Iminium Salts of ω-Dithiafulvenylpolyenals: An Easy Entry to the Corresponding Aldehydes and Doubly Proaromatic Nonlinear Optic-phores

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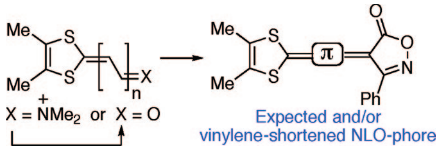

A short, high-yielding route to ω-dithiafulvenylpolyenals (**1**) via the corresponding iminium salts (**2**) and starting from trimethyl-1,3-dithiolium tetrafluoroborate is reported. The Knoevenagel reactions of either **1** or **2** with isoxazolone-containing acceptors afford merocyanines **7** and **9**, in a process that is often accompanied by a vinylene-shortening side reaction. Experimental and theoretical studies reveal that compounds **7** and **9**, featuring two proaromatic end groups, are strongly polarized and show good second-order nonlinear optical responses.

Introduction

Conjugated donor−acceptor (D−π−A) compounds are being actively investigated for their second-order nonlinear optical (NLO) properties and their applications in telecommunications and optical information processing. Their microscopic NLO efficiencies, characterized by their first molecular hyperpolarizabilities (β), depend on the subtle interplay between several factors, such as the strength of the end groups and the connectivity of the π-electron bridge, and the successful design of such NLO-phores relies on the understanding of structure/NLO relationships,[1] many of which were already established in the 1990s. Extensive use of the "two-level" model soon revealed that molecules with strong, low energy intramolecular charge transfer (ICT) transitions were good candidates for second-order NLO studies. The ground state and the first excited state of such molecules can be represented as linear combinations of neutral and zwitterionic (charge-separated) limiting forms, and their contributions can be estimated through the use of structural parameters, prominent among which is bond length alternation (BLA), defined as the difference between the average carbon−carbon single and double bond lengths in the polymethine backbone. Therefore, BLA essentially represents the degree of delocalization of the π-bridge and was found to peak at values of ca. ±0.05 Å.[1b,2]

Not only donor and acceptor strengths but also the nature of the π-spacer has a marked effect on BLA (and, therefore, on β).[3] The limited thermal and photochemical stability of long polyenic chains has led to the introduction of aromatic spacers, but this structural modification usually gives rise to less

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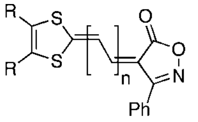
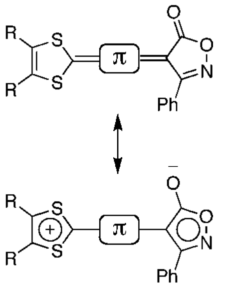
delocalized structures with decreased NLO responses, since the ICT excitation decreases the resonance energy of these molecules on passing from an aromatic ground-state to a quinoid-like excited state. To overcome this tradeoff, Marder advocated the use of fragments gaining aromaticity on charge transfer,[4] and since then, this strategy has been applied to proaromatic electron acceptors,[5] electron donors,[6] and spacers.[7]

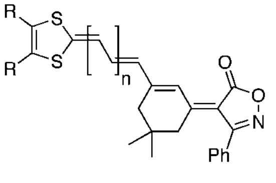
Isoxazolones are powerful proaromatic acceptors that have afforded high nonlinearities when linked to aromatic donors, such as *N,N*-disubstituted anilines[8] and indoles,[9] but NLO-phores featuring an isoxazolone and a proaromatic donor have received only a scant attention.[10]

As the proaromatic character of 1,4-dithiafulvenes has given rise to efficient NLO-phores,[7,11] in this paper we report the synthesis, structural, and optical properties of merocyanines **7** and their ring-locked analogues **9**, which are expected to benefit from the gain in aromaticity at both end groups upon photoexcitation.



7a-c: R = Me; **7'a-c**: R = H

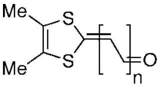




9a-d: R = Me; **9'a-d**: R = H

a: n = 1; **b**: n = 2; **c**: n = 3; **d**: n = 0

Moreover, we describe a very simple synthesis of aldehydes **1b**,**c** (widely used for the preparation of D−π−A compounds and extended tetrathiafulvalenes)[12] from the newly prepared iminium salts **2b**,**c**, and report an unexpected vinylene shortening reaction of merocyanines, a process that remains nearly unnoticed in the literature.



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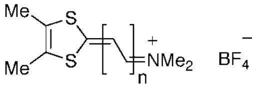

2

a: n = 1; **b**: n = 2; **c**: n = 3

Results and Discussion

Synthesis and Hydrolysis of Iminium Salts 2b and 2c: A New Access to Aldehydes 1b and 1c. The reaction of vinylogous tertiary formamides with acylating agents such as acetic anhydride or acetyl halides generates the corresponding *O*-acetyl derivatives (*ω*-acetoxyiminium salts)[13] which are strongly electrophilic. Nevertheless, the potential synthetic utility of such species remains largely unexplored. In particular, there are very few examples of their reactions with heteroaromatic cations bearing activated methyl groups, which show nucleophilic properties through the corresponding methylene bases (anhydrobases).[14] We have found that the reaction of the easily prepared trimethyl-1,3-dithiolium tetrafluoroborate **3**[15] with 3-dimethylaminoacrolein in Ac_2O at room temperature gives salt **2b** (vinylogous of **2a**)[15] in excellent yield (94%) (Scheme 1).

On the other hand, the reaction of **3** with **5**[16] affords a 3:1 mixture of **2c** and *N,N*-dimethyl-5-acetoxypentadienylideniminium tetrafluoroborate (identified by ^1H NMR and mass spectrometry). Isolation of pure **2c** from this mixture was troublesome, but this problem was easily circumvented through hydrolysis (see below) of the crude product to afford aldehyde **1c** (55% yield) and reaction of the latter with dimethylammonium tetrafluoroborate,[17] affording **2c** in 92% yield (Scheme 1).

It is unfortunate that, contrary to 2-methylbenzothiazolium salts,[18] the reaction of **3** with glutaconaldehyde dianilide hydrochloride does not take place to any appreciable extent, since this reaction would give rise to the anilino analogue of **2c** in a single step and from a commercially available reagent. A related failure, involving the reaction of a 2-methylene-1,3-dithiole derivative with malonaldehyde dianilide hydrochloride, has also been reported.[19]

If desired, **2b** can be easily hydrolyzed to aldehyde **1b** in good yield (79%) (Scheme 1). The only reported synthesis of

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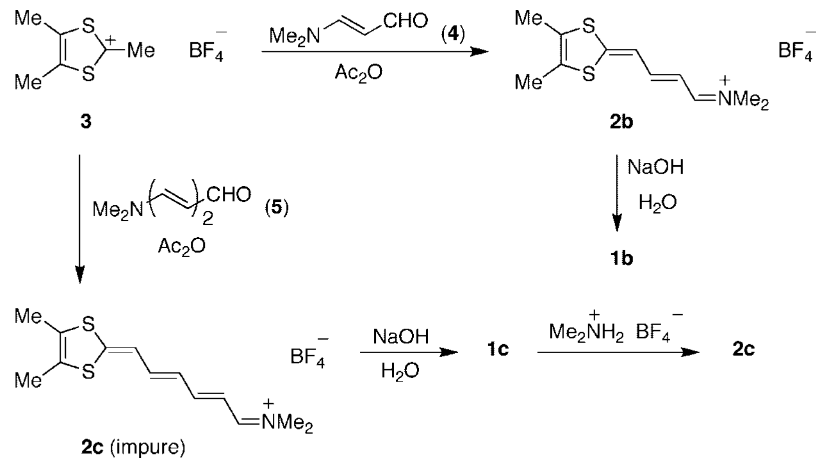
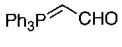
SCHEME 1



