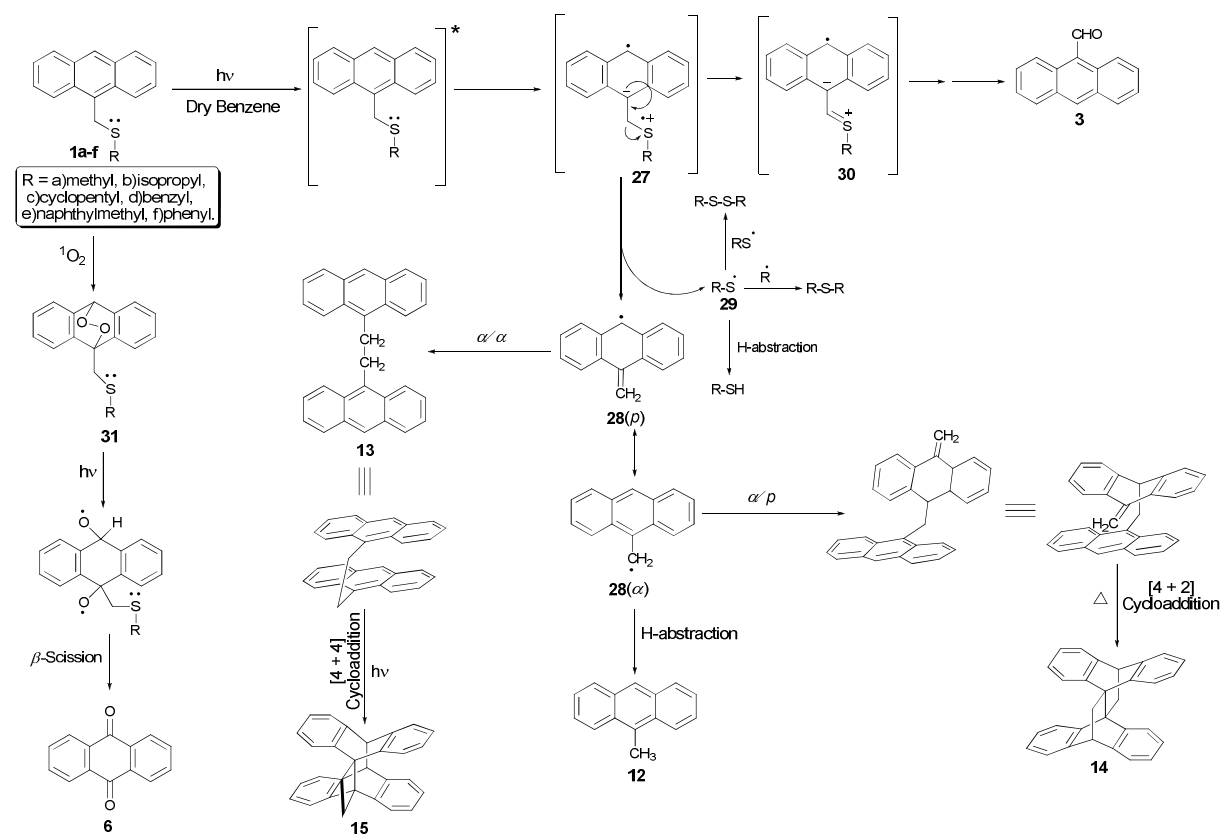
Chart 2. Common products formed in the photolysis of (anthracen-9-yl)methyl sulfides **1a-f**.



Scheme 3. All reaction products for the photochemical reactions of (anthracen-9-yl)methyl sulfides **1a-f**.

Mechanism for the photochemical reaction of (anthracen-9-yl)methyl sulfides **1a-f** can be explained on the basis of intramolecular one-electron transfer which takes place in (anthracen-9-yl)methyl sulfides in the excited state to form intramolecular sulfide radical cation-anthracene radical anion pair **27**. This leads to the destabilization and cleavage of a C-S bond to form the anthracenemethyl radical (**28**) and sulfide radical **29**. Sulfide radical (**29**) undergoes a series of

reactions to form products such as alcohols, thiols, thioethers, disulfides, and even trisulfides in some cases. The chemistry of the anthracenemethyl radical (**28**) is well documented.^{62,67,73} It can be represented as a resonance hybrid of **28(p)** and **28(α)** forms. Hydrogen atom abstraction by **28** leads to the formation of 9-methylantracene (**12**). Lepidoptere (**14**) is formed by the α/p dimerization of **28** followed by intramolecular [4+2] cycloaddition. This is a thermal intramolecular [4+2] cycloaddition, a facile process even at room temperature.⁷⁹ 1,2-Bis(9-anthracenyl)ethane (**13**) is the α/α dimerization product of **28**. Biplanene (**15**) is formed by intramolecular [4+4] cycloaddition of **13** initiated by stray light. Generation of 9-anthraldehyde (**3**) is explained on the basis of initial intramolecular excited-state electron transfer leading intermediate **27** followed by α -H atom loss and bond reorganization to sulfonium cation **30**. Hydrolysis of **30** gives 9-anthraldehyde (**3**). 9,10-Anthraquinone (**6**) is formed through the bond homolysis followed by β -scission of the endoperoxide **31** generated from **1a-f**⁸⁰ by the reaction with singlet oxygen⁸¹ (Scheme 4).



