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### THE SYNTHESIS OF DITHIOLENE DYES WITH STRONG NEAR-IR ABSORPTION

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#### 1. INTRODUCTION

For quite a few years, we have investigated several approaches to create materials which show intense electronic transitions in the 1.0 to 1.6  $\mu$  region of the Near-IR. This Report attempts to place some of this work into focus by describing why we wanted to synthesize such dyes, what we have done, what we have learned from it, and why this is of interest.

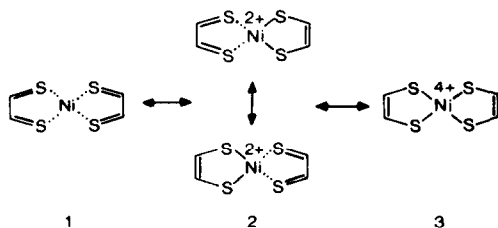
There are several choices in the types of compounds one might consider as candidates for Near-IR dyes. Ours has been the class of square planar transition metal dithiolene complexes, especially those of Ni, because (1) already the unsubstituted parent Ni dithiolene shows a transition at the Near-IR edge of the visible and (2) the dithiolene absorption can be shifted by proper substitution. How far into the Near-IR one can expect to go with this approach is an unanswered question. A further question of more general nature is whether or not we can expect in principle to obtain dyes with transitions at such low energies: there might exist a cut-off beyond which electronic transitions no longer exist. This report will focus on dithiolenes, but it will also include a general discussion of Near-IR dyes and their uses. We will address these points after introducing the class of dithiolenes.

### Structure and general properties of dithiolenes

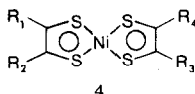
The dithiolenes complexes of transition metals are a class of covalent compounds with a number of unusual properties, the most relevant to this Report being their very intense electronic transition in the Near-IR region. A second important property of the dithiolenes is their ability to exist in several clearly defined oxidation states which are connected through fully reversible redox steps. The third and rather useful characteristic of the dithiolenes is their high thermal and photochemical stability. Very soon after the first syntheses of dithiolenes were reported<sup>1-3</sup> in the early 1960s, these properties were recognized as indications of a type of bonding different from what was previously known for transition-metal complexes.<sup>4</sup> The reason was found to lie in a high degree of electron delocalization in these systems, which also manifests itself in the intense electronic transitions at unusually low energies, not unlike the absorptions seen in extended organic  $\pi$ -systems. One notable characteristic, in which the dithiolenes differ from purely organic dyes such as the cyanines, is the shape of the intense Near-IR band: in all known dithiolenes the band is very broad and shows no vibrational fine structure.

Dithiolenes have aroused interest for several different reasons: in addition to our present work<sup>5,6</sup> to explore them as Q-switch dyes for Near-IR lasers, dithiolenes have been investigated<sup>7-9</sup> as partially oxidized or reduced species with non-integral oxidation states in several types of low-dimensional conducting solids, and others were prepared<sup>10-13</sup> as first examples of transition metal complexes with liquid crystal properties. A recent review on this class of transition metal compounds has summarized their chemistry and a few of these applications.<sup>14</sup>

A qualitative description of the bonding in dithiolenes, as exemplified by the neutral  $d^8$  complex  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2$ , involves the structures 1 to 3, in which the metal assumes formal oxidation states of 0, 2+, and 4+ while the ligands are either neutral 'dithiodiketones' or dinegative 'dithiolates'.

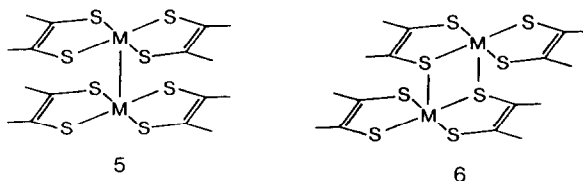


Dithiolenes are best considered to be a resonance hybrid of the limiting structures 1-3. The electron delocalization is not limited to the ligand, but includes the metals to give rise to cyclic delocalization ('aromaticity'). To symbolize this electron delocalization in dithiolenes, they can be represented, similar to the description of benzene, by formulas such as 4, containing a ring inside the framework given by the metal, sulfur, and carbon atoms. It is worth noting that dithiolenes are not unique in this regard: complexes with *o*-benzoquinones and *o*-phenylenediamines appear to possess some delocalization because they have been shown to also undergo reversible redox chemistry.<sup>15,16</sup> Special to the dithiolenes is the extent of delocalization which is made possible by the stronger overlap involving sulfur *d*-orbitals.



In most known bis-dithiolenes the ligands form the strictly square-planar arrangement indicated in 4, with all S-M-S bond angles very close to 90° and with very similar intra- and interligand S-S distances. The planar geometry is also found in the majority of mono- and dianions of these species, but here the dihedral angle between the two ligands can vary up to the tetrahedral extreme. Depending on the central metal, neutral bis-dithiolenes may exist as planar monomers or form

dimers with either metal–metal bonds, as shown in 5, or with metal–sulfur bonds as, for example, the dithiolene 6.



Even the simplest examples of bis-dithiolenes, the diamagnetic  $d^8$  complexes of Ni, Pd, and Pt, show different solid-state properties: the parent Ni dithiolene is a planar monomer<sup>17</sup> of type 4, whereas its Pd and Pt analogues form<sup>18</sup> metal–metal bonded dimers of type 5, which appear to undergo a monomer–dimer equilibrium in solution. This difference in structure may relate to their different degree of electron delocalization and the size of the valence orbitals available for metal–metal bonding. In the dimers, the metal–metal distances are very short (2.79 and 2.75 Å, respectively); the intermolecular S–S distances are 3.03 Å and thus much shorter than the sum of sulfur van der Waals radii and considerably shorter than the intraligand S–S distances of 3.25 Å; the  $C_2H_2$  groups bend away slightly from the central core to achieve more normal intermolecular distances.

A semi-quantitative study<sup>19</sup> of the extent of cyclic electron delocalization in square planar dithiolenes and in the related class of dithio-acetylacetonates (SacSac complexes) of Ni, Pd, and Pt was based on the NMR chemical shift differences observable in mesityl derivatives of these compounds. If a delocalized cyclic structure carries a mesityl substituent, the methyl groups in the *ortho* position experience an upfield shift whereas those in the *para* position do not. Their chemical shift difference can be used as a measure of delocalization.<sup>20</sup> Compounds with a shift difference >0.30 ppm are considered to be ‘aromatic’, i.e. highly delocalized.

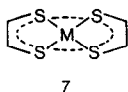
These experiments showed that the Ni dithiolene is highly delocalized, whereas Pd and Pt dithiolenes show less delocalization, a trend which parallels the  $^1H$  chemical shifts and the observation that the latter two form dimers, whereas the Ni complex does not. In the SacSac series, all three complexes show a lower and undifferentiated degree of delocalization. These data are given in Table 1.

Table 1.

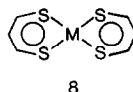
The  $^1H$  chemical shift difference between the *o*- and *p*-methyl groups in mesityl derivatives of dithiolenes and dithio-acetylacetonates. The larger the shift difference, the more delocalized the system.

Metal	Dithiolene	SacSac
Ni	0.40	0.32
Pd	0.31	0.32
Pt	0.34	0.32

Although all SacSac complexes are deeply colored,<sup>21</sup> they lack the intense absorption at low energy found in the class of dithiolenes. The dithiolenes are delocalized throughout the entire complex unit as shown in 7, but the delocalization in the SacSac complexes apparently involves the two ring systems independently, as shown in 8: the cyclic electron delocalization does involve the metal, but there is no crossover of delocalization from one half of the molecule to the other.



7



8

We can thus regard the dithiolenes as subject to some of the rules of substituent effects which are well established in the organic chemistry of aromatic compounds. This knowledge will guide us in the design of dithiolenes with particular properties.

In addition to the planar  $d^8$  dithiolenes with two ligands ('bis-dithiolenes') there also exist the tris-dithiolenes which contain three ligands surrounding a metal such as W or Cr. These complexes show the unusual tendency to prefer trigonal prismatic rather than octahedral coordination geometries.<sup>22</sup> Distortions toward octahedral structures are known to occur especially in anionic tris-dithiolenes, but the preference for trigonal prismatic arrangements is clearly established for the neutral species. The main reason is found in favorable interligand interactions between the sulfur atoms. In  $\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3$  the intra- and inter-ligand S-S distances of 2.10 and 2.11 Å are virtually identical.<sup>22</sup> This difference in electronic structure between bis- and tris-dithiolenes may be connected to the fact that no intense Near-IR absorption has been reported for the tris-dithiolenes. This Report will therefore focus on the planar bis-dithiolenes of Ni (and a few results on Pd and Pt) dithiolenes.

## 2. SYNTHESIS OF DITHIOLENES

Two main synthetic routes are available for the preparation of dithiolenes: in the first and most frequently used method, either the free ethylene dithiol or an appropriate salt of the ethylene dithiolato ligand dianion are reacted with a metal salt to produce anions of the dithiolenes, which may or may not be subsequently oxidized to the neutral species; in the second method, vicinal diones are converted to dithiones, and these are reacted either with zero-valent metals to directly form dithiolenes, or with metal salts to arrive at cationic species which are reduced to the neutral dithiolenes either during the reaction or in a subsequent step. The preparative potential seems to be limited only by the individual's ability to synthesize the desired organic ligand precursors. Once these are in hand, their conversion to dithiolenes generally follows well-established procedures.

