Diarylethenes with Electroactive Substituents: A Theoretical Study to Understand the Effect on the IR Spectrum and a Simple Way to Read Optical Memory in the Mid-IR

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Diarylethenes bearing electro-donating and electro-withdrawing substituents in the 5,5′-positions of the thiophene unit were studied theoretically (DFT, B3LYP) to understand the effect of the substituents on the infrared spectrum in the two stable forms. The photochromic molecule with the electro-donating substituent showed the largest difference in the infrared (IR) spectrum due to the push−pull−push structure. It was chosen to build a memory film with a readout process in the mid-IR. Information written on the photochromic film was read using a setup based on an infrared camera (multibolometer) and a filtered broadband Globar source. The results showed that the readout process worked without matching any specific absorption band. A good contrast was obtained also with a single camera frame (45 ms).

1. Introduction

Because society continues to require better tools to communicate more data at higher rates, optical memories which allow the storage of larger amounts of information are one of the most desired targets for computing technology. Magnetic memory, which is the most stable and versatile method to store information, has substantially reached its limit of capacity. Overtaking this limit implies increasing the size of the system. In the recent past, compact disks (CDs) have revolutionized data storage technology. But this heat mode type of memory lacks molecular resolution and the possibility of erasing single information. Furthermore, the temperature threshold limits the writing speed. Because memories that are characterized by the storage of large amounts of data and versatility of writing and deleting information are in great demand, photon mode recording could be the way of the future.

Switching between the two forms of a photochromic material can be exploited for the design and construction of versatile and innovative devices for molecular electronics, such as optical memories. For such systems, photochromic materials need to fulfill the following fundamental requirements: thermal irreversibility, good conversion, and fatigue resistance. In the last fifteen years the guidelines for obtaining photochromic materials with such properties have been drawn by the group of Irie,[1] and more recently, by some other groups;[2] the family of the 1,2-diarylethenes and particularly 1,2-dithienylperfluorocyclopentenes have gained much attention by these groups.

The most difficult step of a photochromic memory is the readout process, which must preserve the written information. A partial loss of information inevitably accompanies the readout process when it is performed with a laser beam in the visible range. Different approaches have been proposed to solve this problem, such as the use of gated photochromism,[3] photocurrent detection,[4] or using photochromic molecules with very low ring-opening quantum yield read with low power laser. As an alternative, a mid-infrared readout method was initially proposed by Seibold et al.[5] and by Stellacci et al.[6] for fulgides and diarylethenes, respectively. This approach has attracted great interest due to the real feasibility. The basic concept is that IR photons can be used to read the information stored without causing any molecular rearrangement because of their low energy. Irie et al. developed this idea by monitoring an image written with visible light onto a Zeonex film containing 1,2-bis(2-methyl-6-phenyl-1-benzothiophen-3-yl)perfluorocyclopentene using IR light at 1590 cm^{-1} (with a Perkin-Elmer Spectrum Spotlight 300).[7,8]

The aim of this work is to demonstrate the capability of reading, in a nondestructive way, the memory information using a simple setup based on a broadband source and a room-temperature detector (multibolometer). The broadband source is used instead of a monochromatic source matching

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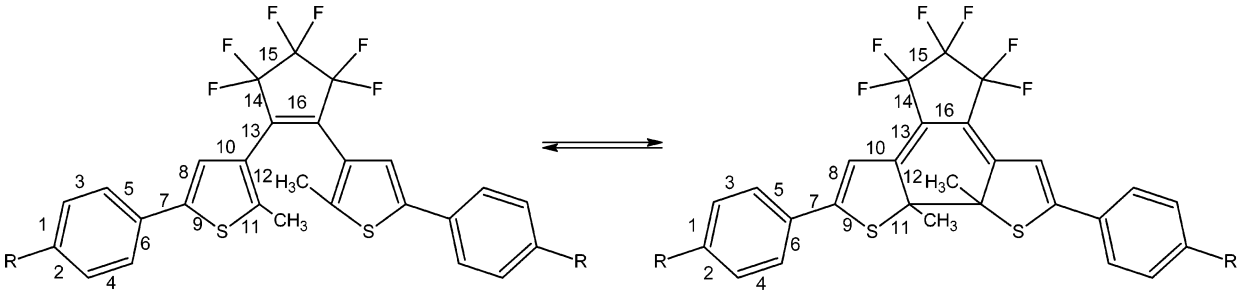

Figure 1. Molecular structure of the open and closed form of the basic diarylethene studied in this work.

the sharp IR band characteristic of one of the two photochromic isomers. The readout method proposed is based on the measurement of the difference of the infrared bands between the two forms in the whole spectral range between 1300 and 2000 cm^{-1}. Due to the simplicity of the setup and the possibility to be used with different photochromic systems, such method can be easily transferred to technology.

