The Synthesis and Characterization of Solvatochromic Maleimide-Fused *N*-Allyl- and *N*-Alkyl-Substituted 1,4-Dithiines and Diels–Alder Reactions with Anthracene

Şirin Gülten*

Department of Chemistry, Faculty of Arts and Sciences, Terzioğlu Campus, Çanakkale Onsekiz Mart University, Çanakkale 17020, Turkey
*E-mail: siringulten@hotmail.com

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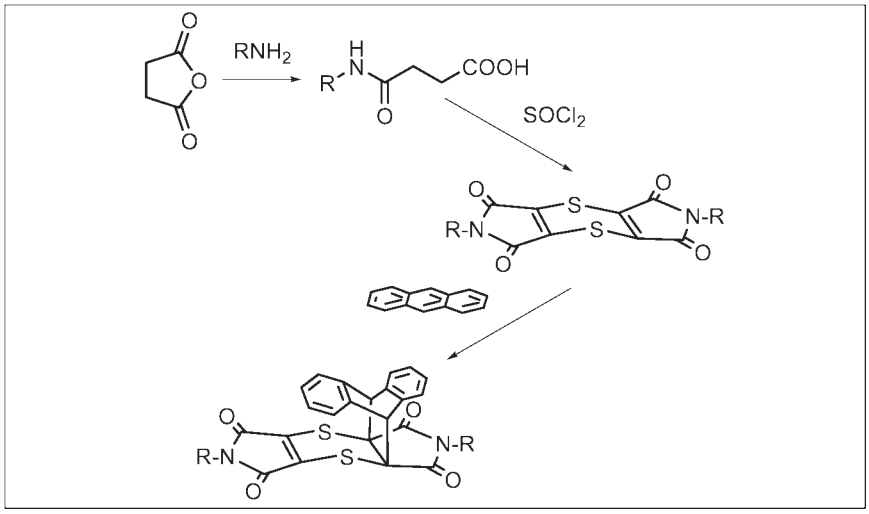

A simple and facile access to new solvatochromic maleimide-fused *N*-allyl- and *N*-alkyl-substituted 1,4-dithiines from the corresponding *N*-substituted succinamic acid derivatives in one-pot with oxidation by thionyl chloride is described. The Diels–Alder reaction of these 1,4-dithiines with anthracene has been investigated. The 1,4-dithiine derivatives react smoothly with anthracene *via* charge-transfer complexes to form the Diels–Alder adducts in excellent yields.

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INTRODUCTION

Sulfur-containing heterocyclic compounds have held the focus of researchers along decades of historical development of organic synthesis. Their biological activities and unique structures allow several applications in different parts of pharmaceutical and agrochemical research or in material science [1].

The synthesis of 1,4-dithiines has recevied much attention because of their biological activity, particularly as fungicides and antibacterials [2], their application in synthetic organic and medicinal chemistry, their structural and electronic properties, their ability to act as electron donors [3], and the wide variety of synthetic transformation they undergo [3]. Some derivatives of 1,4-dithiines show activities as nonpeptide antagonists of the human Galanin hGAL-1 receptors [4], and some 1,4-dithiine-2,3,5,6-tetracarboxydiimides have been used as anthelmintics [5]. Detailed research of 1,4-dithiines has been limited by a lack of suitable synthetic approaches. Some 1,4-dithiines have been known for more than 100 years, although the correct stuctures were assigned recently [1,6,7]. Many polycyclic 1,4-dithiine derivatives are useful as pigments and functional materials for electrooptical applications [7].

For 80 years, the Diels–Alder reaction has remained as one of the best and most powerful methods of synthesis of six-membered rings and bicyclic molecules [8]. Many factors, such as its versatility, its high regio- and stereoselectivity, and its ability to rapidly give polyfunctionality have contributed to the popularity of this reaction in organic syntheses.

Anthracene and its derivatives are among the most useful polycyclic aromatic compounds and efficient photochromic systems. In view of their fluorescent properties, they are of practical interest as sensors and markers in biological or supramolecular systems [9]. Anthracenes are well-known as fairly reactive dienes that easily undergo both thermal and photochemical Diels–Alder cycloadditions with a variety of dienophiles [10]. In the thermal [4+2] cycloaddition reaction mechanism, new

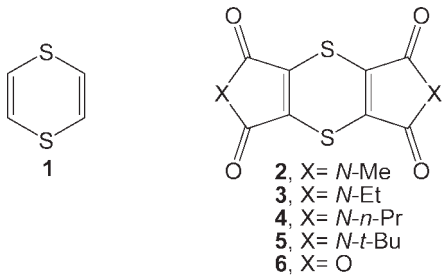


Figure 1. 1,4-Dithiine and its derivatives.

sigma bonds are formed simultaneously, either by direct addition or *via* intermediate charge-transfer (CT) complex (electron donor-acceptor molecular complex). Many studies have indicated the observation of transient color that disappears as the thermal Diels–Alder reaction proceeds. This has been shown to be due to the formation of a CT complex during the course of the reaction [11].