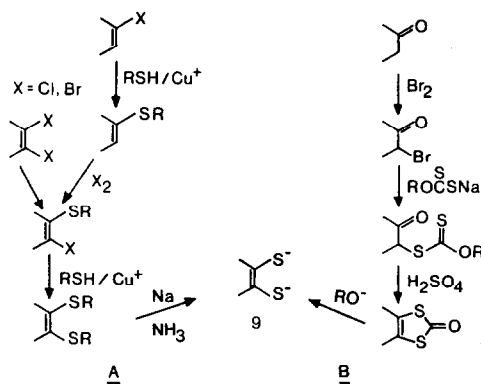
The original synthesis of alkyl- and aryl-substituted dithiolenes used the reaction of acyloins or benzoin with  $\text{P}_4\text{S}_{10}$  in dioxane or toluene and treatment of this mixture with a metal salt.<sup>14</sup> This method is now used only in very rare cases.

### 2.1. Syntheses via ethylene dithiolates

To obtain ethylene dithiols, the various routes described in Scheme 1 are available. Vicinal dithioethers, obtainable from *cis*-dichloro- or dibromo-olefins or from olefins through a stepwise synthesis,<sup>23-25</sup> can be cleaved to produce dithiols (route A). Ethylene dithiocarbonates can be prepared from  $\alpha$ -bromoketones via the xanthate esters<sup>14,26</sup> and by some less general methods<sup>27</sup> as well. Their cleavage by alkali hydroxides or alkoxides leads to salts of ethylene dithiolates (Route B). Their photolysis with loss of CO and generation of a dithioketone has also been described.<sup>28</sup>

The chemistry of tetrathiafulvalene and its derivatives (TTFs) has been widely explored in recent years, because many charge transfer complexes with TTF as the donor component have shown very high and strongly anisotropic electrical conductivity. The flurry of synthetic activity has benefitted the chemistry of dithiolenes, because many of the intermediates leading to TTFs, such as the ethylene dithiocarbonates mentioned above, are equally useful in preparing ethylene dithiols and dithiolates. Independently, the investigation of conductive dithiolenes has led to a series of new complexes with novel ligand types.<sup>29</sup>

Many aromatic dithiols are stable, but others tend to polymerize rather rapidly.<sup>30</sup> Aliphatic enedithiols are very prone to decomposition and polymerization.<sup>23,24</sup> They are best converted to alkali salts or salts of organic cations such as the tetrabutylammonium ion. Alternatively, they can



Scheme 1. Synthetic routes to ethylene dithiolato ligands.

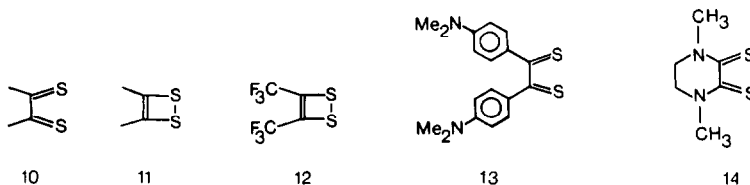
be acylated by acid halides to be stored as thioesters, which can be cleaved again by alkoxides prior to their reaction with a metal salt to form dithiolenes.

## 2.2. Syntheses via dithiones

In our laboratory, an important step has been realized in the synthesis of dithiolenes via  $\alpha$ -dithiones, which we obtained from the corresponding diones. Most of these dithiones are very unstable, but in some dithiolene syntheses, where dithiolates are not available, they are the crucial intermediate. Whereas the chemical literature shows many examples of mono-thiones (thioaldehydes and especially thioketones), dithiones are not part of this repertoire. In several cases, we were able to refine the sulfurization techniques to afford surprising reproducibility, which allowed us to prepare, isolate and characterize dithiones. As will be seen below, however, the synthesis of dithiones is often a major problem. Nevertheless, this route now makes the often much simpler synthesis of diones and their conversion to dithiolenes a pathway of equal importance to the formerly preferred route via dithiolates.<sup>31</sup>

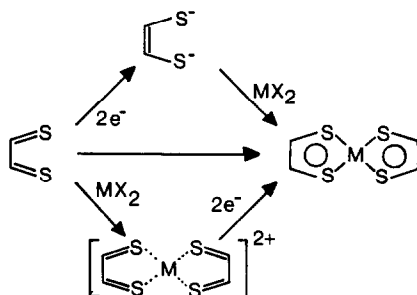
Several 1,2-dithiones can be obtained from 1,2-diones by direct sulfurization with  $P_4S_{10}$  or  $B_2S_3$ . The usually heterogeneous reaction can be accelerated by the use of ultrasound. An alternate thionation using Lawesson's Reagent has been tried in several cases but has generally found to be less successful.

Most dithiones are prone to hydrolysis and decomposition and some cannot be prepared at all under the above conditions. Unless steric and electronic constraints prevail, vicinal dithiones **10** can exist in an equilibrium mixture with their dithiacyclobutene ('dithiete' or 'dithietene') isomers **11**. Strongly electron-withdrawing substituents, such as in **12**, appear to favor the latter form, but the donor-substituted dithione **13** is also known<sup>28</sup> to show such an equilibrium. As a *cis*-fixed dithioamide, the ligand **14** is particularly stable and presumably exists only in the dithione form.



Three main options, described in Scheme 2, exist for the conversion of dithiones to dithiolenes: (1) reaction with a transition metal carbonyl or other reactive zero-valent material; (2) reduction to an ethylene dithiolate and reaction as described above for these species; (3) reaction with a metal

salt to form a cationic dithiolene and reduction of the reaction product to the neutral compounds, whereby a suitable solvent may serve the function of the reducing agent for *in situ* generation of the neutral species.



Scheme 2. Reactions of  $\alpha$ -dithiones to form dithiolenes.

The synthesis of the julolidine substituted dithiolene has been carried out by methods 2 and 3. The reduction according to route 2 of the dithione by  $\text{NaBH}_4$  in THF-MeOH, followed by acidification and reaction with aqueous  $\text{NiCl}_2$  led<sup>32</sup> to the dithiolene in excellent yield. As is evident from the MO diagram of dithiolenes and their established redox properties, method 3 applies only to dithiolenes with strongly electron-donating substituents which may stabilize the cationic intermediates. In the present case this might be true, but only the neutral species was isolated when the reaction between the dithione and Ni salts was carried out in methanol, which can be expected to act as a mild reducing agent. Very good results were also obtained when the reaction between the dithione and a nickel salt was carried out in the presence of  $\text{SnCl}_2$ .

### 3. Q-SWITCHING AND Q-SWITCH DYES

Why would dyes with intense NIR maxima be of interest and why have we put so much work into this area? The answer lies in the fact that dithiolenes seem to be irreplaceable in the application of NIR dyes in Q-switching infrared lasers, which allows the generation of short and very intense pulses. Because of the significance of this application and because most chemists are not very familiar with such processes, we will digress for a moment and discuss the phenomenon of Q-switching and the requirements to be made of materials to be used as reversibly bleachable or saturable absorbers in passive Q-switching.

The lasers in question are the Neodymium, the Iodine, and the Erbium laser. The Nd-glass or Nd-YAG lasers, operating at 1,060 nm, are very powerful systems. Our discovery<sup>33</sup> in 1972 that dithiolenes are particularly suited for Q-switching these lasers has led to the widespread use of these materials. Some dithiolenes are commercially available for this purpose. Further out toward longer wavelength, the iodine laser at 1,300 nm is of great current interest, because it is among the most powerful lasers available. It presently is used in several laboratories in an arrangement where one laser pumps the next one in an array of increasingly intense output in attempts to produce an energy source to initiate nuclear fusion. From experiments carried out with Q-switches of the dithiolene type supplied by us on an experimental basis it appears that dithiolenes will succeed as the material of choice in these applications. The Er laser, as it exists at present, is a low power, solid state laser. It is of major importance in night vision and range finder instrumentation, because at its wavelength of 1.54  $\mu$  the human eye is not very sensitive to radiation. Neodymium and iodine laser radiation can irreversibly damage the retina even at comparatively low power levels, because the vitreous body of the eye transmits their radiation. The 1.54  $\mu$  radiation of the Er laser is strongly absorbed

by the vitreous body and most likely does not reach the retina. Pulsed lasers are necessary for measuring distances in surveying. At present, some such instruments use the dangerous Nd laser, because no Q-switch dye is available in the  $1.54 \mu$  region.

The emission of a laser can generally be of two types: a continuous output of coherent light (CW operation) or compression of the full output energy into ultrashort pulses of extremely high peak power. The latter is commonly called Q-switching, a term, originating from microwave technology, which refers to a sudden change in the 'Quality' of a resonator cavity.

How can such Q-switching in lasers be achieved? Because lasing depends on photons to stimulate the emission, an absorber inside the laser cavity will suppress lasing and will thus allow us to 'load' the laser more strongly by pumping more of the active species into the excited state than are left in the ground state (population inversion). If we then remove the absorber, lasing will be possible, but because of the high population inversion it will be in the form of a short and very powerful pulse.

If an appropriate dye, either in solution or suspended in a transparent matrix, is introduced in the laser cavity, it will absorb the laser radiation and will have the effect of a closed optical shutter. As the pumping of the laser continues and the population inversion increases, the photon flux within the laser cavity will soon reach a level at which the excited state lifetime of the dye molecules is too long to allow enough molecules to return to the ground state at a sufficient rate to sustain the absorption of laser light. When this moment is reached, the dye will temporarily 'bleach out'. In terms of an optical shutter, this means a sudden switch from closed to open. At this moment, the laser output is no longer attenuated and a 'giant pulse' of very short duration and of peak powers exceeding 100 MW is produced. As soon as the pulse has been emitted, the dye molecules return to the ground state and the initial closed shutter situation is restored. Passive Q-switching is thus achieved by a reversibly bleachable absorber, without any need for external controls. This process has great advantages over any mechanical alternatives.