1b is a four-step procedure (overall yield ca. 40%) which involves in the key step the reaction of diethyl 4,5-dimethyl-1,3-dithiol-2-ylphosphonate with fumaraldehyde mono(dimethyl acetal),[20] prepared in turn from furan.[21] Therefore, the two-step synthesis of **1b** from **3** herein reported constitutes a simpler, improved procedure, with an overall yield of 74%. We also want to point out that our attempts to prepare **1b** by vinylogation of the easily available **1a**[22] with a variety of reagents (**A**−**F**)[23−27] did not meet with success.



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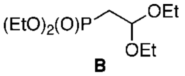

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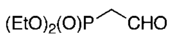

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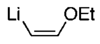

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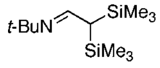

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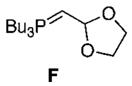

F

In a similar way, the synthesis of **1c** from **3** in 55% yield (Scheme 1) compares favorably to the previously reported syntheses of this compound, involving either vinylogation of **1b** (23% yield)[20] or reaction of 4,5-dimethyl-1,3-dithiol-2-ylidenetributylphosphorane with (*E*,*E*)-mucondialdehyde, also available from furan (overall yield, 28%).[11c]

Synthesis of Isoxazolone-Containing Merocyanines 7 and 9. Besides giving rise to the corresponding aldehydes, iminium salts **2** are also expected to behave as surrogate aldehydes of enhanced electrophilicity in Knoevenagel-type reactions.[28] To confirm these expectations, we have carried out a comparative study of the reactivity of **1** and **2** toward isoxazolone-containing acceptors **6** and **8**.

The reaction of **6** with aldehydes **1a** and **1b** (Scheme 2) affords targets **7a** (94%) and **7b** (74%), and similar yields are obtained from the reactions of **6** with the corresponding iminium salts **2a** and **2b** (**7a**, 91%; **7b**, 62%).

On the other hand, compound **7c** could only be isolated from the reaction of **6** with **2c**, since the corresponding aldehyde **1c** only afforded a complex mixture. It is worth mentioning that even when smooth conditions (absence of base, ice-bath temperature) are used, the reaction of **2c** with **6** affords **7c** together with a small amount of the unexpected product **7b**. In fact, when this reaction is carried out in the presence of base at room temperature, **7b** becomes the major product. Some aspects of this chain-shortening reaction are discussed below.

With a view to study the effect that ring-locking of the π-spacer has on the optical and thermal properties of the corresponding merocyanines, we also decided to study the reactivity of acceptor **8**.

Compound **8** was prepared as previously described,[29] since an alternative procedure[30] did not lead in our hands to the desired compound. As expected,[8b] **8** was obtained as a *Z*/*E* mixture (10:3 ratio). Recrystallization from methanol afforded the (*Z*)-isomer nearly free from the (*E*)-isomer (ca. 10:1 ratio).

According to the expected weaker acidity of **8** when compared to **6** ($pK_a = 4.0$),[31] we have found that its reactions with either **1** or **2** only take place in the presence of a base (Scheme 3). The enhanced reactivity of iminium salts **2**, compared to that of aldehydes **1**, is demonstrated by the much higher yield of **9a** when prepared from **2a** (45%) than when synthesized from **1a** using piperidine in refluxing ethanol (9%).

Similarly, only the reactions of iminium salts **2b**,**c** with **8** led to the isolation of the desired products **9b**,**c** in synthetically useful yields, although the corresponding “degraded” merocyanines (**9a** and **9b**, respectively) were also formed as byproducts. On the other hand, this side reaction became dominant when using aldehydes **1b**,**c** as starting materials, and therefore, this route was abandoned.

For the sake of comparison, compound **9d** was also synthesized, starting from dithiolium salt **10** (prepared following a

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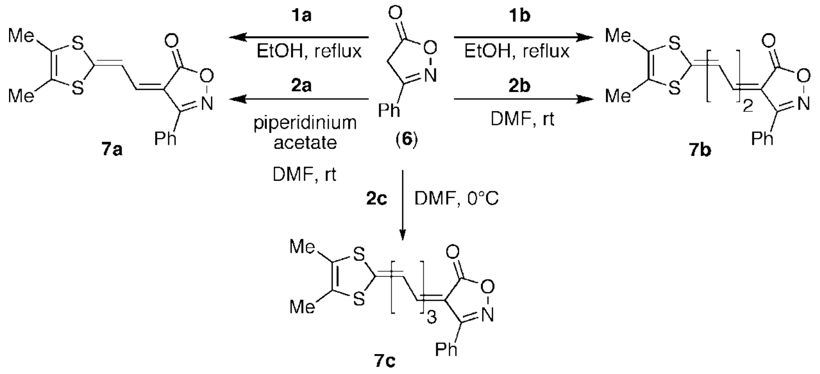
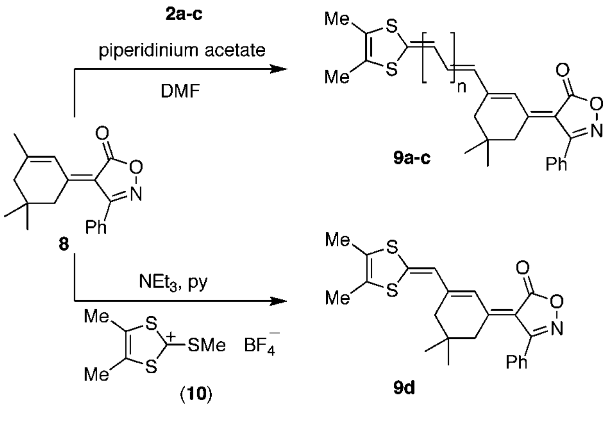
SCHEME 2



SCHEME 3



a: n = 1; **b**: n = 2; **c**: n = 3

general method)[32] and using conditions analogous to those reported for related derivatives.[11d,33]

It has to be mentioned that in every case compounds **9** are formed as ca. 1:1 (*Z*)/(*E*) mixtures around the exocyclic isoxazolone C=C bond, even when nearly pure (*Z*)-**8** is used as starting material. This may result from the loss of stereochemical integrity taking place in the extended enolate derived from **8**. Related isomerizations on isophorone derivatives bearing either moderate or strong exocyclic acceptors have been previously reported.[34] Moreover, calculations indicate only negligible energy differences between the (*Z*)- and (*E*)-isomers of compounds **9** (see the Supporting Information), thus explaining the observed stereochemical outcome of these reactions. Therefore, **8** was used as the nonenriched mixture of stereoisomers for the synthesis of compounds **9**.