Very few articles deal with the synthesis, characterization, reactions, and properties of maleimide-fused 1,4-dithiines [7,12–15]. Hayakawa *et al*. [12] and Kim *et al*. [13] have reported the preparation of the methyl, ethyl, propyl, and *t*-butyl derivatives of maleimide-fused 1,4-dithiine with short experimental details. The mechanistic pathway was not suggested in these reports. Valla *et al*. [14] and Zentz *et al*. [15] have reported the preparation of the propyl, isopropyl, butyl, and benzyl derivatives of maleimide-fused 1,4-dithiine with experimental details and investigated the mechanistic pathway by using a Pummerer rearrangement-like reaction. 1,4-Dithiines **2, 3, 4,** and **5** were used as a dienophile for Diels–Alder reactions by Hayakawa *et al*. [12] and Kim *et al*. [13] (Fig. 1).

1,4-Dithiine **1** and its derivatives undergo thermal elimination of sulfur to produce corresponding thiophene derivatives [16]. Nevertheless, thermal stability of *N*,*N*′-dimethyl-dipyrrole-fused dithiine **2** and the dianhydride **6** was observed by Draber [17], along with the formation of cycloadducts with anthracene (Fig. 1).

Draber [17] has suggested the planar structure of **2** and **6** based on strong ultraviolet absorptions at long wavelenghts, thermal stability, and the ability to form CT complexes. Indeed, various molecular orbital calculations have indicated **2** and **6** to be nearly planar [12]. 1,4-Ditihiine **3** exhibits a planar structure that makes easy the formation of CT crystals with anthracene in alternate donor-acceptor stacks [13].

RESULTS AND DISCUSSION

This study describes synthesis of new solvatochromic maleimide-fused *N*-allyl- and *N*-alkyl-substituted 1,4-dithiines (**9a–d**) from succinamic acid derivatives (**8a–d**) in one-pot with oxidation by thionyl chloride and their subsequent Diels–Alder cycloaddition reactions with anthracene.

Maleimide-fused *N*-allyl- and *N*-alkyl-substituted 1,4-dithiines. The initial study began with the reaction between succinic anhydride **7** and the appropriate amines to give *N*-substituted succinamic acid derivatives. Maleimide-fused *N*-allyl [18] and *N*-alkyl 1,4-dithiines were prepared in high yields from corresponding *N*-substituted succinamic acid derivatives using $SOCl_2$ according to the earlier reported procedure (Table 1) by Michaïlidis *et al*. [19], who reported without experimental details. 1,4-Dithiines **9a–d** are green and deep green crystals, but their solutions in various solvents (diethyl ether, ethanol, chloroform, acetone, and benzene) are coloured yellow (**9a** in diethyl ether, ethanol, and acetone; **9c** in ethanol), green (**9a** in benzene; **9c** in acetone; **9d** in ethanol), deep geen (**9a** in chloroform; **9c** in diethyl ether and chloroform), deep blue (**9c** in benzene; **9d** in diethyl ether), purple (**9b** in acetone), deep blue-green (**9d** in benzene and chloroform), deep blue-purple (**9b** in benzene and chloroform; **9d** in acetone); thus, products **9a–d** are higly solvatochromic. Maleimide-fused *N*-allyl 1,4-dithiine **9a** is partly soluble in diethyl ether and ethanol, whereas **9b** is insoluble in diethyl ether and ethanol.

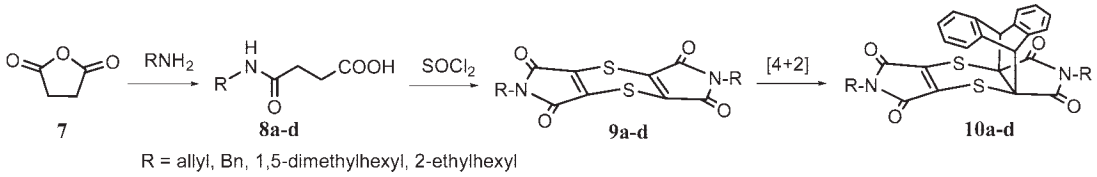
The conjugation of double bond with carbonyl groups in 1,4-dithiines **9a–d** leads to both the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ transitions being shifted to longer wavelengths. The absorptions are found between 300 and 310 nm for $\pi \rightarrow \pi^*$ transition and between 378 and 389 nm for $n \rightarrow \pi^*$ transition in **9a–d**. The $n \rightarrow \pi^*$ transitions are much less intense (ϵ = 1271–1803) than $\pi \rightarrow \pi^*$ transition (ϵ = 1657–2439).

