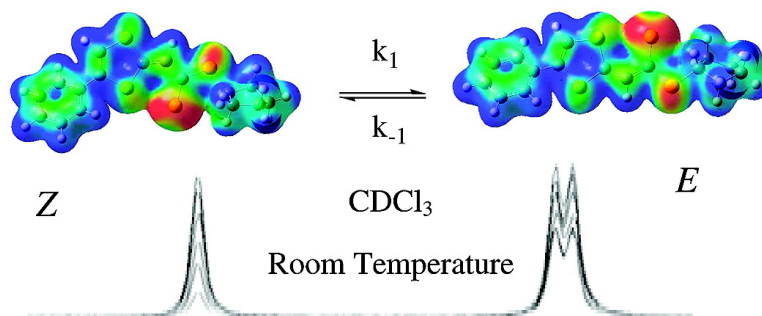


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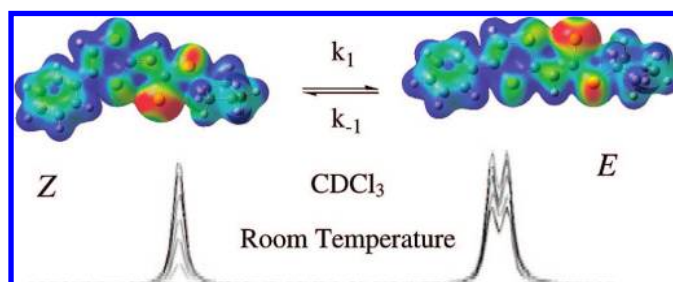
E–*Z* Isomerization and Aggregation Phenomena of Dithiafulvenes in CHCl_3

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The physical–chemical properties of several 1,3-dithiafulvene (DTF) derivatives having a donor and acceptor group in the molecule were studied. The synthesis of these compounds produces selectively the *E* isomer, but when the compound is dissolved in CHCl_3 isomerization to the *Z* isomer takes place with a rate that depends on the substituents. The interconversion rate is slow on the NMR time scale; therefore, two separated signals are observed, and they are used to measure the rate constant of isomerization. The equilibrium constant is, in all cases, very close to 1, and this is coincident with the fact that theoretical calculations of the energy of the two isomers in the gas phase differ by less than 0.1 kcal/mol. The isomerization reaction is completely reversible, and the *E* isomer can be obtained in pure form by selective crystallization. The derivatives with thioalkyl groups have a strong tendency to aggregate in CDCl_3 . The formation of the aggregates is evidenced from the changes in 1D ^1H NMR and DOSY spectra as a function of concentration. The compounds are highly delocalized, and this is reflected by the low activation energy for the isomerization.

Introduction

Smart materials are in demand for applications ranging from the development of electronic devices¹ to drug delivery.² By definition, smart materials respond in a qualitatively different way to different stimuli; nonlinearity is the qualifying property for functional behavior. Delocalized electrons are an obvious source of nonlinearity, and materials based on π -conjugated molecules or polymers combine promising properties with the flexibility of organic synthesis. Materials made up of large π -conjugated molecules are of interest for nonlinear optics (NLO) applications (NLO-phores). Nonlinear functional behavior is, in these materials, a consequence of the large electronic delocalization within each NLO-phore, related to the presence of a large π -conjugated backbone.³

The dithiafulvene unit (1,3-dithiole-2-ylidene group) is a good electron donor currently used in the design and synthesis of new organic materials, especially in the search for extended tetrathiafulvalene derivatives.^{4,5} The design of hybrid extended tetrathiafulvalene oligomers, in which a conjugated *p*-quinodimethane⁶ or vinylogous⁷ spacer separates two or more dithiafulvene units or incorporates some metal–dithiolate fused units,⁸ is an emerging and important area of investigation with exciting prospects which has already afforded materials with a large variety of electronic properties and structural flexibility