The "Degradation" (Vinylene Shortening) of Merocyanines. Many of the above-reported syntheses of compounds **7** and **9** have met with an unexpected side reaction, namely, the formation of a shortened merocyanine lacking a vinylene group. To the best of our knowledge, there are only two papers reporting this kind of reaction,[28b,35] although the chain shortening of cyanines was described a long time ago.[36] It is well-known that cyanines and merocyanines show electrophilic properties at the odd-numbered carbon atoms of the polymethine chain and, therefore, they can be attacked by nucleophiles at these atoms.[37] This process can trigger the observed degradation reactions, which can take place either on the final, expected merocyanines or on the starting iminium salts.

To clarify some of these aspects, we have chosen **2b** and **7b** as model compounds and have carried out a series of experiments, monitored by TLC, HPLC, MS, and comparison with authentic samples, which have revealed the following facts:

The expected merocyanine can undergo degradation under the reaction conditions, since treatment of **7b** with **6**/piperidine (DMF, rt, 4.5 h) gives **7a** as the major product. On the other hand, in the absence of piperidine only trace amounts of **7a** are formed.

The degradation of the starting iminium salt occurs to a much lesser extent, since treatment of **2b** with piperidine (DMF, rt, 13 h), followed by basic hydrolysis, affords **1b** along with only a minor amount of aldehyde **1a**. This result is not very surprising, taking into account that the *N*-linked carbon atom of the iminium salt carries the highest positive charge along the chain and that it has been demonstrated that both hard and soft nucleophiles show a marked preference for the attack at the terminal carbon atoms of cyanines.[38]

Therefore, although chain shortening of the iminium salts cannot be completely ruled out, attack on the initially formed merocyanines seems to be the main pathway leading to the degraded products. But, what is the actual nucleophile? Dimethylamine, generated in the Knoevenagel reactions of salts **2**, could play this role, since it is known to degrade cyanines.[39] Nevertheless, the reaction of **2b** with **6** in the absence of base does not give rise to chain shortening, and therefore, the liberated Me_2NH does not seem to lie at the origin of the unexpected reaction. Piperidine seemed an obvious candidate, since it was reported to be very active at degrading cyanines[36a] and we have observed that the reaction of **2b** with **6** in the presence of

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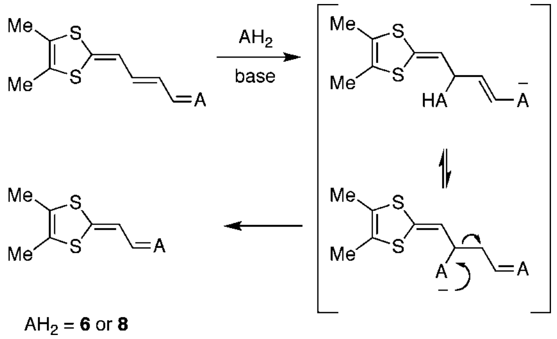
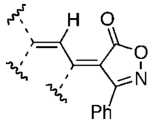
SCHEME 4



piperidinium acetate gives rise to **7b** along with a small amount of **7a**. However, when ethyldiisopropylamine (DIPEA) replaced piperidinium acetate in this reaction, the degraded product **7a** turned out to be the major one. Since DIPEA is a weak nucleophile and cannot form iminium salts, we suggest that the basicity, not the nucleophilicity of the used base, plays a key role through formation of the conjugated base of the acceptor, which is the main nucleophile carrying out the chain shortening reactions (although both factors could be involved in the case of piperidine). These observations can be summarized by the mechanism of Scheme 4, where AH_2 stands for a generalized acceptor (such as **6** or **8**), and which lends support to a tentative mechanism previously proposed for malononitrile dimer.[28b] In turn, this mechanism is reminiscent of the transalkenylation reactions taking place through a Michael/retrograde Michael sequence.[11f]

Thus, in the reactions of iminium salts **2**, chain shortening is observed or greatly increased in the presence of added bases, which are needed for the weak acids, such as acceptor **8**. The degradation observed in the reaction of **2c** with the stronger acid **6** in the absence of base constitutes an exception but is in good agreement with the susceptibility of cyanines toward degradation, which increases with chain length.[36a,39a] The role of the base is confirmed by the reactions of aldehydes **1**, giving rise to chain shortening only in the presence of piperidine.

^{1}H NMR and BLA Studies. As judged from $^3J_{HH}$ values, iminium salts **2b**,**c** have an *all-trans* geometry, like the corresponding aldehydes **1b**,**c**.[20] Similarly, ^{1}H NMR spectra of **7a**−**c** in $CDCl_3$ reveal an *all-trans* configuration of the polyenic chain, except for the C=C bond formed in the Knoevenagel reaction, which has (*Z*)-geometry as shown by the strong deshielding experienced by the H atom located five bonds away from the carbonyl oxygen atom.[40] This assignment was confirmed by an X-ray diffraction study of single crystals of **7a**. Despite the poor quality of the crystals, which did not allow an accurate structural determination, the (*Z*)- configuration of that bond was unambiguously established. This geometry is also found in the solid state of other 3-phenylisoxazol-5-ones bearing polyenylidene substituents at C4.[5a,10a]



On the other hand, compounds **8** and **9** are present as *Z*/*E* mixtures around the isoxazolone-exocyclic C=C bond; again, the vinylic hydrogen atom of the cyclohexene moiety is more deshielded in the (*Z*)- than in the (*E*)-isomers, their ratio being easily determined by integration.

TABLE 1. **$^3J_{HH}$ and ΔJ Values along the Chain**

compd	$^3J_{HH}$(Hz)[a]	ΔJ (Hz)
7a	12.6	
7b	12.1, 13.4, 12.8	1.0
7c	11.8,13.7, 11.8, 14.0, 12.5	1.8

[a] In $CDCl_3$. From donor to acceptor end.

$^3J_{HH}$ coupling constants analysis along the spacer is relevant not only at determining its stereochemistry, but also at providing an estimation of the ground-state polarization of these merocyanines, given the known correlation between $^3J_{HH}$ values and C−C bond lengths.[41] In fact, $^3J_{HH}$ values of compounds **7** (Table 1) indicate an increased (decreased) bond order for the formally single (double) C−C bonds and, therefore, a noticeable degree of equalization due to the contribution of the zwitterionic form to the description of the ground-state of these compounds.

This is confirmed by ΔJ values, defined as the difference between the averaged $^3J_{HH}$ values of the formally double and single bonds along the polymethine chain.[42] Taking into account that $\Delta J \approx 6$ Hz for *all-trans* polyenes and $\Delta J \approx 0$ Hz for cyanines,[43] Table 1 reveals that compounds **7** are strongly polarized and that ground-state polarization decreases on lengthening the spacer. (For the sake of comparison, $\Delta J = 3.6$ Hz for the cinnamylidene analogue of **7b**.)[40]

Theoretical calculations on model compounds **7′**, where the methyl groups on the dithiole ring have been replaced by hydrogen atoms, support the conclusions drawn from ^{1}H NMR studies on **7** and give additional information on their ground-state properties. The molecular geometries of **7′** were optimized at the B3P86/6-31G* level, given the good performance of this hybrid functional at reproducing the geometry of 1,3-dithiole derivatives.[44]

It can be seen (Table 2) that on lengthening the π-spacer, the increase in the SC−S bond lengths is accompanied by a shortening of the exocyclic $S_2C{=}C$ bond and by an increase of the BLA parameter (which remains close to the optimal value maximizing β).[1b] These facts, together with Mulliken population analysis, clearly show that charge transfer decreases as the length of the conjugated spacer increases. In other words, the contribution of the zwitterionic limiting form to the description of the ground-state of compounds **7′** is higher for the shorter derivatives.