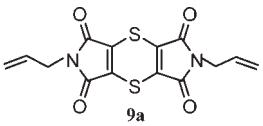
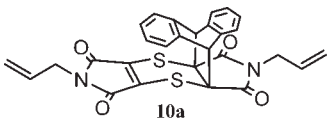
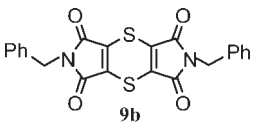
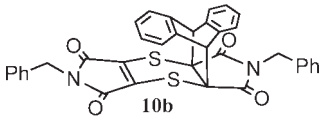
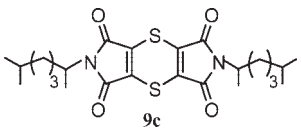
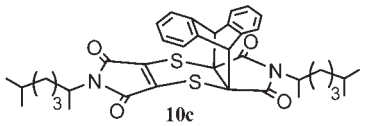
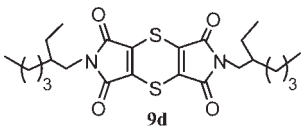
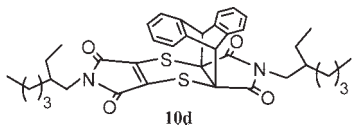
The reaction is straightforward and requires simple and inexpensive starting materials. We have, thus, introduced a highly efficient methodology for the synthesis of maleimide-fused *N*-allyl- and *N*-alkyl-substituted 1,4-dithiines. It may be widely applicable for the preparation of a variety of 1,4-dithiines.

Diels–Alder cycloaddition reactions. When anthracene was allowed to react with 1,4-dithiines **9a–d** in refluxing benzene, the characteristic green, deep blue, deep blue-green, and deep blue-purple colors of **9a–d** disappeared, and the corresponding Diels–Alder cycloadducts **10a–d** were obtained in 95, 89, 94, and 90% yields, respectively (Table 1). Much longer reaction times were needed for **9c** and **9d** than for the reaction of **9a** and **9b**, probably, because of the increased steric bulk. Anthracene and **9a–b** in $CHCl_3$ underwent a slow reaction at room temperature in the dark in 2 weeks, giving the Diels–Alder cycloadducts **10a** and **10b** in 99 and 94% yield, respectively. The same reaction was

Table 1

Formation of 1,4-dithiines and the Diels-Alder cycloadducts.



Entry	1,4-Dithiine	Yield (%)	Diels-Alder cycloadduct	Time	Yield (%)
1	 **9a**	63	 **10a**	24 h 2 weeks	95[a] 99[b]
2	 **9b**	60	 **10b**	22 h 2 weeks	89[a] 94[b]
3	 **9c**	88	 **10c**	5 days 4 weeks	94[a] 74[b]
4	 **9d**	87	 **10d**	3 days 4 weeks	90[a] 79[b]

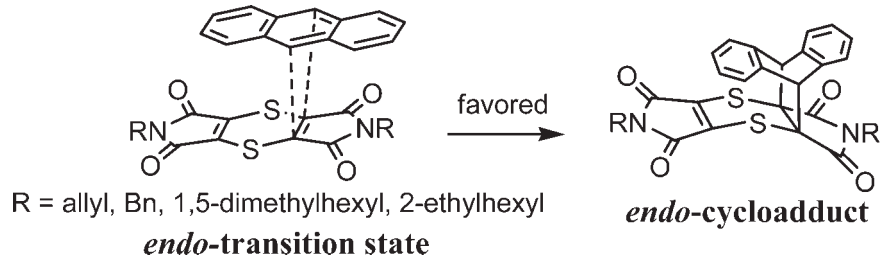
The Diels–Alder reaction conditions: [a]: benzene, reflux; [b]: $CHCl_3$, rt, in the dark.

carried out using **9c** and **9d** under the same reaction conditions but over a time of 4 weeks, giving **10c** and **10d** in 74 and 79% yield, respectively (Table 1). The Diels–Alder cycloadducts **10a–d** were bright yellow crystals, which were reasonably soluble in dichloromethane, chloroform, and ethanol. Only *endo*-cycloadducts **10a** and **10b** were obtained, while the Diels–Alder cycloadducts **10c** and **10d** were shown to be a mixture of two diastereoisomers in a 1:1 ratio as shown by integration of signals in the ^{1}H NMR spectrum. The structure of these adducts **10a–d** were determined on the basis of ^{1}H and ^{13}C NMR spectroscopy, mass spectroscopy, and elemental analysis.

When anthracene and 1,4-dithiine approach each other in the Diels–Alder reaction, the best overlap is achieved when the reactants lie directly on top of one another, a geometry that leads to *endo*- rather than *exo*-product. The kinetically favorable *endo*-Diels–Alder cycloadduct is formed faster (lowest activation energy), even though the thermodynamically favorable *exo*-product is more stable. Secondary orbital overlap in the transition state between the orbitals on the carbonyl groups in the 1,4-dithiine and the orbitals in the anthracene not directly involved in bonding. These interactions do not lead to bond formation, but they do lower the energy of the transition state (Scheme 1).