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for specific applications.^{4,8b} The dithiafulvene unit is also found as part of push–pull donor–acceptor dyads and cruciforms with unprecedented nonlinear optical and redox-controlled characteristics.⁹ The NLO properties of these materials are derived from the electronic delocalization through and extended conjugation in a molecule containing strong donor and acceptor groups. The electrostatic interactions between the different chromophores affect the properties of the material resulting in effects that are cooperative or nonadditive. Another important factor is the interaction of the molecule with the solvent since hyperpolarizable material like the NLO-phores rearranges their electronic distribution in response to the local environment and the NLO properties can be magnified or eliminated. Several groups have initiated programs to engineer functional materials for electronic devices by proper control of the packing of π -conjugated molecules by noncovalent interactions.^{10,11}

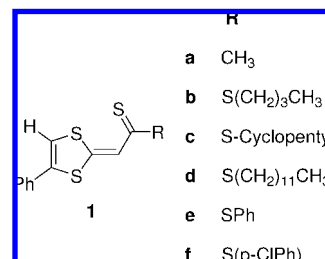
Self-assembly of organic π -conjugated systems in solution can be widely utilized to construct unique, complex supramolecular structures.¹² Thus, π -conjugated molecules with either electron-withdrawing groups or large π -circles and disks self-aggregate in solution by π - π stacking interactions and solvophobic effects.¹³ On the other hand, solid-state and surface organization of π -conjugated molecules is frequently applied to molecular electronics.¹⁴ To control one-, two-, or three-dimensional arrangement of the molecule in the solid state, preaggregation of conjugated π -systems plays an important part.

Recently, tetrathiafulvalene-containing (TTF) oligomers, polymers, and dendrimers have been synthesized to investigate redox-active supramolecular structures.¹⁵ In particular, conjugated TTF oligomers are regarded as candidates for building blocks of supramolecular systems because of their unique electronic properties at neutral, radical cationic, and polycationic

states.¹⁶ Vapor pressure osmometric (VPO) measurements of 1,3,5-tris(tetrathiafulvalenylethynyl) benzene derivatives in chloroform revealed that they self-associate to form higher aggregates than dimers.^{17,18}

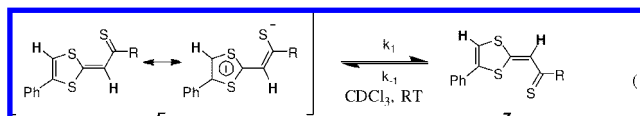
Highly dipolar molecules are excellent candidates on which to base the design of organic electro-optic materials/devices.¹⁹

We have synthesized a series of 1,3-dithiafulvenes (DTF) **1a–f**,²⁰ which have a donor and acceptor group in the same molecule and a high sulfur content. They are promising as candidates for nonlinear optic materials (NLO-phores).²¹ It was reported that there is a close relationship between the structure of the materials and their capacity to produce phenomena of NLO as monomer, aggregates, or solid material. We report here that compounds **1a–f** dissolved in CHCl_3 isomerize at room temperature to an equilibrium mixture of the *E* and *Z* isomers in a process that is fully reversible and also that the compounds form aggregates in the same solvent.



Results and Discussion

General Features. The DTF compounds were obtained according to the published²⁰ methodology through the asynchronous cycloaddition [3 + 2] between 3*H*-1,2-dithiol-3-thione and alkynyl Fischer carbene complexes. The metal-free DTF derivatives were obtained by treating the sample with neutral alumina. Most of the compounds are orange and stable crystalline solids when exposed to normal laboratory conditions. They are very soluble in ether, acetone, chloroform, ethyl acetate, dichloromethane, and dioxane but are sparingly soluble in water and acetonitrile. They have two isomers, the *E* and *Z* (eq 1), but the *E* isomer crystallizes selectively from hexane/dichloromethane mixture (70/30).