Moreover, the electronic structure of push−pull polyenes is quite sensitive to solvent polarity, given the stabilizing effect of polar solvents on the zwitterionic limiting form. Thus, for the vinylic hydrogen atoms of compound **7a**, $^3J_{HH}$ values increase on passing from $CDCl_3$ (12.6 Hz) to acetone-d_6 (12.9 Hz) to DMSO-d_6 (13.2 Hz), indicating an increased bond order and a more pronounced zwitterionic character in more polar solvents. In a similar way, for compound **7b** ΔJ along the spacer decreases from 1.0 Hz (in $CDCl_3$) to 0.3 Hz (in DMSO),

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TABLE 2. B3P86/6-31G* Values for C−S[a], C−C,[b] and C−O[c] Bond Distances, BLA,[d] and Charges in the Dithiole (D), Spacer (π), and Isoxazolone (A) Moieties

compd	C−S (Å)	C−C (Å)	C−O (Å)	BLA (Å)	D charge (e)	π charge (e)	A charge (e)
7′a[e]	1.756	1.370	1.211	0.044	+0.15	+0.05	−0.20
7′a[f]	1.740	1.386	1.220	0.015	+0.32	+0.06	−0.38
7′b[e]	1.760	1.367	1.210	0.049	+0.11	+0.09	−0.20
7′c[e]	1.762	1.365	1.210	0.051	+0.09	+0.11	−0.20
7′c[f]	1.749	1.378	1.221	0.022	+0.23	+0.18	−0.41

[a] Averaged values of the SC−S dithiole bonds. [b] S_2C═C bond. [c] C═O bond [d] Along the polyenic spacer. [e] Gas phase. [f] In DMSO (PCM).

TABLE 3. Cyclic Voltammetric Data[a] and E_{HOMO} and E_{LUMO} Values[b] (eV) for Compounds 7 and 9

compd	E_{ox}	E_{red}	E_{HOMO}	E_{LUMO}
7a	+1.06	−1.12	−6.28	−3.27
7b	+0.77	−0.93	−6.06	−3.39
7c	+0.59	−0.82	−5.88	−3.48
9d	+0.85	−1.16	−5.88[c]	−3.20[c]
			−5.96[d]	−3.21[d]
9a	+0.59	−0.95	−5.77[c]	−3.33[c]
			−5.84[d]	−3.36[d]
9b	+0.50	−0.91	−5.64[c]	−3.39[c]
			−5.71[d]	−3.42[d]
9c	+0.43	−0.86, −1.30	−5.54[c]	−3.44[c]
			−5.60[d]	−3.47[d]

[a] In volts, 10^{-3} M in CH_2Cl_2 vs Ag/AgCl, glassy carbon working electrode, Pt counter electrode, 20 °C, 0.1 M Bu_4NPF_6, 100 mV s^{-1} scan rate. [b] B3P86/6-31G*//B3P86/6-31G* level in the gas phase, calculated for model compounds **7′** and **9′**. [c] Isomer with (*Z*)-C═C bond exocyclic to the isoxazolone ring. [d] Isomer with (*E*)-C═C bond exocyclic to the isoxazolone ring.

pointing to a less alternated structure in the latter solvent. This is confirmed through a comparison of the calculated geometries of **7′a** and **7′c** in the gas phase and in DMSO ($\epsilon = 46.7$, polarized continuum model, PCM; the optimization of **7′b** in DMSO failed to converge), which reveals a strong decrease of the BLA values on inclusion of the solvent (Table 2). Mulliken analyses in DMSO also show that the positive charge on the dithiole ring and the negative charge on the phenylisoxazolone acceptor strongly increase when compared to the values of the gas-phase structures. These facts, together with the calculated lengthening of the C═O bond in DMSO, confirm an increase in the zwitterionic character of these merocyanines on increasing the polarity of the medium.

Electrochemistry. Cyclic voltammetry provides information about the donor/acceptor interaction in D−π−A compounds, and relevant data for merocyanines **7** and **9** are gathered in Table 3, along with calculated E_{HOMO} and E_{LUMO} values.

All compounds (except for **9c**) show two irreversible waves, corresponding to the oxidation of the dithiafulvene donor and the reduction of the isoxazolone fragment, respectively. In compounds **7**, an increase in the length of the π-spacer gives rise to both easier oxidation and reduction processes, indicating a progressively weaker interaction between the D and A moieties because of the less effective electron donation (withdrawal) felt by the acceptor (donor) on passing from **7a** to **7c**. These observations also point to a smaller contribution of the zwitterionic limiting form to the ground-state for the longer derivatives, in good agreement with the results of theoretical calculations. The increase (decrease) of the calculated E_{HOMO} (E_{LUMO}) values on lengthening the polyenic spacer nicely parallels the observed cyclovoltammetric behavior.

Compounds **9** show exactly the same trends as those displayed by their acyclic analogues **7**.

TABLE 4. UV−vis Data

compd	λ_{max}[a] (CH_2Cl_2) (log ϵ)	λ_{max}[a] (DMSO)
7a	547 (4.74)	520,[b] 553
7b	587 (4.73), 621[b] (4.68)	598,[b] 637
7c	633 (4.50)	646, 726[b]
9d	582[b] (4.58), 609 (4.59)	590,[b] 622
9a	606 (4.62)	624
9b	614 (4.62)	626
9c	622 (4.57)	632

[a] In nm. [b] Shoulder.

For a given length of the π-system, locking one of the C═C bonds into the isophorone ring gives rise to more cathodic reduction processes (cf. **7b** and **9d** or **7c** and **9a**), in good agreement with previous comparisons on open-chain and ring-locked merocyanines.[45]

Calculations also reveal that isomers where the double bond connecting the isophorone and isoxazolone rings is (*E*)- show both lower E_{HOMO} and E_{LUMO} values than their (*Z*)-counterparts.

UV−vis Spectroscopy. The electronic absorption spectra of compounds **7** and **9** (Table 4) show a broad, unstructured, low energy ICT band (extending from ca. 500 to 700−800 nm), although a shoulder is discernible in some cases. As expected, the maxima values shift bathochromically with increasing number of conjugated double bonds, although the vinylene shift of compounds **9** is much less marked than that of **7**. When compounds of the same conjugation lengths are compared (**7b** and **9d** or **7c** and **9a**), it can be seen that the ring-locked derivatives **9** show blue-shifted absorptions. In fact, the incorporation of the isophorone-derived fragment usually gives rise to a hypsochromic shift,[45,46] although bathochromic shifts[30,47] or even both effects[48] have been observed. Moreover, both series of compounds (**7** and **9**) show positive solvatochromism, in good agreement with their positive β values (see below).