The IR spectra exhibited characteristic imide bands at 1771 and 1707 cm^{-1} for **10a**, at 1776 and 1708 cm^{-1} for **10b**, at 1773 and 1706 cm^{-1} for **10c**, and at 1767 and 1703 cm^{-1} for **10d**. ^{1}H NMR spectra showed two *N*-allyl or *N*-alkyl proton signals for one isomer, one of them being shifted upfield as a result of shielding effect

Scheme 1. Formation of the *endo*-Diels–Alder cycloadduct.



of the anthracene ring. Characteristic absorptions of anthracene have disappeared, indicating destruction of the anthracene conjugated system by the Diels–Alder cycloadditon. The UV–vis spectroscopic analysis of the Diels–Alder cycloadducts **10a–d** revealed the appearance of new absorption bands at 405, 412, 410, and 411 nm, respectively.

In accordance with the reported early experimental results [13], there are two pathways for the formation of the Diels–Alder cycloadducts of 1,4-dithiines **9a–d** and anthracene (Fig. 2). The choice of these reaction pathways only depends on the electronic properties of dienophile (1,4-dithiine) and diene (anthracene). Electron-rich dienes (anthracene, 9-methylanthracene, 9,10-dimethylanthracene) give a cycloadduct *via* pathway I, modestly electron-deficient diene (9-anthracenecarboxaldehyde) give a cycloadduct *via* pathway II, and no reaction occurs to the strongly electron-deficient diene (9-nitroanthracene) [12]. 1,4-Dithiine derivatives 9a–d act as strong acceptors in CT complex formation and possess high reactivity as planar electron-rich dienes.

According to the preliminary investigation by Draber [17], the reaction of 1,4-dithiines **9a–d** with the electron-rich anthracene occurred *via* CT complexes, as evidenced by unusual color change during the reaction.

We, herein, report new 1,4-dithiine derivatives and their Diels–Alder cycloadducts. The oxidation reaction by thionyl chloride was succesfully applied to **8a–d**, which gave the corresponding ring-closed 1,4-dithiines **9a–d** in good yields. To the best of our knowledge, three of the synthesized 1,4-dithiines, **9a, 9c,** and **9d,** and all Diels–Alder cycloadducts **10a–d** are new compounds. To the best of our knowledge, this method is the first example of a one-step synthesis of maleimide-fused *N*-allyl- and sterically-bulky *N*-alkyl-substituted 1,4-dithiines directly from succinamic acid derivatives by thionyl chloride oxidation. This one-pot reaction converts various succinamic acid derivatives to solvatochromic 1,4-dithiines, which underwent the Diels–Alder reactions with anthracene in excellent yields.

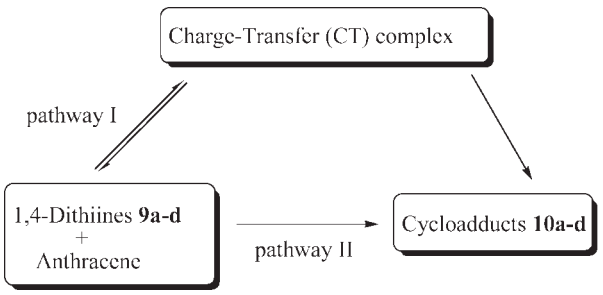


Figure 2. Pathway I: The cycloaddition *via* CT complex, pathway II: Direct cycloaddition.

EXPERIMENTAL

The melting points were measured on an Electrothermal 9100 melting point apparatus and are uncorrected. The UV–vis absorption spectra were determined with a Perkin Elmer Lamda 25 spectrophotometer in chloroform solutions using 10-mm quartz cells. The IR spectra were recorded on a One FTIR ATR Perkin Elmer spectrometer. The ^{1}H and ^{13}C NMR spectra were taken with a Varian NMR Gemini 300 and Bruker 400 Ultra Shield spectrometers and chemical shifts were recorded as ppm downfield from internal tetramethylsilane. The mass spectra were taken on a Waters ZQ Micromass LC/MS spectrometer. Elemental analyses were performed on a Leco 932 CHNS instrument. All chemicals were purchased from commercial suppliers and used directly without any further purification. Organic solvents were dried by standard methods and were distilled before use. All the reactions were performed under a nitrogen atmosphere. Reaction progress was monitored by TLC on precoated aluminum-backed plates (Merck SIL G/UV_{254}), and chromophoric compounds were visualised by UV light and subsequent staining with alkaline potassium permanganate solution or iodine. Petroleum ether refers to light petroleum (bp 40–60°C).

General procedure for the preparation of *N*-substituted succinamic acids (8a–d). Reaction of succinic anhydride **7** (16 mmol) with the appropriate amine (20 mmol) in the presence of the dry appropriate solvent (10 mL, THF, MeCN, acetone, or 1,4-dioxane) at room temperature with stirring for a few hours generated the corresponding *N*-substituted succinamic acids **8a–d**. After the reaction was completed, the solvent was removed under reduced pressure and recrystallized from the appropriate solvent (Et_2O, 1,4-dioxane, or water).