A thorough understanding of the molecular design is necessary to maximize the difference in the infrared intensity between the two isomers. Specifically, it becomes essential to understand the role of the substituents on the basic diarylethenes structure on the modulation of the infrared intensity of some particular bands. Valuable information can be gained using ab initio calculations. For this study, we chose to use DFT calculations with B3LYP functional and 6-31G**. This basis set with polarization functions permits a good description of the conjugated π electrons, which provide peculiar electronic and vibrational properties to the molecules.[9,10] The geometry optimization and the vibrational properties (i.e., IR spectrum and normal modes) were computed for the molecules in the two different photochromic structures. The information derived from the calculations is more abundant than that available from the experiment, where only the spectrum (frequency and intensity) is obtained.

The calculations were performed with the Gaussian 98[11] software on the HP SuperDome64000 at the Consorzio Interuniversitario Lombardo per la Elaborazione Automatica (CILEA).

The basic structures of the diarylethenes studied in the open and closed form are reported in Figure 1. The specific molecules being investigated are shown in Figure 2. They have the same core structure (diarylethene) but different side groups (R) in the para position of the benzene ring:

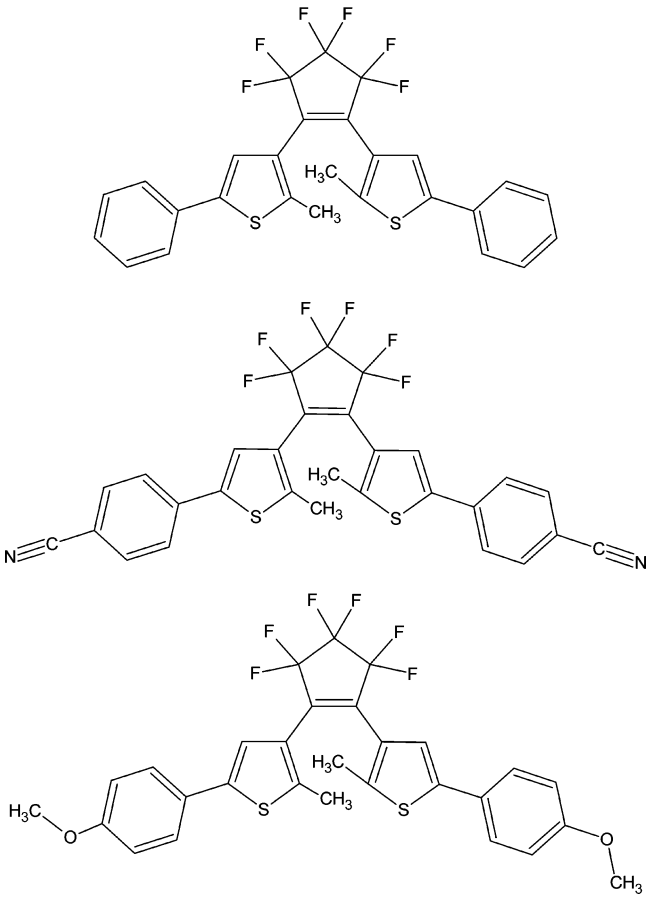

Figure 2. Molecular structure of the studied molecules: from top to bottom, daeph, daecn, and daeome.

Table 1. Dihedral Angles (degrees) between the Phenyl Ring and Thiophene Ring

daeome			daecn			daeph		
open	closed	Δ	open	closed	Δ	open	closed	Δ
27.26	16.06	11.2	23.35	18.78	4.58	26.61	20.03	6.58
26.47	15.69	10.78	22.91	18.02	4.89	26.36	19.36	7.00

−H (daeph), a donor −O−CH_3 group (daeome), a withdrawing −CN group (daecn).