Nonlinear Optical Properties. The second-order NLO properties of compounds **7** and **9** were determined by EFISH measurements at 1907 nm in dichloromethane. The zero-frequency (static) values ($\mu\beta_0$) were calculated using the two-level model, which takes dispersion into account and allows reliable comparisons to be made, since β_0 is an intrinsic value, independent of the used wavelength (for the sake of comparison, $\mu\beta_0 \approx 400 \times 10^{-48}$ esu for Disperse Red 1, a common

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TABLE 5. Experimental[a] and Calculated[b,c] NLO Properties

	experimental		TD-DFT[d]				CPHF[e]		
compd	$\mu\beta$[f]	$\mu\beta_0$[f]	μ_g (D)	μ_e (D)	E (eV)	f	μ_g (D)	β_{tot}[g]	$\mu\beta_0$[f]
7a	250	153	9.55	10.90	3.05	0.6025	10.06	15	74
7b	1100	565	10.90	16.98	2.80	1.0964	10.94	54	387
7c	2193	1091	12.16	23.11	2.57	1.5193	11.71	116	983
9d[h]	719	382	10.69	15.85	2.77	1.0013	11.01	44	213
9d[i]			11.94	18.24	2.82	0.9446	12.26	23	272
9a[h]	2750	1475	11.35	23.27	2.51	1.3197	11.32	94	577
9a[i]			12.84	25.90	2.55	1.2398	12.79	63	794
9b[h]	4252	2229	12.24	28.74	2.34	1.6672	11.78	165	1163
9b[i]			14.00	31.63	2.36	1.5823	13.50	124	1652
9c[h]	5539	2843	13.09	34.24	2.18	1.9650	12.20	251	1944
9c[i]			15.04	37.33	2.20	1.8810	14.09	203	2827

[a] In CH_2Cl_2, at 1907 nm. [b] On B3P86/6-31G* geometries. [c] Calculations carried out on compounds **7′** and **9′** instead of **7** and **9**, respectively. [d] B3P86/6-31G* level. [e] CPHF/6-31G* level. [f] In 10^{-48} esu. Experimental accuracy ± 10%. [g] In 10^{-30} esu. [h] Calculated values for the isomer with (Z)-C=C bond exocyclic to the isoxazolone ring. [i] Calculated values for the isomer with (E)-C=C bond exocyclic to the isoxazolone ring.

benchmark in organic NLO-phores).[49] Inspection of Table 5 reveals the expected increase in $\mu\beta_0$ on lengthening the conjugation path for series **7** and **9**, giving rise to high $\mu\beta_0$ values for the longer derivatives.

Calculated molecular hyperpolarizabilities on model compounds **7′** and **9′** using the coupled perturbed Hartree−Fock (CPHF) method show the same trend, although theoretical $\mu\beta_0$ values are systematically underestimated, probably due to the fact that solvent effects were not considered in the calculations. For compounds **9**, present as (Z)/(E) mixtures around the isoxazolone−exocyclic bond, calculations also show that the (E)-isomers have higher $\mu\beta_0$ values (by ca. 40%) than the (Z)-isomers, a fact which is due to the interplay of several factors: the (E)-isomers have higher dipole moments and lower total hyperpolarizabilities (β_{tot}), but the angle formed by the ground-state dipole moment and the vectorial hyperpolarizability is much smaller for the (E)- than for the (Z)-isomer, resulting in higher $\mu\beta_0$ values for the former. Although calculations on both configurations lead to analogous qualitative conclusions, it is not surprising that the calculated values for the more polar (E)-isomers are closer to the experimental ones, provided that these isomers must be favored at the high electric fields employed during the EFISH measurements.

To get a more intuitive description of the NLO properties of **7** and **9**, we have also carried out TD-DFT calculations which, despite their limited description of charge transfer transitions,[50] allow the determination of the parameters involved in the two-level model ($\beta_0 \propto \Delta\mu_{ge} f/E^3$, where $\Delta\mu_{ge}$ is the difference between the excited and ground-state dipole moments, μ_e and μ_g respectively, f is the oscillator strength, and E is the first excitation energy).[51] Within each series of compounds (**7** and **9**), $\Delta\mu_{ge}$ and f increase, and E decreases on increasing the conjugation path, qualitatively explaining the higher $\mu\beta_0$ values for the longer derivatives. Table 5 also shows that $\Delta\mu_{ge}$ values are positive, in agreement with the observed positive solvatochromism, and that on lengthening the chain there is a much steeper increase in μ_e than in μ_g values. The smooth increase of the latter is a consequence of two opposing trends, namely, the increase in molecular length (L) and the decrease of donor to acceptor charge transfer, which goes down roughly as $1/L$, reflecting the increasing difficulty of separating charges over larger distances.[52] This agrees with the previously discussed decrease in the zwitterionic character of the ground-state for the longer derivatives.

The effect of ring-locking on the NLO (and thermal) properties of these compounds is not clear: when molecules of the same conjugation length are compared it can be seen that the introduction of the isophorone-derived spacer gives rise to either a decrease (cf. **7b** and **9d**) or an increase (cf. **7c** and **9a**) in $\mu\beta_0$. This structural modification usually results in diminished β (or $\mu\beta$) values[11d,30,46b,48b] and a variety of reasons, such as distortions from planarity and poor alignment of the μ and β vectors, have been invoked to account for this behavior. On the other hand, only a weak effect on the $\mu\beta_0$ values upon ring-locking has been reported in other instances.[45] In a similar way, the incorporation of cyclohexene fragments into the spacer has been reported to afford merocyanines with enhanced thermal stabilities,[46,48] but this is not the case with the compounds herein reported. Their thermal stabilities were studied using thermogravimetric analysis (TGA) and their decomposition temperatures (T_d) were estimated as the temperature that is the intercept of the leading edge of the weight loss by the baseline of the TGA scans. When compared to **7b** (T_d = 156 °C), its ring-locked analogue **9d** showed a decreased thermal stability (T_d = 128 °C), and only a negligible increase in stability on ring-locking was observed for compounds **7c** (T_d = 105 °C) and **9a** (T_d = 111 °C).

Finally, it is pertinent to compare the NLO responses of the compounds herein described to those of related derivatives. The donor ability of the dithiafulvene moiety, as judged from the $\mu\beta_0$ values of previously reported isoxazolone-containing merocyanines of the same conjugation length, is similar to that of trimethyl-2-methyleneindoline (Fischer's base)[2b] and *N*,*N*-dimethylaniline[5a] (up to ca. 10 conjugated carbon atoms) and superior to that of tetrathiafulvalene.[53] Comparison with other proaromatic donors is difficult since only

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two compounds, structurally analogous to **7a**, featuring a benzothiazolylidene and a 4-pyridylidene group, respectively, have been described[10a] and their $\mu\beta_0$ values—determined by Hyper-Rayleigh Scattering (HRS)—are presumed to be resonance-enhanced. In any case, the negative $\mu\beta_0$ value measured for the pyridylidene derivative points to this donor as the strongest one in these series. Focusing on the acceptor fragment, when $\mu\beta_0$ values of dithiafulvene-based NLO-phores bearing different acceptors are compared, it can be seen that 3-phenyl-5-isoxazolone is a more efficient electron-withdrawing group than most previously used ones,[11d,e,28b] being only surpassed by 1,1,3-tricyano-2-phenylpropene.[11f]

In summary, the hitherto unreported *N*,*N*-dimethyliminium salts formally derived from *ω*-(2,3-dimethyl-1,4-dithiafulvenyl)polyenals have been easily prepared from trimethyl-1,3-dithiolium tetrafluoroborate. These iminium salts can be smoothly hydrolyzed to the corresponding aldehydes, in what constitutes the shortest, highest-yielding route to these important polyenals so far reported. Moreover, the reactivity of both kinds of electrophiles in Knoevenagel-type reactions has been studied using isoxazolone-containing proaromatic acceptors, and iminium salts show a higher reactivity, especially toward weaker acids. In these reactions, a "degraded" merocyanine, lacking a vinylene group, is usually formed along with the expected one, and a mechanistic rationale to account for this fact is offered. ^{1}H NMR, electrochemical and theoretical studies reveal that the push−pull dithiafulvenes herein reported are strongly polarized and that the contribution of the zwitterionic form to the ground-state decreases on lengthening the π-spacer. These compounds featuring two proaromatic end groups have close to optimal BLA values and display high molecular hyperpolarizabilities.