4-Oxo-4-(prop-2-enylamino)butanoic acid (8a). White crystals; 70% yield (1.76 g); mp 93–94°C; IR-ATR (ν_{max}, cm^{-1}): 3500–2600, 3302, 1690, 1639, 1618, 1544; ^{1}H NMR (400 MHz, DMSO-d_6): 2.54 (t, J = 6.9 Hz, 2H, CH_2CONH), 2.72 (t, J = 6.9 Hz, 2H, CH_2COOH), 3.90 (m, 2H, CONHCH_2), 5.20–5.15 (skew dq, 2H, CH=CH_2), 5.80 (m, 1H, CH=CH_2),

5.97–6.34 (br s, 1H, NH), 7.34–10.45 (br s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): 29.70 (*C*H_2CONH), 30.64 (*C*H_2COOH), 41.55 (CONH*C*H_2), 115.37 (CH=*C*H_2), 135.04 (*C*H=CH_2), 171.63 (CONH), 174.35 (COOH); MS (ESI+): m/z (%): 158 (44, $[M + H]^+$), 152 (14), 140 (100); Anal. Calcd. for $C_7H_{11}NO_3$: C, 53.49; H, 7.05; N, 8.91. Found: C, 53.55; H, 7.19; N, 8.94.

4-Oxo-4-(phenylmethylamino)butanoic acid (8b). White crystals; 83% yield (2.75 g); mp 132–133°C (lit. [20] mp 137.7–138.2°C; lit. [14,15] mp 144°C); IR-ATR (ν_{max}, cm^{-1}): 3300–2500, 3296, 1689, 1639, 1540; ^{1}H NMR (400 MHz, DMSO-d_6): 2.61 (m, 2H, CH_2), 2.46 (m, 2H, CH_2), 3.4 (br s, 1H, NH), 4.36 (d, J = 5.71 Hz, 2H, CH_2NH), 6.02 (br s, 1H, OH), 7.3–7.2 (m, 5H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): 30.17 (CH_2), 31.03 (CH_2), 43.84 (CH_2), 127.78 (CH), 128.71 (CH), 128.84 (CH), 137.77 (Q), 172.43 (CONH), 174.66 (COOH); MS (ESI−): *m/z* (%): 206 (100, $[M - H]^-$); MS (ESI+): *m/z* (%): 208 (35, $[M + H]^+$), 230 (100, $[M + Na]^+$).

4-[(6-Methylheptan-2-yl)amino]-4-oxobutanoic acid (8c). White crystals; 93% yield (3.40 g); mp 79–80°C; IR-ATR (ν_{max}, cm^{-1}): 3200–2500, 3287, 1714, 1648, 1550; ^{1}H NMR (300 MHz, $CDCl_3$): 0.84 (d, J = 6.44 Hz, 6H, CH_3), 1.09 (d, J = 6.44 Hz, 3H, CH_3), 1.10–1.16 (m, 1H, CH), 1.2–1.3 (m, 2H, CH_2), 1.38–1.42 (m, 2H, CH_2), 1.44–1.53 (m, 2H, CH_2), 2.49 (skew t, 2H, CH_2), 2.67 (skew t, 2H, CH_2), 3.30–3.95 (m, 1H, CH), 5.95 (d, J = 8.5 Hz, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$): 20.96 (CH_3), 22.78 (CH_3), 22.81 (CH_3), 23.99 (CH_2), 28.07 (CH), 30.29 (CH_2), 31.12 (CH_2), 37.16 (CH_2), 38.92 (CH_2), 45.99 (CH), 172 (CONH), 176.81 (COOH); MS (ESI−): *m/z* (%): 228 (100, $[M - H]^-$); MS (ESI+): *m/z* (%): 230 (100, $[M + H]^+$), 252 (98, $[M + Na]^+$); Anal. Calcd. for $C_{12}H_{23}NO_3$: C, 62.85; H, 10.11; N, 6.11. Found: C, 62.59; H, 9.71; N, 6.30.

4-[(2-Ethylhexyl)amino]-4-oxobutanoic acid (8d). White crystals; 80% yield (2.92 g); mp 65–67°C; IR-ATR (ν_{max}, cm^{-1}): 3310–2500, 3318, 1691, 1631, 1544; ^{1}H NMR (300 MHz, $CDCl_3$): 0.85–0.88 (m, 6H, CH_3), 1.22–1.32 (m, 8H, CH_2), 1.35–1.45 (m, 1H, CH), 2.5 (skew t, 2H, CH_2), 2.66 (skew t, 2H, CH_2), 3.16 (dt, J = 1.46, 4.7 Hz, 2H, CH_2), 6.00 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$): 11.01 (CH_3), 14.29 (CH_3), 23.20 (CH_2), 24.30 (CH_2), 29.01 (CH_2), 30.20 (CH_2), 31.01 (CH_2), 31.09 (CH_2), 39.40 (CH), 42.87 (CH_2), 172.75 (CONH), 176.89 (COOH); MS (ESI−): *m/z* (%): 228 (100, $[M - H]^-$); MS (ESI+): *m/z* (%): 230 (95, $[M + H]^+$), 252 (100, $[M + Na]^+$); Anal. Calcd. for $C_{12}H_{23}NO_3$: C, 62.85; H, 10.11; N, 6.11. Found: C, 62.50; H, 9.81; N, 6.45.