When the *E* isomer is dissolved in CHCl_3 or CDCl_3 , it spontaneously isomerizes at room temperature to the *Z* isomer to reach an equilibrium mixture of approximately 1:1 content of each one (see below).

Since the isomerization rate is slow on the time scale of the NMR, i.e., the $\Delta\delta$ is larger than the rate of the isomerization reaction, the two isomers gave separated signals (Figure 1).

The vinylic hydrogen of the *E* isomer presents a long-range coupling ($J = 1.25$ Hz for **1b**, R = butylthio) with the hydrogen of the heterocyclic ring, which is not present in the *Z* isomer. This coupling was corroborated by homonuclear proton-decoupling experiments. The observation of this long-range coupling gave information about the electronic structure of the molecule since spin–spin interactions through more than three bonds can take place only when there is a certain disposition of the bonds and nucleus. It is known that this long-range coupling (five

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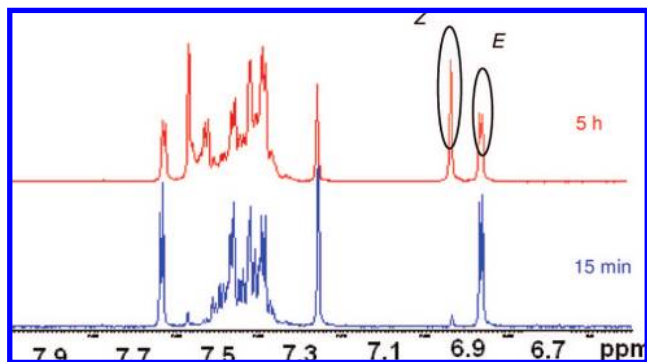


FIGURE 1. Aromatic region of the ^1H NMR spectrum of compound **1b** in CDCl_3 .

bonds) is maximal when there is a zigzag type of configuration among the bonding atoms.²² The planar structure of the compounds was demonstrated by X-ray analysis of the single-crystal structures of DTF **1a** and **1c**, which show the planar structure of the molecule consistent with an important electronic delocalization.²⁰ The eclipsed configuration of the exocyclic S and the S(1) atom of the dithiole ring may suggest a binding interaction like that existing in trithiapentalenes derivatives.²³ In fact, the distance between the two sulfur atoms of ~ 2.95 Å is well below the van der Waals distance (3.7 Å),²⁴ consistent with the presence of some type of weak interaction between the two sulfur atoms.

It is important to remark that the isomerization process is totally reversible since from the mixture of *E*–*Z* isomers after equilibration, the *E* isomer can be recovered completely pure with controlled evaporation of the solvent in the case of the alkylthio derivatives **1b**–**d**. For the compounds with *R* = methyl or arylthio (**1a**, **1e**, and **1f**), the recrystallization of the pure *E* isomer requires more specific conditions (see the Experimental Section). The reversibility of the process has great significance considering its importance in microscopic processes as mentioned in the Introduction.

Self-Aggregation. When we set out to measure the kinetics of the isomerization process, we found that the concentration vs time curves did not show the clean monoexponential behavior expected for a first-order process.²⁵ In addition, the data obtained