It is evident from the above brief description that there exists a set of obvious requirements which a dye has to meet to be usable as a Q-switch, but there also are a few less obvious properties of the dye which turn out to be essential as well. Without going into details, we will describe a few of them.

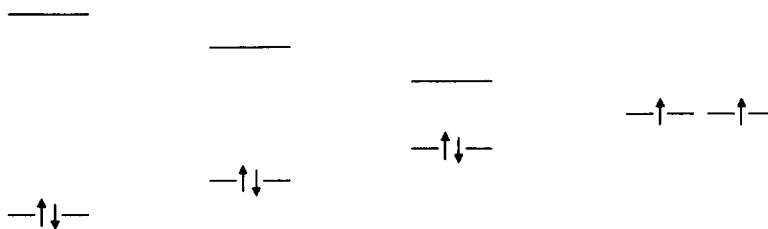
The first requirement is trivial: the dye must have a significant absorption maximum at or near the laser wavelength. The *absorption maximum* does not have to match the laser wavelength exactly, but it is desirable to match the two as closely as possible. The laser may operate at a wavelength which corresponds to 70 or 80% of the maximum absorption of the dye without losing much of the Q-switching effectiveness, if its extinction coefficient is high enough. A less obvious necessity to achieve bleaching of the Q-switch is that the dye must have no higher excitation at the same energy. The lowest energy transition ( $S_0 \rightarrow S_1$  transition) must be energetically well separated from  $S_1 \rightarrow S_2$  or any other higher transition. The *excited state lifetime* of a Q-switch dye is an important constant in this process. If the lifetime is too long, the dye will bleach out too soon, because the molecules will stay in the excited state too long to be available to absorb further radiation. If the lifetime is extremely short, bleaching may not be achieved, because enough molecules continue to return to the ground state to guarantee continuous absorption. *Photochemical stability* to radiation at the laser wavelength as well as to ambient light is a great advantage but not an essential requirement for some Q-switch applications within a laboratory. The dye solution can be kept in the dark and may be circulated from a reservoir through the laser cavity if the dye photodecomposes. In laboratory applications, this is only an annoying inconvenience, but it becomes a serious problem for mobile laser units. *Thermal stability* also must be considered. In the laser cavity, dye decomposition may be accelerated because a significant portion of the absorbed energy can be released through internal conversion to the environment, i.e. the solvent, in the form of thermal energy. Since very short pulses are involved, heat dissipation may be slow and this inhomogeneous situation can lead to vastly increased rates of thermal decomposition. An important criterion is the *solvent choice* and the interaction of the dye with the solvent. The choice of solvents is limited because there always

exists the possibility that the dye molecules may aggregate. Dimers and more complicated aggregates (Scheibe aggregates) may be formed. For some cyanine Near-IR dyes, the existence of distinct dimers with an absorption quite different from that of the isolated, solvated molecule has been demonstrated. The dimer formation is strongly solvent dependent and restricts the solvent choice. In addition, some solvents may not be useful, because they absorb at the wavelength of the laser. Usually, these absorptions are weak overtones of vibrational modes, but they may nevertheless steal enough radiation to suppress lasing.

The obvious focus of our present work on dithiolenes is to shift their intense NIR band to lower energies. We must keep the above criteria in mind when we want to design complexes which we want to be of any use in this regard.

#### 4. ELECTRONIC SPECTRA OF DITHIOLENES

To create a rational basis for any such work, we must correlate what is known about the position of the dithiolenes transitions with what we can see as important structural characteristics. Where suitable quantum chemical results exist, we can utilize them in helping us understand the observed trends. We must also be aware that it may not be possible to shift electronic transitions of the  $\pi-\pi^*$  type indefinitely to lower energies. The reason for such suspicion lies in the simple fact that we are approaching the energy region of the standard IR and that it may be possible to thermally populate the excited state. Another reason for a natural cut-off of electronic transitions at very low energies may be linked to the rearrangement, by minor molecular distortions, of the frontier orbital levels which cause the energy gap between the HOMO and LUMO to either widen or shrink; in the latter extreme we may arrive at a molecule with a triplet ground state. These considerations are expressed in the following scheme:



Scheme 2a.

Where such a cut-off might be found is not exactly predictable. Wherever thermal population of excited states plays a role, we clearly would have to expect a strong temperature dependence of the intensity of this absorption band.

The dithiolenes are of interest for any such study, because they possess a fairly broad but intense ( $\epsilon = 15,000$  to  $40,000$ ) characteristic long-wavelength (above 700 nm) electronic transition. In particular, the intensity of the transition is unmatched in any other transition-metal compound, where low-energy transitions usually are of  $d-d$  character and thus considerably weaker. Early theoretical treatments have been confirmed in their essential results by more refined calculations in assigning this electronic absorption band to a  $\pi-\pi^*$  transition between the relatively high-lying highest filled MO and the lowest vacant MO, which is of unusually low energy. This latter fact is, of course, substantiated by the electron acceptor properties of the properly substituted dithiolenes, and the existence of radical anions and dianions in which this LUMO is filled by one or two electrons.



#### 4.1. Influence of ligand structure on the electronic spectra

In the square-planar dithiolenes of Ni, Pd, and Pt, this transition can be shifted far into the NIR region by proper substitution. In Table 2, the major part of which is taken from our recent review on dithiolenes,<sup>14</sup> the electronic absorption maxima are listed for nickel dithiolenes with a variety of substituents. Their maxima span the range from 720 nm for the parent dithiolene to the present maximum of 1440 nm.

Table 2.

#### LIGAND EFFECTS ON THE LOWEST ENERGY TRANSITIONS IN NICKEL DITHIOLENES.

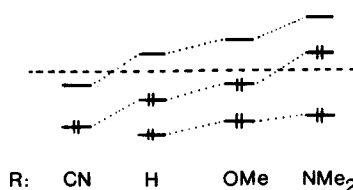
The numbering of  $R_1 - R_4$  refers to formula 4. Values in parentheses have not been determined accurately. In entry #11, DETHQ is *N,N'*-diethyl-6,6'-tetrahydroquinoxalyl. Entry #19 is an estimate, because only the spectrum of the anion is known.

#	Substituents	Solvent	Max. (nm)	$\epsilon$
<b>2.1: Symmetrical ligands (<math>R_1 = R_2 = R_3 = R_4</math>)</b>				
1	H	hexane	720	14300
2	CH <sub>3</sub>	CHCl <sub>3</sub>	774	28200
3	CF <sub>3</sub>	pentane	715	12300
4	S-C <sub>4</sub> H <sub>9</sub>	CHCl <sub>3</sub>	1104	---
5	C <sub>6</sub> H <sub>5</sub>	CHCl <sub>3</sub>	866	30900
6	2-Naphthyl-	CHCl <sub>3</sub>	905	---
7	3-Pyrenyl-	CHCl <sub>3</sub>	910	---
8	2-Thienyl-	CHCl <sub>3</sub>	982	---
9	4-(CH <sub>3</sub> ) <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	1120	28000
10	Julolidine	CH <sub>2</sub> Cl <sub>2</sub>	1270	45000
11	DETHQ	CH <sub>2</sub> Cl <sub>2</sub>	1370	(42000)
11a	DETHQ	DMSO	1440	(42000)
<b>2.2: Cyclic ligands</b>				
12	2,3-Indenedithiole	CH <sub>2</sub> Cl <sub>2</sub>	915	(25000)
13	9,10-Phenanthrenedithiole	CH <sub>2</sub> Cl <sub>2</sub>	966	(30000)
14	9,10-Acenaphthylenedithiole	CH <sub>2</sub> Cl <sub>2</sub>	1140	(30000)
<b>2.3: Unsymmetrical ligands (<math>R_1 = R_3, R_2 = R_4</math>)</b>				
	$R_1, R_4$	$R_2, R_3$		
15	H	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> Cl <sub>2</sub>	805 (25000)
16	H	4-octyl-C <sub>6</sub> H <sub>4</sub>	hexane	850 (25000)
17	H	Julolidine	CH <sub>2</sub> Cl <sub>2</sub>	1180 (35000)
18	C <sub>6</sub> H <sub>5</sub>	4-(CH <sub>3</sub> ) <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	1060 28000
<b>2.4: Dithiolenes with two different ligands (<math>R_1 = R_2, R_3 = R_4</math>)</b>				
	L <sub>1</sub>	L <sub>2</sub>		
19	S <sub>2</sub> C <sub>2</sub> (CN) <sub>2</sub>	S <sub>2</sub> C <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	---	( $\approx$ 900) (20000)
20	S <sub>2</sub> C <sub>2</sub> (CN) <sub>2</sub>	S <sub>2</sub> C <sub>2</sub> (NCH <sub>3</sub> ) <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	775 (20000)

By closer inspection of the data in Table 2 we can glean important information concerning the influence of ligand structure on the peak position and thus learn a lesson in general dye chemistry and in planning the synthesis of new materials with Near-IR absorptions. In this spectral range, judging ligand effects by the wavelength shift they produce can at best be qualitative; more relevant comparisons must be made by using an energy-linear scale. For this reason, the peak maxima are listed also in eV and our conclusions must be based on this scale.

Looking at the data in Table 2.1 we see that alkyl groups produce a modest bathochromic shift (0.12 eV) and that aryl groups are more effective in this regard (0.29 eV). This is explainable in terms of the weak donor properties of alkyl groups and the fact that the delocalized arenes extend the  $\pi$ -system and thus shift the absorption to lower energy. Noteworthy is the fact that very large  $\pi$  systems, such as the pyrene nucleus, have no drastic additional shift (0.36 eV). The bathochromic effect of donor groups is juxtaposed in Table 2.3 to the absence of any shift when electron acceptor substituents are incorporated in the dithiolenes: all listed donors have a strong effect ( $>0.60$  eV).