Scheme 4. Proposed mechanistic sequences for the photochemical reactions of (anthracen-9-yl)methyl sulfides **1a-f**.

Conclusion

We have illustrated the single electron-transfer oxidation reaction of (anthracen-9-yl)methyl sulfides via chemical electron transfer as well as intramolecular excited-state electron-transfer methods. We have established that multiple pathways operate in the CAN-mediated and photochemical transformations of anthracenemethyl sulfides. These include single electron-transfer mediated transformations, C-S bond fragmentation, nitration and oxidation as major pathways.

Experimental Section

General. All reactions were carried out in oven-dried glassware. All experiments used 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. All the reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Aluminium sheets coated with silica gel (Merck) were used for thin layer chromatography. Separation and purification of compounds was achieved by column chromatography using silica gel (Spectrochem Chemicals, 60-120 mesh). The products were further purified by recrystallization from suitable solvent systems. Melting points are uncorrected and were determined on a Neolab melting point apparatus. Infrared spectra were recorded using Jasco 4100 and ABB Bomem (MB Series) FT-IR spectrometers. The ^1H 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 electrospray ionization (ESI) using GC-MS (Agilent GC-7890A, Mass-5975C) and fast atom bombardment (FAB) using *JMS 600 JEOL* mass spectrometers. All new compounds were identified on the basis of spectroscopic and analytical data. Relevant references are cited for known compounds.

Synthesis of (anthracen-9-yl)methyl sulfides.

(Anthracen-9-yl)methyl sulfides **1a-f** were prepared by adaptation of known procedures.^{57,58,82,83}

General experimental procedure for the chemical electron-transfer reactions of (anthracen-9-yl)methyl sulfides 1a-f with CAN. To a solution of (anthracen-9-yl)methyl sulfide **1a-f** (0.38g, 1 equiv.) in MeCN–H₂O (5:1, 6 mL), CAN (2.1 equiv.) was added and the mixture was refluxed for 3 h. After completion of the reaction, the reaction mixture was poured into H₂O and extracted with CH₂Cl₂. The organic layer was separated, washed with H₂O and dried over anhydrous Na₂SO₄. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture of hexane and CH₂Cl₂ separated twelve products such as compounds **2-9**. Compounds **2b-f** were obtained by the elution

using hexane. Compounds **3-6** were obtained by elution using a mixture of hexane and CH₂Cl₂ (3:2). Elution using hexane and CH₂Cl₂ (3:7) yielded **7** and **8**. Elution using hexane and CH₂Cl₂ (1:4) yielded the compound **9**.

General experimental procedure for the photoinduced electron-transfer reaction of (anthracen-9-yl)methyl sulfides 1a-f. A degassed solution of (anthracen-9-yl)methyl sulfides **1a-f** (0.8 mM) in dry benzene (200 mL) was irradiated at 350 nm lamp under argon or nitrogen atmosphere in a Rayonet photochemical reactor. Progress of the reaction was monitored by TLC. Solvent was removed under reduced pressure and the residue was purified by column chromatography over silica gel. Elution with hexane gave **2b-d**, **2f** and **12**. Compounds **13** and **17-26** were obtained by elution with hexane and CH₂Cl₂ (9:1). Compounds **14** and **15** are obtained by elution using hexane-CH₂Cl₂ (4:1) mixture. Elution with hexane and CH₂Cl₂ (3:2) yielded **3**, **6** and **16**. The reaction time for different (anthracen-9-yl)methyl sulfides is indicated in Scheme 3. The presence of volatile components was established by GC-MS analysis of the photolysate.

1,2-Diisopropyl disulfide (2b).^{84,85} Colorless liquid; MS: *m/z* 150 (*M*⁺).

1,2-Dicyclopentyl disulfide (2c).⁸⁶ Colorless liquid; MS: *m/z* 202 (*M*⁺).

1,2-Dibenzyl disulfide (2d).⁸⁷ White crystalline solid; mp 67-69 °C; MS: *m/z* 246 (*M*⁺).

1,2-bis(Naphthalen-1-ylmethyl)disulfide (2e).⁸⁸ White crystalline solid; mp 145-147 °C; IR *v*_{max} (KBr): 3092, 2986, 2883, 646, 586, 479 cm⁻¹; ¹H NMR (CDCl₃): δ 8.04–7.24 (m, 14H), 4.47 (s, 4H); MS: *m/z* 346 (*M*⁺); Anal. Calcd for C₂₂H₁₈S₂: C, 76.26; H, 5.24; S, 18.51; Found: C, 76.18; H, 5.17; S, 18.43.