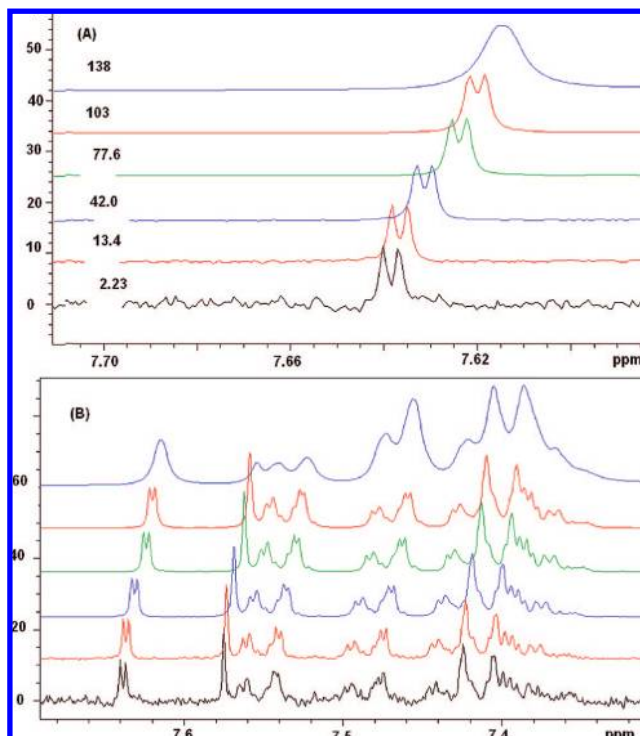


FIGURE 2. ^1H NMR spectrum of **1d** in CDCl_3 at different concentrations as indicated in spectrum (A) (in mM). Heterocyclic hydrogen of the *E* isomer (A); aromatic region (B).

with **1b** at different temperatures (27, 32, and 37 °C) gave an estimated activation energy of 30–40 kcal/mol that was completely inconsistent with the fact that the isomerization process takes place at room temperature in a period of time of approximately 240 min.

In order to determine whether the compounds might be aggregated in solution, we perform ^1H NMR spectra of solutions of **1d** (*R* = dodecylthio) at different concentrations within 2.23 and 138 mM. As can be seen in Figure 2, there is a noticeable change in the spectrum with concentration. In the aromatic region, there is a significant signal broadening and a slight shift of the signal to higher field. In addition, the heterocyclic hydrogen also broadens and moves from 7.64 to 7.61 ppm as the concentration increases from 2.25 to 138 mM. It is known that in systems where monomer and aggregates exchange at a high rate on the NMR time scale, the two signals coalesce into one broad signal.^{26–28}

The observed NMR signal in a system containing monomer and aggregates can be expressed by eq 2,²⁶ where δ_{obs} , δ_{mon} , and δ_{agg} are the observed chemical shift, the value corresponding to the monomer, and the value corresponding to the compound aggregated, respectively. c_T is the total concentration of the compound and c_{mon} the monomer concentration.

$$\delta_{\text{obs}} = (c_{\text{mon}}/c_T)(\delta_{\text{mon}} - \delta_{\text{agg}}) + \delta_{\text{agg}} \quad (2)$$

The observed value of δ was plotted vs the reciprocal of the concentration (Figure 3), and from this plot we can conclude that the compound is aggregated at concentrations higher than 13 mM.

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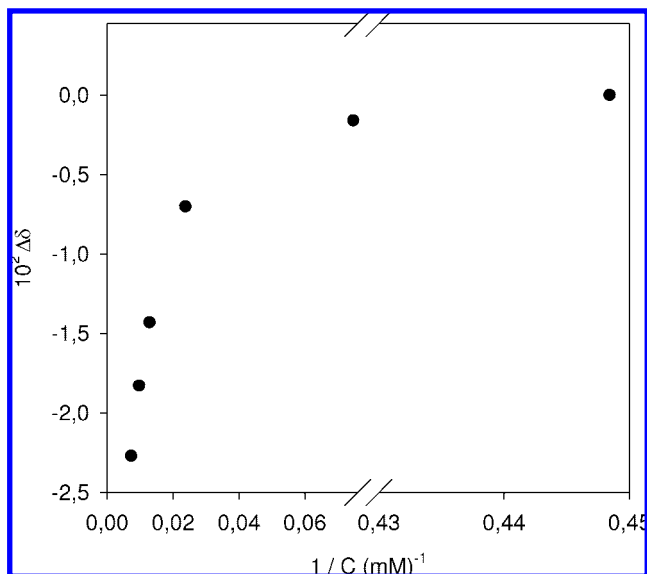


FIGURE 3. Plot of the observed $\Delta\delta$ for the heterocyclic hydrogen of **1d** vs the reciprocal of the concentration.