The simplified diagram in Scheme 3 of the frontier MOs of substituted dithiolenes, based on EHT results,<sup>34</sup> helps to explain this trend.



Scheme 3. EHT frontier MO energies in dithiolenes as a function of donor and acceptor substituents R.

The highest occupied orbital lies in a not at all unusual energy range but the lowest vacant orbital has very low energy, giving rise to the observed allowed electronic transition.

Acceptor substituents lower the energy of the highest occupied and the lowest vacant orbital by roughly the same amount and no drastic shift in the absorption maximum is observed; however, in accord with what is known from the electrochemistry of dithiolenes, their electron acceptor strength is drastically increased.

Donor substituents also affect both MOs, but they raise the energy of the highest occupied MO more than that of the lowest vacant one. Consequently, they cause a bathochromic shift of the lowest energy transition. Very strong donor substituents cause the strongest shift to lower energies but they also force the HOMO to become antibonding. This is a very undesirable effect: it introduces into the compound a tendency to lose one or both of the electrons in this MO, leading to the formation of a radical cation or a dication, both of them without much interest in the context of strong IR absorbers. In addition, the increased reactivity drastically reduces the usefulness of such materials.

Table 2.1 also shows what the combination of donor substituents and an extended  $\pi$ -system will do: large shifts of up to 0.82 eV are observed. We can inspect all of these effects in detail by investigating each ligand functionality and structure individually. This is done in Tables 2.3 and 2.5. One phenyl group produces a shift by 0.18 eV; two phenyl groups added up to less than twice this shift (0.29 eV). The absence of additivity has a very good reason: one phenyl group can easily be coplanar with the dithiolene and thus exert a maximum effect. However, two phenyl substituents find themselves in a *cis*-stilbene environment where coplanarity is impossible and their individual effect is reduced as a function ( $\cos^2$  dependence) of the twist angle.

When one of these rings carries a donor substituent, we can expect the substituted ring to be more coplanar with the dithiolene at the expense of the unsubstituted ring, which will have to twist

out of the way. A case in point is the series exemplified by the compounds listed under the numbers 3, 18, and 9: the diphenyl-substituted dithiolenes # 3 has a maximum at 1.43 eV; addition of one dimethylamino group to the *para* position of the phenyl groups has a very strong effect, producing a maximum at 1.17 eV ( $\delta E = 0.26$ ) for compound # 18; introduction of a second *para*-dimethylamino group to produce the bis-dimethylaminophenyl dithiolenes leads to a symmetrically substituted system # 9, structurally just like the parent diphenyl dithiolenes, which absorbs at 1.10 eV, constituting a rather modest additional gain of 0.07 eV. Clearly, the substituted ring in # 18 must be more aligned in coplanarity with the dithiolenes to produce such a dramatic shift.

To maximize whatever effect a substituent may have it is thus necessary to bring it into coplanarity with the dithiolenes. Table 2.4 shows what we can and cannot learn from this. Compared to the monophenyl system # 13 in Table 2.3 with a maximum at 1.54 eV the fixed indene derivative # 15 is shifted to 1.35 eV. If we subtract from this shift that portion which may be ascribed to the CH<sub>2</sub> group (0.08 eV as in # 13), the effect of holding the phenyl ring rigidly in coplanarity amounts to 0.11 eV. Bringing two phenyl rings into coplanarity means going from a *cis*-stilbene system to a phenanthrene ring by incorporating a C–C single bond between the rings. This change, # 3 to # 16, moved the peak from 1.37 to 1.28 eV, a significant shift of 0.09 eV, but less than what we might have assumed from the previous case of comparing # 13 with # 15. This simply means that we cannot expect a phenanthrene to act like two disconnected phenyl rings. Table 2.4 also included the acenaphthylene system # 17 as a highly promising candidate to NIR dyes based on dithiolenes. The appearance of its peak at 1.08 eV emphasized the dependence of these shifts upon more than just additive increments.

Nevertheless, we can make use of some of the additive effects in analyzing the rest of these dyes. Clearly, the presence of aromatic rings and of electron donor substituents is beneficial to our purposes. An important additional fact can be learned from Table 2.3 by comparing the extinction coefficients of compounds # 9 and # 10, which are electronically comparable but which differ in one important aspect: in # 9 the dialkylamino groups are free to rotate, but in the julolidine derivative # 10 they are rigidly fixed into coplanarity with the phenyl rings (which themselves are not coplanar with the dithiolenes). This drastically increases the peak intensity: the extinction coefficient jumps from 28,000 to over 40,000. We can understand this effect qualitatively in that a fixed dialkylamino substituent is more available (on a time averaged basis) than a freely rotating one and that the elimination of some vibrational modes leads to a sharpening of the absorption band. A similar increase in extinction coefficient is seen in Table 2.5 for unsymmetrical systems, in which the fixed donor group increases the extinction coefficient in a substantial way.

It should be noted that dithiolenes do not fluoresce, nor do they show any other type of emission when irradiated in solution at the lowest energy transition. There also exists no evidence for photochemical reactions upon excitation of this transition. All absorbed energy must therefore be transmitted to the environment as heat. As long as the surrounding solution remains stable, this irradiation does not lead to decomposition of the dithiolenes.

Toward higher energy, the intense first band is followed by a weak *d-d* type transition near 600 to 700 nm and then by a series of very intense UV absorptions. Dithiolenes are more sensitive to irradiation into these latter bands and can undergo photoreactions. Their decomposition by exposure to strong UV light is not uncommon.

#### 4.2. Conclusions

If we analyze the information presented in Table 2 in terms of which structural factors contribute to the desired band shifts, we can extract a strategy for the design of NIR dyes. Considering only nickel complexes for the moment, we can summarize the effect of substituents as offering an opportunity to shift the absorption and to enhance it at the same time by providing electron-donating groups in one or several of the positions on the dithiolenes nucleus.

It is clear from the above and from other work not listed in Table 2 that the following factors

are important in any attempt to shift the absorption maximum of the dithiolenes to lower energy :

1. Coplanarity of ligand  $\pi$ -system and dithiolene ;
2. Presence of an extended  $\pi$ -system ;
3. Presence of electron donating substituents ;
4. Fixing of the substituents into rigid coplanarity with the ligand ;
5. Attachment of sterically bulky substituents to increase solubility ;
6. Variation of the central metal to obtain different shifts and to tune the relaxation time.

With these options and constraints in mind, new types of ligands can be designed. While it may be relatively simple to produce dithiolenes with one of these properties, to combine all of them into a particular ligand structure amounts to a major synthetic effort. There can be little doubt that the manipulation of dithiolenes with the goal of producing NIR dyes with high absorbance at energies as low as 0.8 eV (1.5  $\mu$ ) is a reasonable proposition.

## 5. SYNTHESIS OF NEW DITHIOLENES

### 5.1. General strategy

In Section 4, we summarized most of the information we have at present on how structural factors influence the NIR transition of the dithiolenes. In particular, it has become clear that dithiolenes containing planar polycyclic aromatic rings, carrying fixed donor groups in the proper positions, may be a good choice in synthesizing stable Near-IR dyes. How can we put this knowledge to use in producing new dyes with absorptions e.g. at the wavelength of the Er laser, and which synthetic routes are available to obtain such dithiolenes?

We have explored several approaches to the preparation of Near-IR dyes based on the planar dithiolenes of Ni as the central core. Of the planar ring systems of Table 2, the acenaphthylene and the phenanthrene derivatives clearly suggest themselves as a good basis for amino-substituted aromatic ligands for new dithiolenes. As described below in some detail, the synthesis of our acenaphthylene-based target did not succeed at all, but the second approach, the synthesis of phenanthrene-based dithiolenes, brought several of the desired results.

An important related area of research would be the synthesis of dithiolene ligands substituted by *non*-benzenoid aromatics. Not much at all is known about the possibilities in this approach, but the drastic effects of the thiophene ring (entry # 8 in Table 2) is noteworthy in this regard.

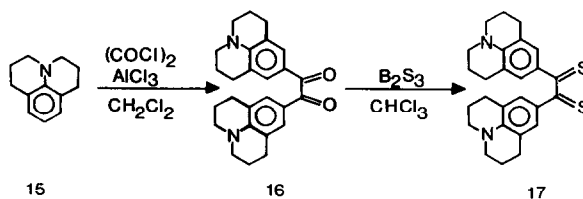
A very new approach to dithiolenes with strong Near-IR absorption is based on using totally different electron donor functions as substituents in dithiolene ligands: this involves the synthesis of metallocene-substituted dithiolenes. This area is still almost unexplored but our research group has contributed to both areas, metallocene and dithiolene chemistry, with some success. It has become clear that the chemistry of metallocenes and of related compounds offers great structural variety and that its combination with the chemistry of dithiolenes may provide an important alternative to the first approach.

### 5.2. Synthesis of JUL2 (Tetra-julolidinyl nickel dithiolene)

Because several of these syntheses were expected to make use of dithiones as the precursors to the dithiolenes, it was deemed important to improve, if possible, the known methods which lead to dithiones as well as their conversion to the target complexes so that we might profit from these results in the synthesis of the more complex ligands.

The material to be made in these preliminary studies was JUL2, listed as entry # 10 in Table 2, and shown in Fig. 1. JUL2 is the trivial name for the tetra-julolidinyl nickel dithiolene, in which the amino groups are fixed into coplanarity with the phenyl group by two saturated, six-membered rings. It was first synthesized<sup>35,36</sup> in our laboratories in 1977 as a Q-switch dye for the iodine laser (1315 nm). The synthesis used the not very efficient direct conversion of the dione

precursor to JUL2 by reaction with  $P_4S_{10}$  in dioxane and treatment of the resulting solution with nickel chloride in water; its success in these applications led to several studies regarding the solvent dependence of its Near-IR transition, which can be shifted from 1150 to 1450 nm.<sup>37,38</sup> A second synthesis was reported,<sup>38,39</sup> but its yield was only 1–2%. We believed that this left room for significant improvement by better control of the sulfurization and isolation of the dithione.