Experimental Section

Compounds **1a**,[22] **2a**,[15] **3**,[15] **5**,[16] and **10**[32] were prepared as previously described.

(*E*)-*N*,*N*-Dimethyl 4-(4,5-Dimethyl-1,3-dithiol-2-yliden)but-2-enylideniminium Tetrafluoroborate (2b). To a solution of trimethyl-1,3-dithiolium tetrafluoroborate (**3**) (734 mg, 3.15 mmol) in Ac$_2$O (6 mL) 3-dimethylaminoacrolein (929 mg, 9.37 mmol) was added. The mixture was stirred under argon at room temperature for 30 min. The resulting solution was added to ice-cooled Et$_2$O (125 mL), and the resulting solid was filtered off, washed with cold Et$_2$O, and dried. Yield: maroon solid (930 mg, 94%). Mp: 207−208 °C. IR (Nujol, cm^{-1}): 1635 (*C*=N). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.27 (d, J = 11.1 Hz, 1H), 7.53 (t, J = 12.8 Hz, 1H), 6.76 (d, J = 12.4 Hz, 1H), 6.26 (dd, J = 13.0 Hz, J' = 11.1 Hz), 3.41 (s, 3H), 3.27 (s, 3H), 2.17 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 165.8, 165.6, 151.9, 127.7, 127.6, 110.3, 110.2, 47.2, 39.2, 13.2, 12.9. MS (MALDI$^+$): *m*/*z* 226 ($C_{11}H_{16}NS_2$)$^+$. Anal. Calcd for $C_{11}H_{16}BF_4NS_2$: C, 42.19; H, 5.15; N, 4.47. Found: C, 41.81; H, 4.82; N, 4.79.

(*E*)-4-(4,5-Dimethyl-1,3-dithiol-2-yliden)but-2-enal (1b). To a solution of **2b** (313 mg, 1.0 mmol) in CH$_2$Cl$_2$ (20 mL) was added aqueous NaOH (5 N, 15 mL). The mixture was stirred at room temperature for 20−30 min (TLC monitoring), and the organic layer was separated, washed with saturated aqueous NaCl (20 mL) and water (20 mL), and dried (MgSO$_4$). The crude product was purified by flash chromatography on silica gel using hexane/AcOEt (9:1). Yield: 156 mg, 79%. The product was identical in all respects to an authentic sample prepared as previously reported.[20]

(*E*,*E*)-6-(4,5-Dimethyl-1,3-dithiol-2-yliden)hexa-2,4-dienal (1c). To a solution of salt **3** (197 mg, 0.85 mmol) in Ac$_2$O (3 mL) was added dropwise a solution of (*E*,*E*)-5-(dimethylamino)penta-2,4-dienal (**5**, 106 mg, 0.85 mmol) in anhydrous CH$_2$Cl$_2$ (3 mL). The mixture was heated under argon at 70 °C for 3 h and then allowed to cool to room temperature. The solution was added to ice-cooled Et$_2$O (75 mL), and the resulting dark blue precipitate was isolated by filtration, washed with cool Et$_2$O, and dried. Hydrolysis of this crude iminium salt **2c** and subsequent purification of the final product (**1c**) was carried out exactly as described above for the preparation of **1b**. Yield from **3**: 104 mg, 55%. The product was identical in all respects to an authentic sample prepared as previously reported.[20]

(*E*,*E*)-*N*,*N*-Dimethyl 6-(4,5-dimethyl-1,3-dithiol-2-yliden)hexa-2,4-dienylideniminium Tetrafluoroborate (2c). To a solution of aldehyde **1c** (265 mg, 1.18 mmol) in absolute ethanol (30 mL) was added dimethylammonium tetrafluoroborate (157 mg, 1.18 mmol). The mixture was refluxed for 7 h and cooled and the solvent distilled. Et$_2$O (100 mL) was added, and the resulting precipitate was filtered off, washed with Et$_2$O, and dried. Yield: dark blue solid (370 mg, 92%). Mp: 110−112 °C. IR (KBr, cm^{-1}): 1653 (*C*=N). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 7.92 (d, J = 11.3 Hz, 1H), 7.53 (t, J = 12.8 Hz, 1H), 7.10 (t, J = 12.8 Hz, 1H), 6.40 (d, J = 12.3 Hz, 1H), 6.30 (t, J = 12.8 Hz, 1H), 6.17 (dd, J = 13.4 Hz, J' = 11.3 Hz, 1H), 3.48 (s, 3H), 3.27 (s, 3H), 2.11 (s, 6H). ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz): δ 165.7, 162.8, 161.9, 147.7, 128.4, 128.2, 123.5, 112.4, 111.9, 48.2, 40.0, 14.0, 13.6. MS (ESI$^+$): *m*/*z* 252 ($C_{13}H_{18}NS_2$)$^+$. Anal. Calcd for $C_{13}H_{18}BF_4NS_2$: C, 46.03; H, 5.35; N, 4.13. Found: C, 45.64; H, 5.08; N, 4.49.

Compounds 7a,b from 1a,b: General Procedure. 3-Phenyl-5-isoxazolone (**6**, 94 mg, 0.58 mmol) was added to a solution of 0.58 mmol of the corresponding aldehyde (**1a**,**b**) in absolute ethanol (10 mL). The solution was refluxed under argon with exclusion of light for 1.5−2 h (TLC monitoring) and then allowed to cool to room temperature. The resulting solid was filtered off, washed with cold ethanol, and dried.

(*Z*)-4-[2-(4,5-Dimethyl-1,3-dithiol-2-ylidene)ethylidene]-3-phenyl-5-isoxazolone (7a). Yield: purple solid (143 mg, 78%). Evaporation of the filtrate and column chromatography (silica gel) using CH$_2$Cl$_2$/Et$_2$O (9:1) as eluent gave a second fraction (30 mg, 16%). Mp: 238−239 °C. IR (Nujol, cm^{-1}): 1745 (C=O). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.79 (d, J = 12.6 Hz, 1H), 7.59−7.49 (m, 5H), 7.32 (d, J = 12.6 Hz, 1H), 2.13 (s, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 171.9, 170.9, 162.4, 140.6, 130.2, 129.0, 128.8, 128.5, 128.3, 128.1, 108.6, 103.9, 13.7, 13.6. MS (EI$^+$): *m*/*z* 315 (M$^{+\cdot}$, 100), 159 (30), 114 (45). HRMS (EI$^+$): calcd for $C_{16}H_{13}NO_2S_2$ 315.0388, found 315.0399. Anal. Calcd for $C_{16}H_{13}NO_2S_2$: C, 60.93; H, 4.15; N, 4.44. Found: C, 61.23; H, 4.22; N, 4.63.