We also determined the UV-vis spectra of **1f** and **1d** at different concentrations, $(3.49\text{--}11.6) \times 10^{-5}$ M for **1f** and $(0.73\text{--}75) \times 10^{-5}$ M for **1d**, and we found that the shape of the spectra do not change with the concentration and that they follow the Lambert-Beer law; therefore, at those concentrations they are most likely in the monomeric form.

To confirm the presence of aggregates, 2D NMR experiments and DOSY (diffusion-ordered spectroscopy) were carried out. In these experiments, ^1H chemical shifts are correlated with the diffusion coefficient of the different species present in solution. The diffusional behavior is proportional to the individual properties of the molecules such as size, shape, mass, and charge as well as temperature and solvent. These experiments show that when a solid *E* isomer is added to CDCl_3 , different types of species are formed and they change with time as can be seen in Figure S1, Supporting Information.

We carried out DOSY experiments with derivatives with $\text{R} = \text{cyclopentylthio}$, methyl, and *p*-chlorophenylthio under two dissolution conditions: (a) the solid compound was placed in the NMR tube, the solvent was added, and the spectrum was taken at different times; (b) the compound was dissolved at 15°C , and after 30 min when we considered all the sample to be in solution, 0.1 mL of this solution was added to 0.5 mL of CDCl_3 .²⁹ The DOSY spectra (see Figures S2 and S3 in the Supporting Information) show that under conditions (a) all the derivatives except **1a** form aggregates during the process of dissolution; in addition, the *Z* isomer is also aggregated in the case of the dodecylthio derivative **1d**. On the other hand, the DOSY spectra under condition (b) show a uniform distribution of only one type of species for all the compounds.

From the DOSY experiments, we calculated the approximate hydrodynamic radius of all the compounds related to **1a**. The values obtained are summarized in Table 1.

It is interesting to note that the ratios for **1e** and **1c** are remarkably similar to the theoretical values, whereas the calculated hydrodynamic radius of compound **1d** is significantly larger than that of **1a**.

Equilibrium Constants and Molecular Interactions. Based on the relative areas of the signal corresponding to the *E* and *Z* isomers in the equilibrium mixture, the equilibrium constant

TABLE 1. Ratio of Hydrodynamic Radii Obtained from DOSY Experiments and Calculated Theoretically

compd	DOSY	theoretical ^a
$(r_{1c})/(r_{1a})$	1.096	0.998
$(r_{1e})/(r_{1a})$	1.122	1.116
$(r_{1d})/(r_{1a})$	3.437	1.118

^a Calculated using B3LYP with 6-31+G* basis set.

TABLE 2. Rate and Equilibrium Constants for the *E-Z* Isomerization of **1a-f**^a

derivative (R) (concn, mM)	K_{eq}	ΔE^b (kcal/mol)	$k_{\text{obs}},^c 10^{-3} \text{ s}^{-1}$
1a (methyl) (28.0)	1.136	0.13	5.9 ± 0.3
1b (butylthio) (18.5)	1.051	nc ^d	0.098 ± 0.001
1c (cyclopentylthio) (2.5)	1.047	0.08	0.098 ± 0.003
1d (dodecylthio) (6.9)	1.059	nc ^d	0.063 ± 0.002
1e (phenylthio) (9.7)	1.041	0.07	2.03 ± 0.07
1f (<i>p</i> -Cl-Phenylthio) (9.7)	1.075	-0.06	3.0 ± 0.6

^a Temperature: 300 K, solvent: CDCl_3 . ^b Energy difference of isomers *E-Z* calculated theoretically as indicated in the Experimental Section. ^c Determined by ^1H NMR. ^d Not calculated.

was calculated and the values are summarized in Table 2. It can be seen that for all the derivatives the value is very close to 1. The isomerization takes place also in other solvents such as dioxane and $\text{CHCl}_3/\text{CCl}_4$ 85/15 mixtures and the equilibrium concentration is in all cases about 1.