From commercial julolidine **15**, the dione **16** was synthesized with oxalyl chloride and aluminum chloride under normal Friedel–Crafts conditions. The usual problems associated with Friedel–Crafts reactions of aromatic amines were aggravated by the bifunctional acid chloride reagent and the yield in this step was expected to be low. Control of the reaction (slow addition at 0° of the acid chloride to a mixture of aluminum chloride and julolidine and reflux for 2 hours) gave the best yield with 28%. Invariably the reaction mixture contained considerable amounts of unreacted julolidine. The bright yellow, crystalline dione **16** was separated by column chromatography.

The dione could best be converted to the dithione by the reaction with  $B_2S_3$  in dry chloroform. This sluggish, heterogeneous reaction was very much accelerated by applying ultrasound. After 12 hours at room temperature and hydrolysis in ice-water, the deep red dithione was separated from a minor amount of the monothione by column chromatography and recrystallized from methylene chloride/carbon tetrachloride to give a 68% yield of long, thin, red plates with a green sheen. It was shown that the monothione as well can be converted to the dithione in a second sulfurization reaction.

With the dithione, JUL2 was synthesized by several methods. In the reaction with nickel perchlorate in acetone, JUL2 was obtained as an olive green precipitate in 48% yield. A much higher yield was obtained when the dithione was reacted with nickel chloride in ethanol in the presence of one equivalent of stannous chloride.<sup>32</sup> In this case, the green complex was isolated in 80% yield. This constituted a significant improvement over the previously published methods. Based on this success, the synthesis of the Pd and Pt analogues was also carried out. The NIR spectrum

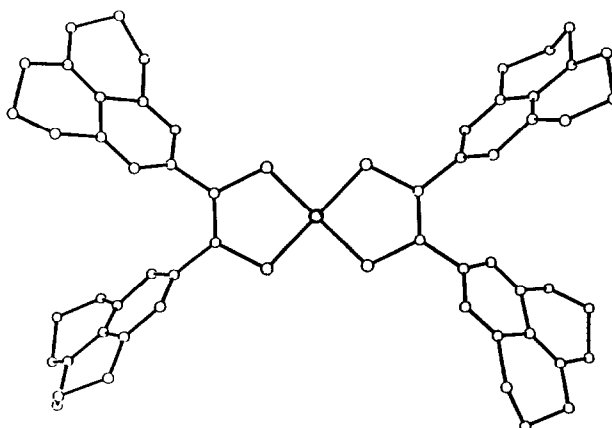


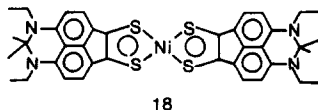
Fig. 1. The X-ray crystal structure of the JUL2 complex.

in methylene chloride for all three complexes shows a strong absorption band at  $1.27 \mu$  and hardly noticeable differences in the maximum between them.

Single crystals were grown by the interdiffusion of an acetone/ $\text{CH}_2\text{Cl}_2$  solution of the ligand with an acetone solution of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in a U-tube fitted with a glass frit during a period of over six months. The X-ray crystal structure<sup>40</sup> of the JUL2 complex shows the expected twist of the phenyl ring out of the dithiolene plane and the puckered nature of the saturated rings (Fig. 1).

### 5.3. Dithiolenes with acenaphthylene-based substituents

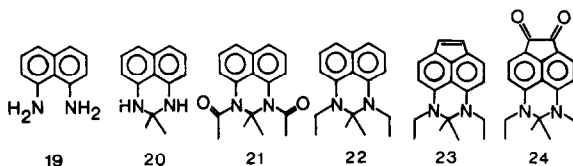
From Table 1, it can be seen that of the unsubstituted hydrocarbon ligands the acenaphthylene dithiolate had the longest wavelength absorption. We have therefore attempted many different routes to a planar and fixed bis-dialkylamino-substituted derivative of this ring system, but it appears that we underestimated the difficulties which such structures would pose. In particular, ring strain effects in the original target molecule **18** now appear to prohibit its synthesis. We have, at least for the moment, abandoned this approach. The reason will become clear from the following.



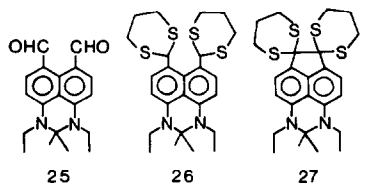
The target molecule **18** was chosen because it contains two fixed dialkylamino groups in coplanarity with the acenaphthylene system in a position *para* to the dithiolene nucleus, thus providing maximum donor effect to the complex.

Two general routes can be proposed for the synthesis of this target. The first would start from 1,8-diaminonaphthalene to construct the donor portion of the ligand and to then incorporate the acenaphthenequinone function. The second one would take acenaphthenequinone as the starting material, introduce nitrogen functions on the opposite side and build up the donor half.

Our first synthetic approach looked deceptively simple: the reaction of 1,8-diamino naphthalene **19** with acetone under acid catalysis produces the cyclic acetone-bridged system **20** (2,2-dimethyl-2,3-dihydropyrimidine). Alkylation of **20**, either directly with bromoethane or, more cleanly, via the diacetyl derivative **21** led to the diethyl derivative **22**. With **22** as starting material, several routes were explored to obtain either the substituted acenaphthylene **23** or the corresponding acenaphthene-1,2-dione **24**.



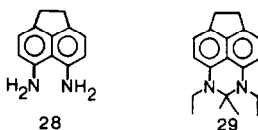
Double Vilsmeier formylation of **22** led to the 6,7-dialdehyde **25** (together with small amounts of the 4,7-isomer and traces of a 4,6,7-trialdehyde). All attempts to cyclize this dialdehyde to **23** failed, including the reaction with hydrazine in acetic acid, which works well in the synthesis of phenanthrenes (see below). The dialdehyde was next converted to its bis-dithioacetal **26**. Double deprotonation by butyl lithium and oxidative coupling of the dianion by iodine to generate the bis-dithioketal **27** of acenaphthenequinone was not successful. Only the unchanged starting material was recovered.



The attempts to achieve a double Friedel–Crafts reaction with oxalyl chloride as an alternate route to the quinone, again a reaction which works very well with phenanthrenes, failed to generate the desired product. Only the anhydride of the 6,7-dicarboxylic acid was obtained. The stepwise Friedel–Crafts acylation of **22** with Cl–CO–CO–OEt led to the 6-substituted product, but its cyclization to the desired quinone **24** failed.

The failure of all these reactions to generate the tetracyclic systems indicated that considerable ring strain could be present in the desired products, more than a simple structural formula would predict. This was even more obvious from the results of our second approach.

In this strategy, we would ideally start from acenaphthenedione. However, no good synthetic routes are known to functionalize the positions in which we are interested. A 5-nitro derivative can be easily obtained, but it would be very difficult to prepare a 5,6-dinitro compound. We thus were forced to start from acenaphthene, which can relatively easily be converted to the 5,6-dinitro-acenaphthene, reduction of which leads to the 5,6-diamino derivative **28**. Cyclization of the diamine by acetone/HCl led, just as in the case of diamionaphthalene, to the dihydropyrimidine ring system **29**.



The functionalization at the CH<sub>2</sub>–CH<sub>2</sub> bridge was where the problems started. Attempts to oxidize the bridge led to few identifiable products, but in one case, a species was isolated, in which the perimidine ring had opened; the <sup>1</sup>H-NMR spectra showed a N–H proton and an isopropyl group.

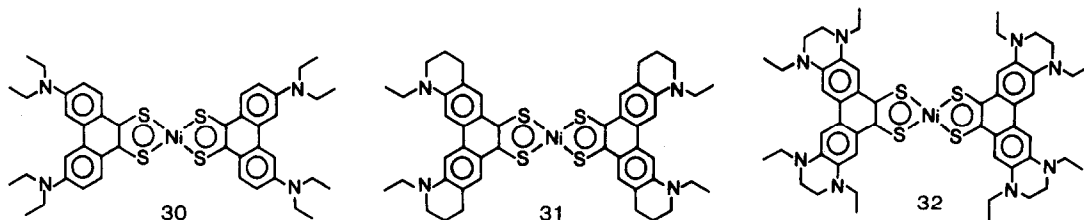
The next attempt was to abstract a hydride from the bridge and to introduce an OH group by hydrolysis of the intermediate carbenium ion. However, there was no observable reaction between the acenaphthylene bridge and triphenylcarbenium tetrafluoroborate.

The lesson from this second approach is that the conversion of the sp<sup>3</sup> hybridized bridge carbons to any form of sp<sup>2</sup> hybridized carbon(s) apparently has no driving force. This could be related to the shorter C–C bond length in the unsaturated system, which leads to an energetically unfavorable product due to increase in ring strain.