General procedure for the preparation of maleimide-fused *N*-allyl- and *N*-alkyl-substituted 1,4-dithiines (9a–d). To a solution of *N*-substituted succinamic acid **8a–d** (3.82 mmol) in dry 1,4-dioxane (10 mL) was added dropwise a solution of thionyl chloride (30.56 mmol) in dry 1,4 dioxane (2 mL) at room temperature with stirring. The solution was heated at 50°C for 6 h. After the reaction was completed, the solution was concentrated *in vacuo*, column chromatography of the residue over silica eluting with petroleum ether-EtOAc (9:1) furnished **9a–d**.

The same reactions of **8a–d** were conducted at room temperature with stirring overnight.

2,6-Di(prop-2-en-1-yl)-1H,5H-[1,4]dithiino[2,3-c:5,6-c′]dipyrrole-1,3,5,7(2H,6H)-tetrone (9a). Dark green crystals; 63% yield (400 mg); mp 225–227°C; UV ($CHCl_3$) λ_{max} : 300 nm sh (Є 1657), 378 (1271), 600 (29); IR-ATR (ν_{max}, cm^{-1}): 1777, 1710, 1661, 1566; ^{1}H NMR (400 MHz, DMSO-d_6): 4.02 (skew dt, 4H, CH_2CH=CH_2), 5.17 (dt, J = 1.22, 18.6 Hz, 4H, CH=CH_2), 5.80 (m, 2H, C*H*=CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): 40.86 (*C*H_2CH=CH_2), 117.30 (CH=*C*H_2), 131.08 (*C*H=CH_2), 132.20 (Q), 164.39 (CO); MS (API−): *m/z* (%): 334 (100, $[M^+]$); Anal. Calcd. for $C_{14}H_{10}N_2O_4S_2 \cdot 1.07H_2O$: C, 47.55; H, 3.46; N, 7.92; S, 18.18. Found: C, 47.42; H, 3.21; N, 7.52; S, 18.16.

2,6-Dibenzyl-1H,5H-[1,4]dithiino[2,3-c:5,6-c′]dipyrrole-1,3,5,7(2H,6H)-tetrone (9b). Dark green pellets; 60% yield (500 mg); mp 216–218°C (lit. [14,15] mp 224°C); UV ($CHCl_3$) λ_{max}: 301 nm sh (Є 1980), 387 (1300), 594 (40); IR-ATR (ν_{max}, cm^{-1}): 1775, 1707, 1693, 1596; ^{1}H NMR (400 MHz, DMSO-d_6): 4.6 (s, 4H, CH_2), 7.34–7.45 (m, 10H, Ar); ^{13}C NMR (100 MHz, DMSO-d_6): 42.53 (CH_2), 128.36 (CH), 128.67 (CH), 128.88 (CH), 131.65 (Q), 135.03 (Q), 163.66 (CO); MS (API−): *m/z* (%): 434 (100, $[M^+]$).

2,6-Di(6-methylheptan-2-yl)-1H,5H-[1,4]dithiino[2,3-c:5,6-c′]dipyrrole-1,3,5,7(2H,6H)-tetrone (9c). Green solid; 88% yield (800 mg); mp 99–100°C; UV ($CHCl_3$) λ_{max}: 310 nm sh (Є 1955), 388 (1636), 595 (45); IR-ATR (ν_{max}, cm^{-1}): 1771, 1692, 1573; ^{1}H NMR (400 MHz, $CDCl_3$): 0.77 (d, J = 6.6 Hz, 6H, CH_3), 0.79 (d, J = 6.6 Hz, 6H, CH_3), 1.07–1.13 (m, 8H, CH_2), 1.26 (d, J = 6.93 Hz, 6H, CH_3), 1.41–1.53 (m, 4H, CH_2), 1.73–1.79 (m, 2H, CH), 3.84–4.19 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): 18.54 (CH_3), 22.45 (CH_3), 22.61 (CH_3), 24.39 (CH_2), 27.75 (CH), 33.81 (CH_2), 38.32 (CH_2), 48.89 (CH), 131.35 (Q), 164.21 (CO); MS (API−): *m/z* (%): 478 (100, $[M^+]$); Anal. Calcd. for $C_{24}H_{34}N_2O_4S_2 \cdot 0.8H_2O$: C, 58.46; H, 7.28; N, 5.68; S, 13.00. Found: C, 58.15; H, 7.19; N, 5.62; S,12.87.