We calculate the energy of both isomers using the density functional theory (DFT) B3LYP with 6-31+G* basis set, contained in the Gaussian 03 package. These values are collected in Table 2.

It can be seen that the difference in energy of both isomers is very small ($\Delta E < 0.1$ kcal/mol), consistent with the equilibrium constant that approaches 1. Although the calculations have been done in the gaseous state, the fact that there were not significant changes in the equilibrium constants measured in different solvents (see above) may indicate that the solvent affects both isomers in a similar way. It is interesting to note that the methyl derivative is the one that has a higher energy difference coincident with the higher value of the equilibrium constant.

As mentioned above, all of the compounds crystallized selectively as the *E* isomer, although in solution and in the gas phase both isomers have about the same energy; therefore, the selective crystallization must be attributed to specific interactions in the crystal. In order to identify the interactions present in the crystal, we analyzed the X-ray structure of the compounds.³⁰ Looking at the unit cell for the derivative with $\text{R} = \text{cyclopentylthio}$, we can see that the distance C-H...S between the thiocarbonyl sulfur and the vinylic hydrogen is quite short (2.9 Å) and it may indicate a hydrogen bond between these two groups. It is known that in many systems there are hydrogen bonds of the type C-H...X.³¹ The probability of the existence of such hydrogen bonds depends mainly on three factors: (i) the hydrogen bond donor ability of the donor, (ii) the hydrogen bond acceptor ability of the electronegative atom, and (iii) the stereochemistry of the crystalline structure. In the structure of

(29) Although some isomerization takes place during this time at 15°C , the reaction is still far from the equilibrium and the rate of conversion can be measured.

(30) This X-ray structure is published in ref 20.

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1e, the alkyl chain (cyclopentyl in this case) is oriented toward the internal face of the unit cell; therefore, van der Waals interactions are also possible. There exist no face-to-face π - π stacking nor edge-to-face interactions such as aromatic C-H \cdots π -hydrogen bonding as was observed in the crystal structure of other systems.³²

It is important to note that in the derivative **1a**, where R = methyl, we do not see the van der Waals interactions as in **1c**. The differences found in the crystals are consistent with the different behavior of the two types of compounds in the process of selective recrystallization and in the aggregation behavior in CDCl₃ solution as well.

Isomerization Kinetics. The UV spectra of most of the *E* and *Z* isomers are not different enough to allow rate determination by this technique, and only in a few cases could we do the measurement in this way. The rate constants measured for **1a** (0.049 mM), **1b** (0.076 mM), and **1c** (0.052 mM) using the change in UV-vis absorption with time were 3.8, 3.8, and $0.4 \times 10^{-3} \text{ s}^{-1}$, respectively. Comparing these values with those shown in Table 2, we see that there are important differences with the values obtained by the two techniques. Part of the difference may be attributed to the fact that the maximum change in the absorbance was very small (at most 0.025) and to the possible temperature difference between the NMR probe and the UV-vis experiments. However, these two reasons cannot justify a factor of 40 and 4 in the case of derivatives **1b** and **1c**, respectively; we believe that the differences arise from the fact that the concentrations used were very different and consequently the aggregation state is also different under the experimental conditions. It is well-known that the rate of reactions decreases when the reactants are aggregated.³³ The concentrations used for the UV-vis experiments are significantly lower than those used for the NMR experiments (see Table 2).

Since the isomerization of DTF might be acid catalyzed by traces of acid present as impurity in the chloroform,³⁴ we performed an experiment using CDCl₃ previously treated with basic alumina and another in a solution containing acetic acid 0.0087 M. There were no significant differences in the rates measured under these two conditions.

The rate of isomerization was determined by ¹H NMR by measuring the changes in area of the signals corresponding to the vinylic proton of the *E* and *Z* isomers with time (Figure 4 is representative).