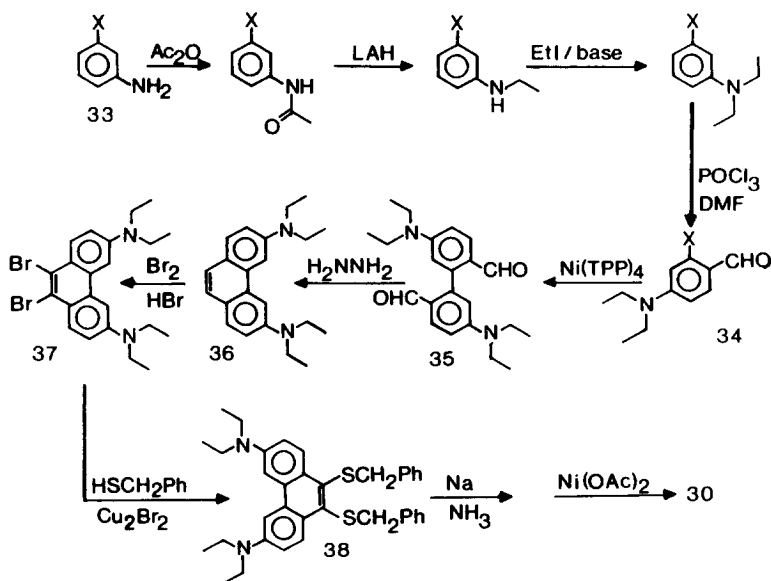
We therefore felt it to be best to abandon, at least for now, the acenaphthylene-based system and to pursue the initially second best choice, ligands using a phenanthrene ring system as the core.

#### 5.4. Dithiolenes with phenanthrene-based substituents

In the series of phenanthrene-based dithiolenes, we have investigated two main examples. Both carry two dialkylamino substituents in the 3 and 6 positions, which in the first case, the bis-3,6-diethylaminophenanthrene based system **30**, are free to rotate, while they are fixed in the second example, compound **31**, in which a saturated six-membered ring holds the substituent in conjugation with the phenanthrene rings. A further target was **32**, which is structurally related to **31** but contains four nitrogen donor groups. It is the planar analog of compound # 11 in Table 2, which showed the lowest energy absorption of all the dithiolenes in that Table.



*Synthesis of bis-(3,6-bis-diethylaminophenanthrene-9,10-dithiolato) nickel (30).* Compound **30** was synthesized following the route outlined in Scheme 4. Starting from commercially available 3-chloro-aniline **33** or the much more costly 3-bromo-aniline, acetylation and reduction by  $\text{LiAlH}_4$  produced the *n*-ethyl derivative, which was converted to *N,N*-diethyl 3-chloro-aniline either by a second acetylation and again reduction by  $\text{LiAlH}_4$  or by direct alkylation using iodoethane and diisopropyl ethylamine in acetonitrile. Its Vilsmeier formylation to **34** was followed by coupling using  $\text{Ni}(\text{TPP})_4$  in DMF to yield the biphenyl derivative **35**. The dialdehyde **35** was cyclized to the substituted phenanthrene **36** by hydrazine in acetic acid under reflux. Compound **36** was quite sensitive to oxidation, but it was nevertheless possible to brominate it in good yields by bromine in 48%  $\text{HBr}$ , yielding the 9,10-dibromo derivative **37**. Its conversion to the bis-benzylmercapto derivative **38** was achieved in standard ways using  $\text{Cu}_2\text{Br}_2$  as a catalyst and lutidine as solvent. Cleavage by sodium dissolving in  $\text{EtOH}$  or by sodium in liquid ammonia led to the dithiolate **39**, which was converted to the desired complex **30**. For some not evident reasons, the cleavage reaction gave poor yields and the resulting dithiol was very prone to polymerization. This only allowed the formation of the dithiolene in small quantities of a very hard to purify material. No full characterization was possible for these reasons.



Scheme 4. Synthesis of bis-3,6-diethylaminophenanthrene-9,10-dithiolato nickel (**30**).

The NIR spectrum of **30** in methylene chloride solution (Fig. 2) showed a strong, broad absorption centered at 1340 nm. Compared to the parent phenanthrene-substituted dithiolene (see Table 1), this peak is shifted by 0.35 eV. This is an impressive shift, but nevertheless a disappointing one in that it is only marginally larger than the one observed in going from the tetraphenyl-substituted dithiolene to its tetra-dimethylaminophenyl counterpart, where this difference is 0.32 eV.

This route to **30**, which was successful in spite of the very disappointing last step, was actually not our first choice, but it in the end became the only one. The first attempts were directed at preparing 2,7-bis-diethylamino biphenyl (tetraethyl benzidine), which then was to be subjected to a double Friedel–Crafts reaction with oxalyl chloride. No matter how the  $\text{Ni}(0)$  mediated coupling of reactions 3-chloro-*N,N*-diethylaniline or of 3-bromo-*N,N*-diethylaniline were conducted, the biphenyl derivative could be isolated only in very low yields. The major products always were the



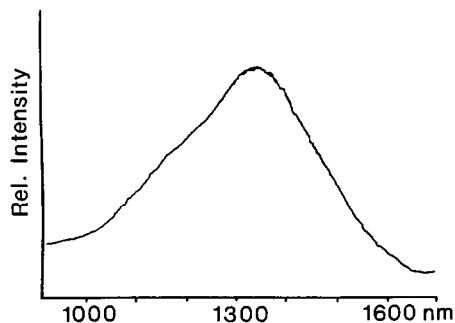


Fig. 2. Near-IR spectrum of **30** in  $\text{CH}_2\text{Cl}_2$  solution.

debrominated materials. Using the corresponding acetanilides brought some improvement in the coupling. The resulting diacetyl benzidine was then reduced to the tetraethyl derivative. It appears that the presence of a carbonyl, either an aldehyde or the N-acyl derivative, deactivates the amino function sufficiently that it will coordinate less strongly to the catalyst so that insertion into the C-halogen bond is possible. The double Friedel-Crafts reaction of the tetraethyl benzidine with oxalyl chloride to generate the phenanthrenequinone derivative unfortunately also produced major amounts of the fluorenone as a decarbonylation product. This already bad situation was made even worse when it was found that the quinone did not want to react with  $\text{B}_2\text{S}_3$  to form the dithione. The starting material was used up, but no identifiable products resulted. This approach was then abandoned in favor of the one described above.

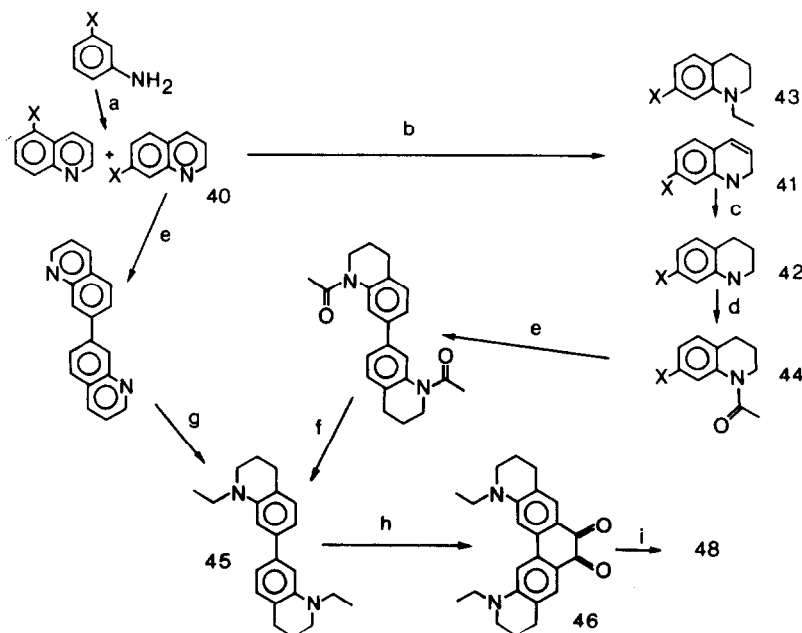
*Synthesis of bis-(1,12-diethyl-1,2,3,4;9,10,11,12-octahydro-1,12-diaza-pentaphene-6,7-dithiolato)nickel (31).* Our next goal was the synthesis of compound **31**, a fixed derivative with the same electronic structure as compounds **30**. As one might expect, the general synthetic scheme has some similarity with that outlined for **30**, but there exist notable and significant differences. The synthesis (Scheme 4) thus can be summarized as follows.

Initial attempts to substitute tetrahydroquinoline, N-acetyl-tetrahydroquinoline, or 6-formyl-tetrahydroquinoline, even when some procedures which claim *meta*-directing substitution were followed, showed that it was not possible to introduce a halogen substituent in position 7. It was thus necessary to again start from the commercially available 3-chloroaniline **33** and to introduce first the quinoline ring system following a Skraup synthesis. As expected, both possible isomers with the halogen in the 5- or 7-position were formed, but their separation was easy to achieve by fractional crystallization from  $\text{HNO}_3$  as the nitrate salts. The free base **40** was regenerated by strong alkali.

When 7-chloro-quinoline **40** was reduced by pyridine-borane in acetic acid, a mixture of three products was obtained: the partially reduced 7-chloro dihydroquinoline **41**, the completely reduced 7-chloro tetrahydroquinoline **42**, and its N-ethyl derivative **43**, which appeared to be formed by acylation under reducing conditions. The first two products were obtained as a hard to separate mixture. However, the acetylation of this mixture and reduction by sodium borohydride in the presence of Raney nickel in warm EtOH led to N-acetyl-tetrahydroquinoline **44** as the only product.

The reduction of 7-chloroquinoline was also carried out in a two-step procedure, first using DIBALH to obtain the dihydro derivative **41** and then reducing with  $\text{NaBH}_4$  or  $\text{NaBH}_3\text{CN}$  in acetic acid, which led to the N-acetyl tetrahydroquinoline **44**.

The Ni(0) mediated coupling of **43** again produced considerable amounts of dehalogenated product, and the coupled biphenyl derivative **45** was obtained only in very small yield. Much more advantageous was the coupling of the acetyl derivative **44** and subsequent reduction with LAH. This generated the benzidine derivative **45** with fixed amino groups.