2. Theoretical Calculations

The first step of the calculation was the geometry optimization. It was carried out without symmetry constraints. We paid particular attention to the torsional angle between the thiophene ring and the benzene ring, since it is an important parameter to understand the conjugation along the molecule.

The values are reported in Table 1, both for the open and the closed forms. As expected, the torsional angle is larger

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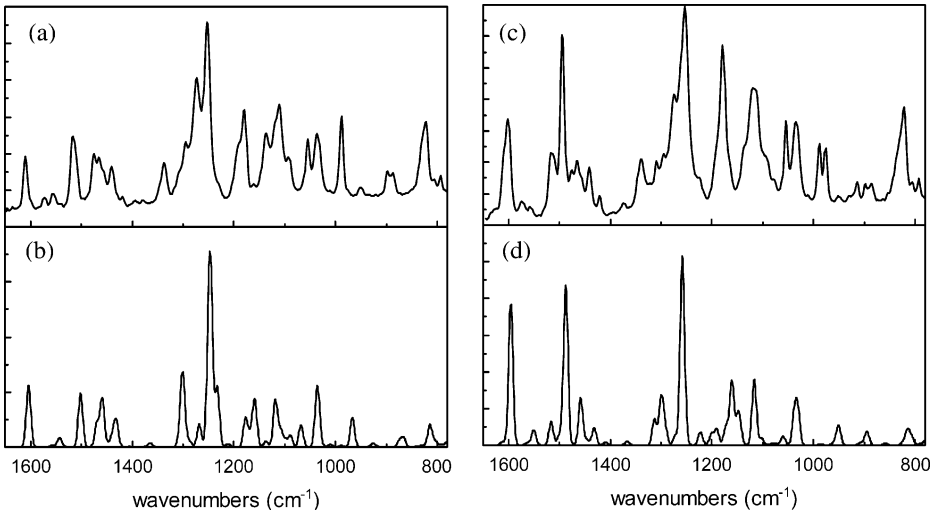

Figure 3. IR spectra of daeome between 1650 and 780 cm^{-1}: (a) open form, experimental, (b) open form, calculated, (c) closed form, experimental, (d) closed form, calculated. The calculated spectra are shifted in frequencies by a factor of 0.96.

in the open form, thus showing that the steric effect between the hydrogen atoms of the thiophene and the phenyl ring is predominant on the conjugation of the π electrons between the two rings. In the closed form, on the other hand, the angle decreases noticeably because, in this case, the conjugation extends along the whole molecule and becomes competitive with the steric hindrance. Comparing the three molecules, daeome has the largest change in angle and the value in the closed form is the smallest, thus indicating that the methoxy group favors the electronic delocalization. Consequently, we expect an enhancement of the properties that depend on it.

The next step was the calculation of the infrared spectrum and the analysis of the normal modes. The comparison between the calculated and experimental spectra for the daeome molecule is shown in Figure 3. A difference that must be taken into account between the theoretical calculation and the experimental results is that, in the latter, a mixture of open and closed form is always present in the spectra (due to the incomplete conversion between the two isomers). Even so, the main features both in the open and in the closed forms are well described, showing the reliability of the computational model used.

Changes in the spectrum between the two forms are clearly found in various spectral ranges. We will focus our attention in the 1500−1600 cm^{-1} range where greatest differences occur.

The calculated infrared spectra of the open form for the three molecules are shown in Figure 4 with the same intensity scale. The spectra are very similar especially in the region 900−1250 cm^{-1} (both for band positions and intensity). In this region, the normal modes involved are the in-plane and out-of-plane bendings that are generally not affected by the different side group. A large difference appears near 1300 cm^{-1}: here not only does the C−C stretching (of the perflourocyclopentene) take place but also the stretching of C−O (which is strong). It follows that in the daeome, an overlap of the bands due to the two modes takes place, thus complicating the issue. In the other two molecules, there are only the C−C stretchings and the intensity turns to be very similar. The region of CC (double bonds) stretching, between