The change in the relative integrated value of the signals follows a first-order behavior (Figure 4 A) from which the observed rate constant was calculated.³⁵ The observed rate constant for the equilibration reaction is given by eq 3, and considering that the equilibrium constant is ~ 1 , $k_1 = k_{-1}$:

$$k_{\text{obs}} = k_1 + k_{-1} = 2k_1 \quad (3)$$

The values of k_{obs} for derivatives **1a-f** are collected in Table 2, where it can be seen that the isomerization rate constant of

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(35) In order to have good pseudo-first-order plots, the solutions must be prepared as indicated in the Experimental Section. When we attempted to measure the rate from a solution prepared by adding the solvent on the crystals of the compounds, the first-order behavior was followed only in the last portion of the curve.

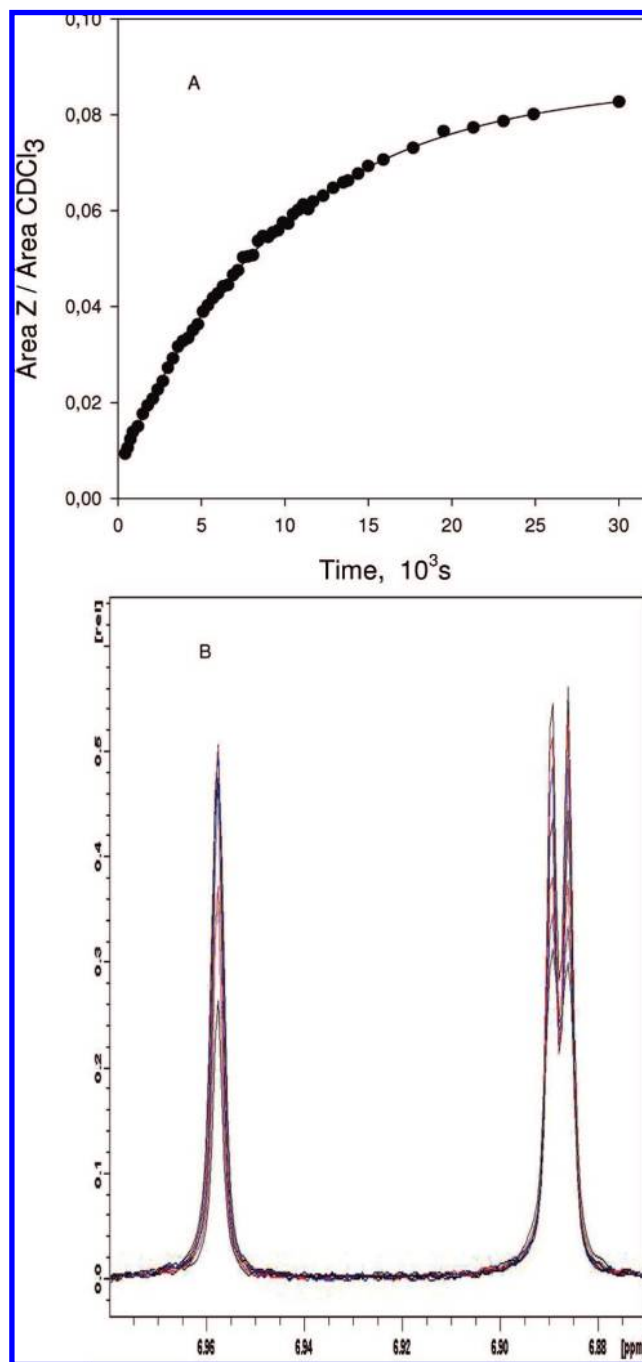


FIGURE 4. Change in relative intensities of the vinylic protons of the *E* and *Z* isomer for **1b** at 300 K. The line in A was calculated with $y = y_0 + a(1 - e^{-bt})$ using $y_0 = 5.87 \times 10^{-3}$, $a = 8.06 \times 10^{-2}$, and $b = 1.2 \times 10^{-4}$.

the arylthio and methyl derivatives is 20–60 times faster than that corresponding to the alkylthio derivatives. These differences are probably due to the fact that compounds **1a**, **1e**, and **1f** are less aggregated than **1b**, **1c**, and **1d**. In addition, the value of the rate constant for **1a** > **1e** is in agreement with the calculated bond orders in the derivatives.