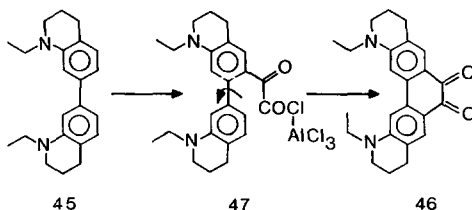
Scheme 5. Synthesis of 1,12-diethyl-1,2,3,4,9,10,11,12-octahydro-1,12-diaza-pentaphene-6,7-dithione (**48**). [X = Cl, Br; a: Skraup reaction; b:  $\text{BH}_3$ -pyridine/AcOH or DIBALH; c:  $\text{NaBH}_3\text{CN}$ ; d:  $\text{AcCl}/\text{CH}_2\text{Cl}_2$ , then  $\text{NaBH}_4$ -Raney Nickel/EtOH; e:  $\text{Ni}(\text{Ph}_3\text{P})_4/\text{DMF}$ ; f:  $\text{LiAlH}_4/\text{ether}$ ; g:  $\text{NaBH}_3\text{CN}/\text{HOAc}$ ; h:  $(\text{COCl})_2/\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ ; i:  $\text{P}_4\text{S}_{10}/\text{dioxane}$ .]

The coupling of the unreduced 7-chloroquinoline **40** was investigated as a shorter route to this compound. However, this is not a very efficient process, presumably because coordination of nickel at the quinoline nitrogen changes the course of the reaction. Unexpected by-products were isolated in substantial yield, among them 7-diphenylphosphinoquinoline, bis(7-quinolyl)phenylphosphine, and 7-phenylquinoline. Reduction of the biquinolyl by sodium cyanoborohydride in acetic acid did produce the benzidine derivative with an ethyl group already attached, but the overall reaction was less efficient than the alternate preparation via the N-acetyl tetrahydroquinoline.

This product is a strong electron donor and as such is very air sensitive. Even under nitrogen and in the dark, **45** turns deep red or black within a short while. Immediate reaction with oxalyl chloride and aluminum chloride to generate the more stable phenanthrenequinone derivative **46** was therefore indicated.

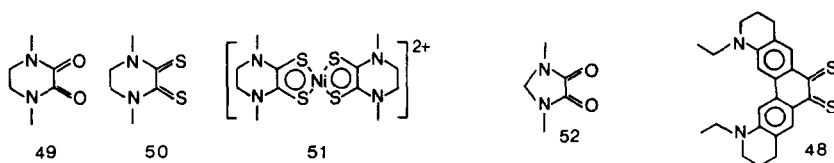
This cyclization to **46** is somewhat unusual and deserves a comment. While Friedel-Crafts reactions are well known to lead only to mono-substitution, biphenyls can undergo double Friedel-Crafts reactions because the two phenyl rings communicate only poorly due to the loss of conjugation upon twisting the rings from coplanarity. This fact together with the steric and electronic requirements in this particular case make a double Friedel-Crafts reaction with oxalyl chloride a very successful next step, leading directly to the substituted phenanthrenequinone **46**. The first attack by the oxalyl chloride-aluminum chloride complex leads to the intermediate **47**, in which the two phenyl rings must be twisted into near-orthogonality for steric reasons alone. This sets up an ideal situation for the second attack by the activated oxalyl chloride group: it is situated directly above the position in which it will substitute. The overall yield is poor (17–18%), but the fact that arylamines generally are poor and erratic substrates for Friedel-Crafts reactions lets this step appear relatively efficient. In the electronically very similar case of the tetraethyl benzidine described above,

the concomitant formation of the fluorenone derivative was observed. This may have been the result of unfavorable reaction conditions rather than a point of principle. Since that case was less interesting in view of the general goals, that reaction was not further optimized.



Sulfurization of the dione **46** to produce the dithione **48** unfortunately is quite another story. The reaction was sluggish and required drastic conditions, which resulted in considerable loss of material. This is similar to what was observed for the tetraethyl case as well.

This also merits some comment. We have observed that it is easy to convert the cyclic oxamide **49** to its dithio-analogue **50**, from which the dithiolene dication **51** was obtained. By contrast, it is not possible at all to convert the oxamide **52** to a dithione. All available methods have been tried to at least effect partial conversion, but all attempts have failed. This result contains a lesson on sulfurization of  $\alpha$ -diones—but we only have a not very specific idea what this message might be, because the detailed mechanism of thionation by  $P_4S_{10}$ , by  $B_2S_3$ , or by Lawesson's Reagent is not known. Nevertheless, this uncertainty is bothersome, but some hint may be found in the rigidity of the diones which do not want to be sulfurized as compared to the relative flexibility of those which react readily. As shown above, the julolidine analog of benzil reacts very nicely, whereas the electronically similar but rigid phenanthrenequinones do not.



For the case at hand, trial and error had to be the choice in finding a method of thionation for **46** which worked at all. Since whatever dithione was formed seemed to instantly revert to the dione on a silica plate, TLC was useless in assessing the progress of the reaction and the isolation of a dithione by column chromatography seemed without promise. Conversion of the reaction mixture to the dithiolene by addition of a nickel salt was one useful way to monitor the thionation.

The only choice to generate the dithione **48** turned out to be the reaction with  $P_4S_{10}$  in boiling dioxane. Reaction of this solution with  $NiCl_2$  in water is similar to the now superseded low-yield procedure used earlier for JUL2. It was therefore not surprising that it produced an impure dithiolene and in low yield. Attempts to recrystallize this material led to further losses. Extraction with methylene chloride and precipitation of the product from the concentrated solution by addition of methanol led to the crude complex **31**, which was filtered and washed several times with methanol. This product clearly is not analytically pure and only a qualitative Near-IR spectrum was recorded (Fig. 3). The maximum is 1380 nm in methylene chloride. It is worth noting that the Near-IR peak is much sharper than that of the electronically very similar complex **30**, in which the amino groups are free to rotate. Apparently, the fixation of the donor substituents does have the effect of narrowing the absorption band while maintaining the transition moment. The result is a more intense peak.

*Synthesis of bis-(1,4,9,12-tetraethyl-1,2,3,4;9,10,11,12-octahydro-1,4,9,12-tetraaza-pentaphene-6,7-dithiolato nickel (32).* In making this complex one of our targets, we looked at the fact that its non-planar analog (entry 11 in Table 2) was the dithiolene with the longest wavelength absorption

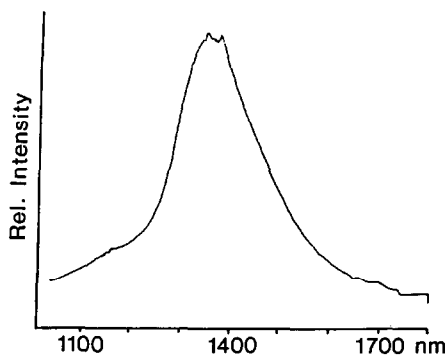
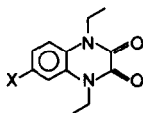


Fig. 3. Near-IR spectrum of **31** in  $\text{CH}_2\text{Cl}_2$  solution.

known so far. It was therefore surmised that the planar system would allow another substantial gain in bathochromic shift.

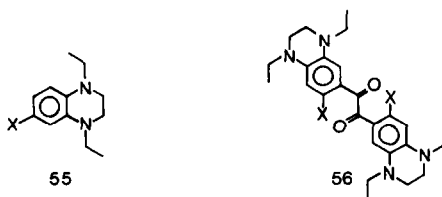
The synthesis of this complex was, by necessity, closely related to the methods used in the preparation of the dithiolenes described above. Starting from commercially available 4-chloro-1,2-phenylenediamine, double acetylation and LAH reduction led to the *N,N'*-diethyl derivative which was cyclized with oxalyl chloride in methylene chloride to give compound **53**. In a parallel route, the bromo compound **54** was obtained by bromination of 1,4-diethyl-1,2,3,4-tetrahydro-2,3-dioxo-quinoxaline (which in turn was available from 1,2-phenylenediamine by the same reaction sequence employed above for the chloro derivative) by reaction with NBS in 20%  $\text{H}_2\text{SO}_4$  at  $80^\circ$ . A side product was the 6,7-dibromo derivative, formation of which could be decreased by slow addition of NBS in small portions.



**53**: X = Cl

**54**: X = Br

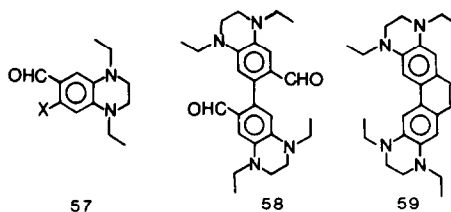
The first attempts to build up the phenanthrene system were not successful at all. The reduced 6-halo-*N,N'*-diethyl-tetrahydro-quinoxaline **55** was coupled with oxalyl chloride—aluminum chloride to the dione **56** which was then subjected to Ni(0) mediated coupling. However, the major product of this reaction was the dehalogenated tetrahydro-quinoxaline. Whereas one other case of an intramolecular coupling of a related compound has been reported<sup>41</sup> for a saturated analog, it appears that the rigidity of the system is disadvantageous for coupling in this specific case.