2,6-Di(2-ethylhexyl)-1H,5H-[1,4]dithiino[2,3-c:5,6-c′]dipyrrole-1,3,5,7(2H,6H)-tetrone (9d). Dark green solid; 87% yield (790 mg); mp 57–58°C; UV ($CHCl_3$) λ_{max}: 310 nm sh (Є 2439), 389 (1803), 601 (45); IR-ATR (ν_{max}, cm^{-1}): 1776, 1703, 1571; ^{1}H NMR (400 MHz, $CDCl_3$): 0.78–0.84 (skew t, 12H, CH_3), 1.10–1.22 (m, 16H, CH_2) 1.60 (m, 2H, CH), 3.30 (d, J = 7.12 Hz, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): 10.23 (CH_3), 14.03 (CH_3), 22.93 (CH_2), 23.65 (CH_2), 28.37 (CH_2), 30.30 (CH_2), 38.19 (CH), 42.79 (CH_2), 131.42 (Q), 164.42 (CO); MS (API−): *m/z* (%): 478 (100, $[M^+]$); Anal. Calcd. for $C_{24}H_{34}N_2O_4S_2 \cdot 0.4H_2O$: C, 59.33; H, 7.22; N, 5.77; S, 13.20. Found: C, 59.04; H, 6.89; N, 5.84, S, 13.20.

General procedure for the Diels–Alder cycloadditions (10a–d). To a solution of anthracene (0.49 mmol) in benzene (15 mL) was added 1,4-dithiines 9a–d (0.45 mmol), and the reaction mixture was refluxed until the green, deep blue, deep blue-green, and deep blue-purple colors of 9a–d faded away, indicating the complete consumption of 9a–d. The solution was concentrated *in vacuo*, purification by column chromatography on silica, eluting with petroleum ether-EtOAc (9:1) gave the corresponding *endo*-cycloadducts **10a** and **10b** and a 1:1 mixture of diastereoisomers of **10c** and **10d**.

The same reactions of **9a–d** were conducted at room temperature in $CHCl_3$ and in the dark for 2 and 4 weeks.

5,10-Dihydro-2,13-di(prop-2-en-1-yl)-5,10[1′,2′]-benzeno-4a,10a-(methaniminomethano)-1H-naphtho[2′,3′:5,6][1,4]dithiino[2,3-c]pyrrole-1,3,12,14(2H)-tetrone (10a). Bright yellow solid; 95% yield (218 mg); mp 258–260°C (melts with dec.); UV ($CHCl_3$) λ_{max}: 292 nm sh (Є 2060), 405 (440); IR-ATR (ν_{max},

cm^{-1}): 1771, 1707, 1650, 1579; ^1H NMR (400 MHz, $CDCl_3$): 3.76 (d, $J = 3.7$ Hz, 2H, CH_2), 3.88 (d, $J = 3.7$ Hz, 2H, CH_2), 4.68 (s, 2H, CH), 4.80–4.85 (m, 2H), 5.12–5.15 (m, 2H, CH), 5.60–5.75 (m, 2H, CH), 7.03–7.05 (m, 2H, Ar), 7.08–7.10 (m, 2H, Ar), 7.20–7.23 (m, 2H, Ar), 7.26–7.29 (m, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): 40.60, 41.76, 55.84, 68.80, 118.64, 119.43, 125.76, 127.22, 127.88, 128.04, 128.79, 131.11, 136.99, 137.50, 137.66, 164.14, 172.57; MS (API+): *m*/*z* (%): 513 (38, $[M + H]^+$); Anal. Calcd. for $C_{28}H_{20}N_2O_4S_2 \cdot 1.7H_2O$: C, 61.91; H, 4.34; N, 5.16; S, 11.81. Found: C, 61.54; H, 4.67; N, 5.29; S,12.20.

5,10-Dihydro-2,13-dibenzyl-5,10[1′,2′]-benzeno-4a,10a-(methaniminomethano)-1H-naphtho[2′,3′:5,6][1,4]dithiino[2,3-c]pyrrole-1,3,12,14(2H)-tetrone (10b). Bright yellow crystals; 89% yield (244 mg); mp 278–280°C (melts with dec.); UV ($CHCl_3$) λ_{max}: 290 nm sh (Є 2583), 412 (569); IR-ATR (ν_{max}, cm^{-1}): 1776, 1708, 1581; ^1H NMR (400 MHz, $CDCl_3$): 4.33 (s, 2H, CH), 4.42 (s, 2H, CH_2), 4.6 (s, 2H, CH_2), 6.50–6.54 (m, 2H, Ar), 6.79–6.81 (m, 4H, Ar), 7.02–7.09 (m, 7H, Ar), 7.25–7.35 (m, 5H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): 42.10, 43.43, 55.67, 68.87, 125.32, 126.93, 127.66, 127.93, 127.99, 128.22, 128.44, 128.60, 128.64, 129.46, 133.63, 135.42, 136.77, 137.11, 137.40, 164.24, 172.75; MS (API+): *m*/*z* (%): 613 (85, $[M + H]^+$); Anal. Calcd. for $C_{36}H_{24}N_2O_4S_2$: C, 70.57; H, 3.95; N, 4.57; S, 10.47. Found: C, 70.69; H, 3.96; N, 4.55; S, 10.02.