For derivative **1b** (R = butylthio), the rate was determined at several temperatures (27, 32, 37, and 42 °C), and from these data we calculated an approximate activation energy for the isomerization of 12.7 kcal/mol.³⁶ This value is similar to the observed energy in systems having push-pull groups or captodative ethylenes that isomerize at room temperature.³⁷

From the data at different temperatures we calculate the equilibrium value which is ~ 1 at all temperatures indicating a ΔH° close to zero consistent with the theoretical calculated values (Table 2).

Conclusions

We have determined that the DFT **1b–f** have a tendency to form aggregates in an organic solvent such as chloroform and that the interactions are stronger for the *E* isomer than for the *Z* isomer; this allows the selective crystallization of the *E* isomer. The compounds isomerize at room temperature in a reversible way. The phenomenon might be of interest for the use of this type of compounds as molecular switches. The fact that the dithiafulvenes are highly polarized and are rich in sulfur might be useful to coordinate Au or Ag nanoparticles and for future uses. Molecules that can be bonded to metal nanoparticles are very important in the field of molecular motors.³⁸

Experimental Section

The synthesis of compounds **1** was carried out as reported previously,²⁰ and the pure *E* isomer was obtained as indicated below.

Compounds **1b–d** were dissolved in hexane/dichloromethane mixtures (70:30) and placed in a small vial closed with a septum that has a small capillary tube to allow the slow evaporation of the solvent at room temperature. In order to selectively crystallize compounds **1a**, **1e**, and **1f** dissolved in the same solvent, the solution was placed in a refrigerator at -20°C where the solvent evaporate more slowly, besides the capillary tube used was of smaller diameter. Compound **1d** is obtained as a powder and all the others as crystals.

All NMR spectra were recorded in a 400 MHz instrument equipped with a variable temperature unit. A 5 mm probehead with Z-axis gradient coil was used. CDCl₃ and CHCl₃ were commercial samples stabilized with laminated Ag. TMS was employed as internal standard, and Topspin 2.0 software was used to process the spectra.

(36) It is important to keep in mind that under the conditions of the rate measurements **1b** is aggregated; therefore, the calculated activation parameters have contributions from the thermodynamics of the association process.

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The DOSY experiments were carried out at 300 K with maximum gradient strength 0.055 T/mA. Bipolar spoil gradients were used with total duration of 2–5 ms. Gradient recovery delays were 0.1–1 ms and diffusion times were within 20 and 60 ms. The gradient field was linearly increased in 32 steps resulting in an attenuation of ¹H NMR of 95%.

Kinetic Procedures. The pure *E* isomer of compounds **1** was dissolved in CDCl₃ at 15 °C and after 30 min 0.1 mL of this solution was added to 0.5 mL of CDCl₃ contained in the NMR tube that was at the temperature of the experiment in a constant temperature bath. The tube was then placed in the NMR probe controlling the temperature with the variable temperature unit (VTU) of the instrument. The ratio of the areas of the vinylic proton of the *Z* isomer and the residual signal of the CHCl₃ at different times was processed with the *multi_integ3* software incorporated in the Topspin 2.0 of Bruker Biospin. The measuring frequency was 400.16 MHz (¹H).

Computational Methods. They were done using the software contained in the Gaussian 03 package.³⁹ The geometry optimization was done using the functional density method (DFT) with a functional hybrid B3LYP and 6-31+G* basis set.

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Supporting Information Available: NMR and DOSY spectra of compound **1** and calculated values of dipolar moments and bond orders. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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