**55**

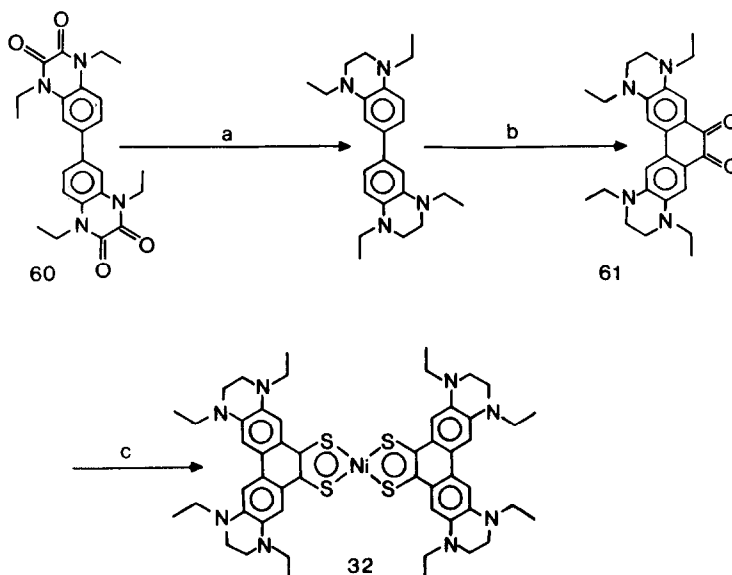
**56**

The next choice, formylation of **55** by standard Vilsmeier techniques led to the aldehyde **57**, which was successfully coupled to the biphenyl derivative **58** by  $\text{Ni}(\text{TPP})_4$  in DMF. Cyclization by hydrazine in acetic acid generated the tetra-amino substituted phenanthrene system **59**. This compound was, however, found to be so extremely sensitive to oxidation that further reactions, such as bromination to functionalize the 9,10 positions, were almost impossible to bring about. This problematic route was not pursued further.



A more successful route again proved to be the coupling of the carbonyl group containing species and their conversion to a phenanthrenequinone. Either of the two halides **53** or **54** were amenable to Ni(0) mediated coupling to the same biphenyl derivative **60**, which was then reduced by LAH and subjected to a double Friedel–Crafts reaction with oxalyl chloride and aluminum chloride in methylene chloride to yield red–black crystals of the phenanthrenequinone derivative **61**.

Thionation of this quinone with  $P_4S_{10}$  or Lawesson's reagent in refluxing dioxane and addition of aqueous nickel chloride to this solution led to the dithiolenic complex **32**.



Scheme 6. Synthesis of 1,4,9,12-tetraethyl-1,2,3,4;9,10,11,12-octahydro-1,4,9,12-tetraaza-pentaphene-6,7-dithiolato nickel (**32**) [a:  $LiAlH_4$ /ether; b:  $(COCl)_2-AlCl_3/CH_2Cl_2$ ; c:  $P_4S_{10}$ /dioxane followed by  $Ni(OAc)_2/H_2O$ .]

This dithiolenic, obtained as a microcrystalline, black powder, showed an intense absorption maximum at 1440 nm in methylene chloride solution (Fig. 4). Compared to the absorption maximum, under the same conditions, of its non-planar analog (1370 nm) the shift by 70 nm (0.044 eV) is less than what we know to occur when two phenyl groups are forced into coplanarity (going from # 3 to # 16 in Table 2, leads to  $\delta E = 0.12$  eV) and thus reinforces the caveat applied there that we can not expect a phenanthrene ring to act like two separate, but coplanar, phenyl substituents. However, this is a substantial step toward the 1.54  $\mu$  target we had set out to meet and, while we are not able to exactly correlate the magnitude of this shift to the results presented at the beginning of this article, we accept it as a bonus in our efforts to produce dyes with strong absorption at the Er laser wavelength. The broadness of the peak of **32** shows that over 80% of the maximum absorption still exists at 1.54  $\mu$ .

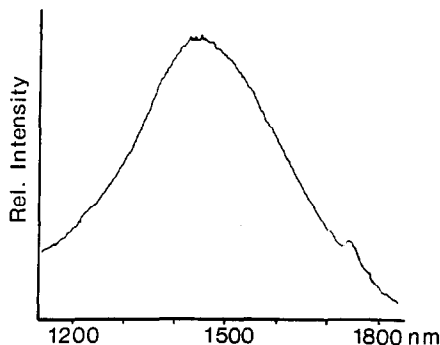


Fig. 4. Near-IR spectrum of **32** in  $\text{CH}_2\text{Cl}_2$  solution.

Unfortunately, this complex also proved to be a very unstable and apparently air sensitive compound. For example, a solution in  $\text{CH}_2\text{Cl}_2$  lost 50% of its characteristic Near-IR absorption during a few hours in a closed spectrometric cuvette.

## 6. SUMMARY AND OUTLOOK

Most of the above work was geared to the synthesis of Near-IR dyes with benzenoid ligands carrying donor substituents. This approach was chosen because we had seen that strong donor groups alone would destabilize the HOMO to such an extent that it would become non-bonding or even anti-bonding and thus produce a high degree of reactivity in the resulting dithiolenes. Whereas benzenoid aromatics extend the overall delocalized  $\pi$ -system and thus lead to the wanted bathochromic shift, they alone will not suffice to bring the absorption maximum to the desired  $1.5 \mu$  range. Coplanarity of the aromatic substituent with the dithiolenes core was recognized as an essential ingredient of the ligand structure to effect low energy transitions. Thus, the combination of coplanar  $\pi$ -systems linked to the dithiolenes core and the presence of donor substituents on the ligand was deemed to be the best compromise to generate the necessary shifts while stability was maintained.

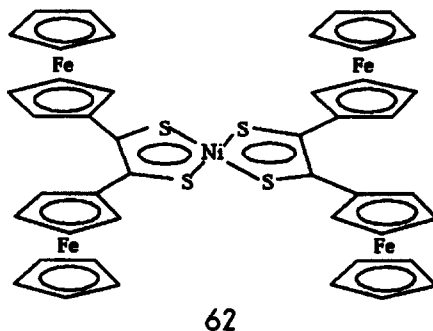
The results confirm our expectations in part. It is possible to approach the  $1.5 \mu$  range, but the stability of the dithiolenes products is not at all what we would want it to be. We attribute their high degree of reactivity to the presence of the amino functions. These donor groups certainly are conjugated to the dithiolenes as evidenced by the resulting bathochromic shifts, but they nevertheless remain susceptible to oxidation. They may therefore possess a more negative effect in adding to the reactivity than their positive effect of shifting the Near-IR transition would merit.

It thus appears that the approach of using the typical manipulation of aromatic compounds as ligand for dithiolenes has reached its limit. It is fortunate that we have arrived at this conclusion at the same time at which a new avenue has opened for further progress in this area. This new approach is based on metallocenes as the donor ligands.

While the above work on dithiolenes with benzenoid ligands was in progress, we have also begun to explore a very different approach to the synthesis of dithiolenes using donor ligands other than the ones described above. Our experience with metallocenes and metallocenophanes has led us to explore the synthesis of dithiolenes which contain organometallic ligands. Ferrocene and ruthenocene are the classical organometallics and their chemistry has been widely investigated. Ferrocene and several of its analogs are strong electron donors which can be reversibly oxidized at low potentials. They also are able to stabilize adjacent positive charges as in carbenium ions and can be used as the donor component in charge transfer complexes. Our own work has helped in under-

standing the properties of cyclic, binuclear metallocene systems<sup>42</sup> and it is this class of ferrocene and ruthenocene derivatives we eventually want to utilize as ligands in dithiolenes.

As a trial balloon, we undertook the synthesis of the tetra-ferrocenyl dithiolene **62** and were most pleasantly surprised by the results. First of all, the new complex showed an absorption maximum at 1,310 nm (0.95 eV) in CH<sub>2</sub>Cl<sub>2</sub> solution—at much lower energy than we had expected, because there exists no possibility for the ferrocenes to arrange themselves in a way that the ligands could maximize their overlap with the dithiolene core. The donor potential of the ferrocene substituents thus cannot possibly be fully utilized, and yet we see a drastic shift. Furthermore, the product appears to be perfectly stable in the solid state and in solution. Solid samples were exposed to laboratory environment for several months without any apparent change in composition or in loss of absorption at 1310 nm.



This substantiates to some degree the suspicion that donor strength (and thereby increase in the HOMO energy of the resulting dithiolene) is not the only important criterion for the stability of the dithiolenes, but that the reactivity of the amino groups in the compounds **30–32** may be the cause of their high reactivity. The metallocene-substituted dithiolene shows the electron donor effect of the metallocenes in the very large shift it produces in the Near-IR transition, but without an increase in reactivity.

These latest results appear to open up an entirely new set of possibilities. Knowing the relative donor potentials of metallocenes and metallocenophanes and adding to this what we have learned about the importance of co-planarity between substituents and the dithiolene central core, we may envision some interesting compounds to investigate.

We can now state that dithiolenes indeed have come through with almost all of what we expected of them and they represent a class of materials which are of interest beyond just a special synthesis of a dye with particular properties. Our search for dyes with still lower energy absorption maxima will continue to rely on dithiolenes as the central core.

*Acknowledgements*—This work has spanned several years during which a number of colleagues have made their valuable contributions. At the IBM Research Laboratory in San Jose, now the Almaden Research Center, Adel Nazzal has been a long term associate who demonstrated many important synthetic skills and produced many of the dithiolenes mentioned here and many other ones as well; among the postdoctoral fellows who contributed to this field, Fritz Heinrich, Arnold Alscher and Bob Lane deserve much credit for their efforts. The recent work at the University of Connecticut involved Blake Vance as a postdoctoral fellow and Dong Ihl Yoon, now a postdoctoral fellow at Berkeley, during his time as a graduate student. The synthesis of the dithiolenes **30** to **32** was possible only because of determination and skill of D. I. Yoon. Kristy Plourde has begun her thesis with new work on the metallocene-substituted dithiolenes. The financial support by the U.S. Army Center for Night Vision and Electro-Optics, especially the interest and encouragement provided by Dr. J. Pohlmann at CNVEO, has been a major asset throughout the last years.

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