5,10-Dihydro-2,13-di(6-methylheptan-2-yl)-5,10[1′,2′]-benzeno-4a,10a-(methaniminomethano)-1H-naphtho[2′,3′:5,6][1,4]dithiino[2,3-c]pyrrole-1,3,12,14(2H)-tetrone (10c). Yellow oil slowly crystallized to bright yellow crystals; 94% yield (277 mg); mp 99–101°C; UV ($CHCl_3$) λ_{max}: 284 nm sh (Є 1895), 410 (313); IR-ATR (ν_{max}, cm^{-1}): 1773, 1706, 1580; ^1H NMR (400 MHz, $CDCl_3$): 0.71 (d, $J = 6.5$ Hz, 6H, CH_3), 0.73 (d, $J = 6.7$ Hz, 6H, CH_3), 0.76 (d, $J = 6.6$ Hz, 6H, CH_3), 0.77 (d, $J = 6.6$ Hz, 6H, CH_3), 0.94–0.97 (m, 8H, CH_2), 1.03–1.08 (m, 8H, CH_2), 1.20 (d, $J = 6.9$ Hz, 12 H, CH_3), 1.33–1.44 (m, 8H, CH_2), 1.63–1.68 (m, 4H, CH), 3.75–3.84 (m, 2H, CH), 3.86–3.95 (m, 2H, CH), 4.67 (s, 4H, CH), 7.04–7.06 (m, 4H, Ar), 7.08–7.11 (m, 4H, Ar), 7.22–7.24 (m, 4H, Ar), 7.28–7.30 (m, 4H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): 16.85, 18.29, 22.49, 22.57, 23.89, 24.43, 25.52, 27.74, 29.70, 30.94, 32.31, 33.91, 38.17, 38.45, 48.22, 49.33, 55.89, 55.91, 67.94, 67.96, 125.73, 125.79, 126.98, 127.25, 127.87, 127.90, 134.14, 135.98, 136.28, 137.64, 137.67, 137.91, 137.93, 164.68, 164.74, 173.23, 173.33; MS (API+): *m*/*z* (%): 657 (100, $[M + H]^+$); Anal. Calcd. for $C_{38}H_{44}N_2O_4S_2$: C, 69.48; H, 6.75; N, 4.26; S, 9.76. Found: C, 69.22; H, 6.58; N, 3.88; S, 9.55.

5,10-Dihydro-2,13-di(2-ethylhexyl)-5,10[1′,2′]-benzeno-4a,10a-(methaniminomethano)-1H-naphtho[2′,3′:5,6][1,4]dithiino[2,3-c]pyrrole-1,3,12,14(2H)-tetrone (10d). Bright yellow crystals; 90% yield (265 mg); mp 188–189°C; UV ($CHCl_3$) λ_{max}: 288 nm sh (Є 4328), 411 (852); IR-ATR (ν_{max}, cm^{-1}): 1767, 1703, 1581; ^1H NMR (400 MHz, $CDCl_3$): 0.62–0.66 (t, $J = 7$ Hz, 6H, CH_3), 0.77–0.84 (m, 18H, CH_3), 1.06–1.21 (m, 24H, CH_2), 1.48 (m, 4H, CH), 3.07 (d, $J = 6.97$ Hz, 4H, CH_2), 3.16 (d, $J = 6.97$ Hz, 4H, CH_2), 4.68 (s, 4H, CH), 7.03 (m, 4H, Ar), 7.09 (m, 4H, Ar), 7.22 (m, 4H, Ar), 7.27 (m, 4H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): 10.31,10.34, 14.03, 14.09, 22.88, 23.01, 23.33, 23.64, 28.03, 28.41, 30.02, 30.30, 37.55, 38.47, 42.23, 43.75, 55.64, 68.54, 68.60, 125.63, 125.68, 127.11, 127.14, 127.49, 127.54, 128.04, 128.06, 136.50, 136.52, 136.57, 137.76, 137.77, 137.79, 165.04, 173.47, 173.49; MS (API+): *m*/*z* (%): 657 (38, $[M + H]^+$); Anal. Calcd. for $C_{38}H_{44}N_2O_4S_2 \cdot 0.4H_2O$: C, 68.79; H, 6.81; N, 4.22; S, 9.66. Found: C, 68.39; H, 6.46; N, 4.26; S, 9.40.

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