(*Z*)-4-[(*E*)-4-(4,5-Dimethyl-1,3-dithiol-2-ylidene)but-2-enylidene]-3-phenyl-5-isoxazolone (7b). Yield: dark blue solid (146 mg, 74%). Mp: 203−204 °C. IR (Nujol, cm^{-1}): 1746 (C=O). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.63−7.45 (m, 6H), 7.29 (d, J = 12.7 Hz, 1H), 6.94 (t, J = 12.8 Hz, 1H) 6.44 (d, J = 11.9 Hz, 1H), 2.07 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 170.1, 161.5, 158.4, 148.2, 146.7, 129.3, 128.0, 127.7, 127.2, 125.7, 125.4, 119.7, 110.8, 108.3, 12.7, 12.3. HRMS (ESI$^+$): calcd for $C_{18}H_{16}NO_2S_2$ (M + H) 342.0617, found 342.0627. Anal. Calcd for $C_{18}H_{15}NO_2S_2$: C, 63.32; H, 4.43; N, 4.10. Found: C, 63.57; H, 4.70; N, 4.38.

Synthesis of 7a from 2a. To a solution of iminium salt **2a** (53 mg, 0.18 mmol) in anhydrous DMF (2 mL) were added 3-phenyl-5-isoxazolone (**6**) (32 mg, 0.198 mmol) and piperidinium acetate (29 mg, 0.198 mmol). The mixture was stirred under argon at room temperature for 1 h. AcOEt (30 mL) was then added, and the resulting organic layer was washed with water (3 × 30 mL), dried (MgSO$_4$), and evaporated. The residue was purified by flash chromatography (silica gel) using CH$_2$Cl$_2$/Et$_2$O (9:1). Yield: 53 mg, 91%.

Synthesis of 7b from 2b. To a solution of iminium salt **2b** (44 mg, 0.14 mmol) in anhydrous DMF (2 mL) was added 3-phenyl-5-isoxazolone (**6**) (24 mg, 0.15 mmol). The mixture was stirred under argon for 7 h. AcOEt (30 mL) was then added, and the resultant organic layer was washed with water (3 × 30 mL), dried

($MgSO_4$), and evaporated. The residue was purified by flash chromatography (silica gel) using hexane/AcOEt (8:2). Yield: 30 mg, 62%.

(*Z*)-4-[(2*E*,4*E*)-6-(4,5-Dimethyl-1,3-dithiol-2-ylidene)hexa-2,4-dienylidene]-3-phenyl-5-isoxazolone (7c). To a solution of iminium salt **2c** (112 mg, 0.33 mmol) in anhydrous DMF (7 mL) was added 3-phenyl-5-isoxazolone (**6**, 55 mg, 0.34 mmol). The mixture was stirred under argon at 0 °C for 2 h. AcOEt (60 mL) was added, and the resultant organic layer was washed with water (3 × 50 mL), dried over $MgSO_4$, and evaporated. The residue was purified by flash chromatography (silica gel) using hexane/AcOEt (8:2). Yield: dark blue solid (30 mg, 25%). Mp: 119−120 °C. IR (Nujol, cm^{-1}): 1748 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (dd, J = 13.7 Hz, J' = 12.4 Hz, 1H), 7.62−7.45 (m, 5H), 7.30 (d, J = 12.4 Hz, 1H), 7.01 (dd, J = 13.7 Hz, J' = 11.8 Hz, 1H), 6.63 (dd, J = 13.7 Hz, J' = 11.8 Hz, 1H), 6.31 (dd, J = 13.7 Hz, J' = 11.8 Hz, 1H), 6.25 (d, J = 11.8 Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.5, 162.4, 154.1, 151.2, 149.1, 140.7, 130.4, 129.0, 128.3, 128.1, 125.9, 124.6, 124.6, 124.5, 111.7, 111.1, 13.6, 13.2; HRMS (ESI$^+$): calcd for $C_{20}H_{18}NO_2S_2$ (M + H) 368.0773, found 368.0765. Anal. Calcd for $C_{20}H_{17}NO_2S_2$: C, 65.37; H, 4.66; N, 3.81. Found: C, 65.04; H, 4.79; N, 4.10.

4-(3,5,5-Trimethyl-2-cyclohexen-1-ylidene)-3-phenyl-5-isoxazolone (8). Compound **8** was prepared as previously reported[29] and obtained as a *Z*/*E* mixture (10:3 ratio). Mp: 161−163 °C. Recrystallization from methanol afforded the (*Z*)- isomer nearly free from the (*E*)-isomer (10:1 ratio). Mp: 168−169 °C (lit.[29] mp 168−170 °C). IR (Nujol, cm^{-1}): 1728 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (*Z*)-isomer: 7.96 (s, 1H), 7.54−7.38 (m, 5H), 2.09 (s, 2H), 2.04 (s, 3H), 1.99 (s, 2H), 0.76 (s, 6H); δ (*E*)-isomer: 7.54−7.38 (m, 5H), 6.12 (s, 1H), 3.06 (s, 2H), 1.68 (s, 3H), 1.25 (s, 2H), 1.02 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.5, 163.6, 162.9, 161.7, 161.4, 159.8, 131.0, 130.8, 130.1, 130.0, 128.7, 128.6, 121.9, 121.0, 111.1, 110.8, 45.8, 45.5, 41.9, 38.9, 32.4, 32.0, 28.2, 27.8, 25.9, 25.7. MS (EI$^+$) *m/z* 281 (M$^{+\cdot}$, 21), 266 (100), 248 (70), 220 (31), 117 (22), 105 (21), 91 (21), 77 (33).

4-[3-(4,5-Dimethyl-1,3-dithiol-2-ylidenemethyl)-5,5-dimethyl-2-cyclohexen-1-ylidene]-3-phenyl-5-isoxazolone (9d). To a solution of 4,5-dimethyl-2-methylthio-1,3-dithiolium tetrafluoroborate (**10**) (264 mg, 1 mmol) in pyridine (5 mL) were added compound **8** (mixture of isomers) (281 mg, 1 mmol) and triethylamine (0.4 mL). The mixture was refluxed with exclusion of light for 30 min and cooled, and the solvents were distilled. The crude product was dissolved in CH_2Cl_2 and washed with HCl 1 N (3 × 100 mL) and water (2 × 100 mL). The organic layer was dried ($MgSO_4$), evaporated, and purified by chromatography (silica gel) using CH_2Cl_2/Et_2O (9:1) as eluent. Yield: dark blue solid (143 mg, 35%). Mp: 191−195 °C. IR (Nujol, cm^{-1}): 1701 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.86 (s, 1H, (*Z*)-isomer), 7.49−7.40 (m, 10H), 6.34 (s, 1H), 6.29 (s, 1H), 5.89 (s, 1H, (*E*)-isomer), 3.08 (s, 2H, (*E*)-isomer), 2.26 (s, 2H, (*Z*)-isomer), 2.15 (s, 2H, (*Z*)-isomer), 2.05 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.30 (s, 2H, (*E*)-isomer), 1.03 (s, 6H, (*E*)-isomer), 0.77 (s, 6H, (*Z*)-isomer). ^{13}C NMR spectrum was not registered due to its low solubility. MS (EI$^+$): *m/z* 409 (M$^{+\cdot}$, 100), 394 (38), 131 (36), 105 (20), 84 (47), 59 (21). Anal. Calcd for $C_{23}H_{23}NO_2S_2$: C, 67.45; H, 5.66; N, 3.42. Found: C, 67.68; H, 5.54; N, 3.70.