1,2-Diphenyl disulfide (2f).⁸⁹ Colorless crystalline solid; mp 57-59 °C; MS: *m/z* 218 (*M*⁺).

9-Nitroanthracene (4).^{90a} Yellow crystalline solid; mp. 153-157 °C; IR *v*_{max} (KBr): 3056, 2923, 1516, 1317, 1440, 725 cm⁻¹; ¹H NMR (CDCl₃): δ 8.59-7.56 (m, 9H); ¹³C NMR (CDCl₃) δ 130.9, 130.4, 128.9, 128.4, 126.2, 122.7, 121.5; MS: *m/z* 223 (*M*⁺); Anal. Calcd for C₁₄H₉NO₂: C, 75.33; H, 4.06; N, 6.27; Found: C, 75.25; H, 3.98; N, 6.21.

9,10-Dinitroanthracene (5).^{90b} Yellow crystalline solid; mp. 292-294 °C; IR *v*_{max} (KBr): 2955, 2926, 1540, 1519, 1363, 1283, 831, 768 cm⁻¹; ¹H NMR (CDCl₃): δ 7.90-7.88 (m, 4H), 7.70-7.68 (m, 4H); MS: *m/z* 268 (*M*⁺); Anal. Calcd for C₁₄H₈N₂O₄: C, 62.69; H, 3.01; N, 10.44; Found: C, 62.60; H, 2.91; N, 10.35.

2-Nitro-9,10-anthraquinone (7).^{90c,e} Yellow crystalline solid; mp. 185-186 °C; IR *v*_{max} (KBr): 3060, 1675, 1585, 1525, 1321, 1290, 696 cm⁻¹; ¹H NMR (CDCl₃): δ 9.06-7.80 (m, 7H); ¹³C NMR (CDCl₃) δ 181.6, 181.1, 151.3, 137.0, 134.9, 133.3, 133.2, 131.4, 129.2, 128.0, 127.8, 127.7, 127.3, 122.7, 120.8; MS: *m/z* 253 (*M*⁺); Anal. Calcd for C₁₄H₇NO₄: C, 66.41; H, 2.79; N, 5.53; Found: C, 66.36; H, 2.68; N, 5.42.

2,7-Dinitro-9,10-anthraquinone (8).^{90d} Pale yellow crystalline solid; mp 290-291 °C; IR *v*_{max} (KBr): 3092, 3038, 1677, 1539, 1356, 1329, 1301, 736 cm⁻¹; ¹H NMR (CDCl₃): δ 9.19-8.59 (m, 6H); ¹³C NMR (CDCl₃) δ 180.24, 179.46, 151.58, 122.83, 136.56, 134.44, 129.64, 128.72; MS:

m/z 298 (M^+); Anal. Calcd for $C_{14}H_6N_2O_6$: C, 56.39; H, 2.03; N, 9.39; Found: C, 56.28; H, 1.94; N, 9.32.

9,9'-Bianthracene-10,10'(9H,9'H)-dione (9).⁴² White crystalline solid; mp 255-256 °C; IR ν_{\max} (KBr): 3076, 2966, 1675, 1595, 1334, 1288, 811, 690 cm^{-1} ; 1H NMR ($CDCl_3$): δ 7.95-6.85 (m, 16H), 4.77 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 183.0, 139.9, 133.8, 132.2, 128.5, 127.9, 126.7, 54.4; MS: m/z 386 (M^+); Anal. Calcd for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69; Found: C, 86.91; H, 4.62.

Anthracen-9(10H)-one (16).⁹¹ Light yellow crystalline solid; mp 154-155 °C; MS: m/z 194 (M^+).

1,3-Diisopropyl trisulfide (17).⁸⁵ Colorless liquid; MS: m/z 182 (M^+).

1,3-Dicyclopentyl trisulfide (18).⁹² Colorless liquid; MS: m/z 234 (M^+).

Benzyl thiol (19).⁹³ Colorless liquid, MS: m/z 124 (M^+).

Dibenzyl sulfide (20).⁹⁴ Colorless crystalline solid; mp: 46-48 °C; MS: m/z 214 (M^+).

1,3-Dibenzyl trisulfide (21).⁹⁵ Colorless liquid; MS: m/z 278 (M^+).

1-Naphthylmethylthiol (22).⁹⁶ Colorless liquid; MS: m/z 174 (M^+).

1-Naphthylmethylalcohol (23).⁹⁷ Colorless liquid; MS: m/z 158 (M^+).

1-Naphthaldehyde (24).⁹⁷ Colorless solid; MS: m/z 156 (M^+).

1-Methylnaphthalene (25).⁹⁸ Colorless liquid; MS: m/z 142 (M^+).

Thiophenol (26).⁸⁹ Colorless liquid, MS: m/z 110 (M^+).

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