4-{3(*E*)-[(4,5-Dimethyl-1,3-dithiol-2-ylidene)prop-1-enyl]-5,5-dimethyl-2-cyclohexen-1-ylidene}-3-phenyl-5-isoxazolone (9a). To a solution of iminium salt **2a** (120 mg, 0.418 mmol) in anhydrous DMF (4 mL) were added compound **8** (129 mg, 0.45 mmol) and piperidinium acetate (65 mg, 0.45 mmol). The mixture was stirred under argon at room temperature for 2 h. AcOEt (50 mL) was added, and the organic layer was washed with water (3 × 50 mL), dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography (silica gel) using hexane/AcOEt (9:1, then 7:3). Yield: dark blue solid (83 mg, 45%). Mp: 169−170 °C. IR (Nujol, cm^{-1}): 1724 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz, −20 °C): δ 8.05 (s, 1H, (*Z*)-isomer), 7.56−7.36 (m, 10H), 6.67 (dd, J = 14.4 Hz, J' = 11.8 Hz, 1H), 6.56 (dd, J = 14.4 Hz, J' = 11.8 Hz, 1H), 6.30 (d, J = 14.4 Hz, 1H), 6.22 (d, J = 11.8 Hz, 1H), 6.20 (s, 1H, (*E*)-isomer), 6.09 (d, J = 11.8 Hz, 1H), 5.54 (d, J = 14.4 Hz, 1H), 3.08 (s, 2H, (*E*)-isomer), 2.27 (s, 4H), 2.01 (s, 6H), 1.99 (s, 3H), 1.98 (s, 3H), 1.22 (s, 2H, (*E*)-isomer), 1.03 (s, 6H, (*E*)-isomer), 0.77 (s, 6H, (*Z*)-isomer). ^{13}C NMR spectrum was not registered due to its low solubility. MS (MALDI$^+$): *m/z* 436 (M + H). Anal. Calcd for $C_{25}H_{25}NO_2S_2$: C, 68.93; H, 5.78; N, 3.22. Found: C, 68.67; H, 5.92; N, 3.51.

4-{3-(1*E*,3*E*)-[5-(4,5-Dimethyl-1,3-dithiol-2-ylidene)penta-1,3-dienyl]-5,5-dimethyl-2-cyclohexen-1-ylidene}-3-phenyl-5-isoxazolone (9b). To a solution of iminium salt **2b** (227 mg, 0.725 mmol) in anhydrous DMF (8 mL) were added compound **8** (204 mg, 0.725 mmol) and piperidinium acetate (105 mg, 0.725 mmol). The mixture was stirred under argon at 0 °C for 4.5 h. AcOEt (80 mL) was added, and the organic layer was washed with water (3 × 80 mL), dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography (silica gel) using hexane/AcOEt (8/2). Yield: dark blue solid (57 mg, 17%). Mp: 198−201 °C. IR (Nujol, cm^{-1}): 1731 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (s, 1H, (*Z*)-isomer), 7.57−7.39 (m, 10H), 6.82 (dd, J = 15.0 Hz, J' = 11.2 Hz, 1H), 6.66 (dd, J = 15.0 Hz, J' = 11.3 Hz, 1H), 6.52 (d, J = 15.0 Hz, 1H), 6.40 (dd, J = 14.3 Hz, J' = 11.5 Hz, 1H), 6.33 (dd, J = 14.3 Hz, J' = 11.7 Hz, 1H), 6.28 (s, 1H, (*E*)-isomer), 6.16 (d, J = 11.5 Hz, 1H), 6.15 (dd, J = 14.3 Hz, J' = 11.2 Hz, 1H), 6.08 (d, J = 11.7 Hz, 1H), 5.98 (dd, J = 14.2 Hz, J' = 11.3 Hz, 1H), 5.76 (d, J = 15.0 Hz, 1H), 3.10 (s, 2H, (*E*)-isomer), 2.28 (s, 2H, (*Z*)-isomer), 2.01 (s, 2H, (*Z*)-isomer), 1.98 (s, 6H), 1.95 (s, 6H), 1.25 (s, 2H, (*E*)-isomer), 1.04 (s, 6H, (*E*)-isomer), 0.79 (s, 6H, (*Z*)-isomer). ^{13}C NMR spectrum was not registered due to its low solubility. HRMS (ESI$^+$): calcd for $C_{27}H_{28}NO_2S_2$ (M + H) 462.1556, found 462.1547. Anal. Calcd for $C_{27}H_{27}NO_2S_2$: C, 70.25; H, 5.90; N, 3.03. Found: C, 70.01; H, 6.22; N, 3.38.

4-{3-(1*E*,3*E*,5*E*)-[7-(4,5-Dimethyl-1,3-dithiol-2-ylidene)hepta-1,3,5-trienyl]-5,5-dimethyl-2-cyclohexen-1-ylidene}-3-phenyl-5-isoxazolone (9c). To a solution of iminium salt **2c** (137 mg, 0.4 mmol) in anhydrous DMF (5 mL) was added compound **8** (123 mg, 0.44 mmol) and piperidinium acetate (64 mg, 0.44 mmol). The mixture was stirred under argon at 0 °C for 3 h. AcOEt (60 mL) was added, and the organic layer was washed with water (3 × 50 mL), dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography (silica gel) using hexane/AcOEt (9:1). Yield: dark blue-green solid (41 mg, 21%). Mp: 194−195 °C. IR (KBr, cm^{-1}): 1722 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.13 (s, 1H, (*Z*)-isomer), 7.57−7.39 (m, 10H), 6.78 (dd, J = 14.9 Hz, J' = 10.9 Hz, 1H), 6.65 (dd, J = 14.9 Hz, J' = 11.3 Hz, 1H), 6.59−6.41 (m, 3H), 6.40−5.95 (m, 9H), 5.79 (d, J = 15.0 Hz, 1H), 3.10 (s, 2H, (*E*)-isomer), 2.29 (s, 4H), 1.97 (s, 6H), 1.94 (s, 6H), 1.31 (s, 2H, (*E*)-isomer), 1.05 (s, 6H, (*E*)-isomer), 0.80 (s, 6H, (*Z*)-isomer). ^{13}C NMR spectrum was not registered due to its low solubility. HRMS (ESI$^+$): calcd for $C_{29}H_{30}NO_2S_2$ (M + H) 488.1712, found 488.1716. Anal. Calcd for $C_{29}H_{29}NO_2S_2$: C, 71.42; H, 5.99; N, 2.87. Found: C, 71.20; H, 6.28; N, 3.09.

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Supporting Information Available: General experimental methods, NMR spectra of new compounds, computed energies, and Cartesian coordinates of optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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