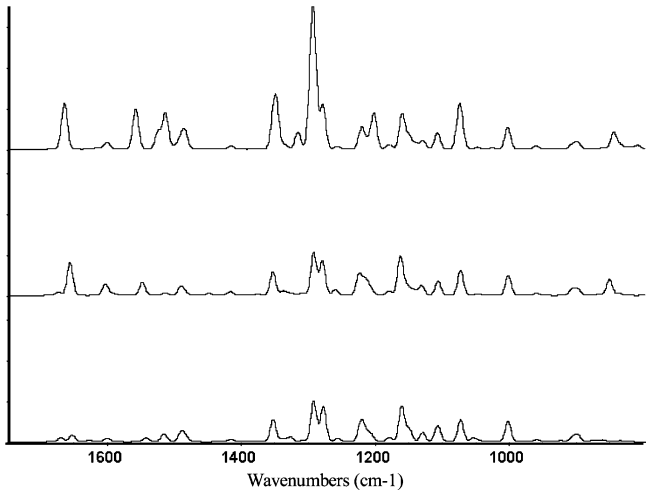

Figure 4. B3LYP 6-31G** calculated infrared spectra of the three molecules in the open form with the same intensity scale: from top to bottom, daeome, daecn, daeph.

1400 and 1700 cm^{-1}, shows noticeable differences especially in terms of intensity. In this case, the normal modes involve a combination of stretching of the double bonds of the benzene and thiophene rings. In particular, the 1660 cm^{-1} band is the CC stretching (bonds 3−4, see Figure 1) of benzene and it is strong only for the daeome and daecn. Only in the daeome do we find other bands (1500−1600 cm^{-1}) as strong as the 1660 cm^{-1}. We observe that the effect of the side groups is noticeable also for the open form of these molecules.

The IR spectra of the closed form are shown in Figure 5. For all compounds, a comparison with the spectra of the corresponding molecules in the open form shows that there are large differences, especially in the region 1500−1700 cm^{-1}. This fact is not surprising if we consider that the main change in the structure between the open and closed form is the redistribution of the double bonds. Going toward a more detailed analysis, the IR spectra of the closed form of the three molecules show different patterns, which can be related to different dynamic coupling and bond polarization. Here the three molecules behave in different ways. In the daeome there are two very strong bands which are the stretching of

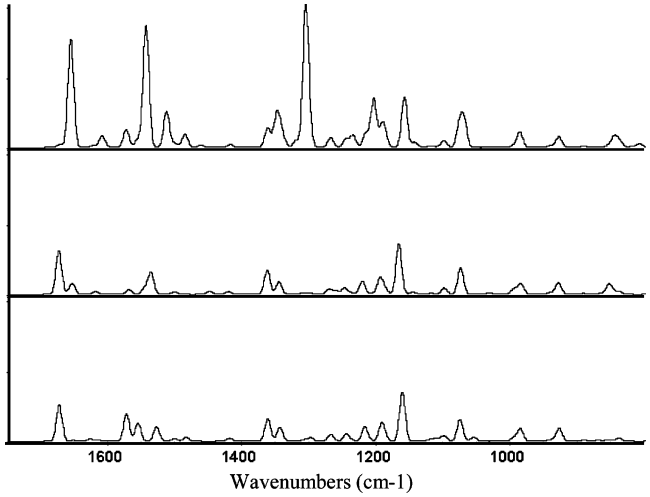

Figure 5. B3LYP 6-31G** calculated infrared spectra of the three molecules in the closed form with the same intensity scale: from top to bottom, daeome, daecn, daeph.

the benzene rings (bonds 3−4) coupled with the inter ring double bonds (bond 7) and the stretching of the double bond of thiophene (bond 8). The vibrations of the two phenyl rings and the thiophene rings are out of phase. In the daecn and daeph, the stretching of benzene ring is decoupled from the inter ring double bond; therefore the corresponding band has a very low intensity. On the basis of these results, it can be stressed that, for these two molecules, the presence of the benzene ring plays a small role in the enhancement of the intensity of the IR spectrum.

Table 2 reports the calculated IR intensities for the three different molecules and the ratio between the open and closed form in different spectral ranges. It is apparent that the CH stretching bands do not change in intensity on going from the open to the closed forms.

It is obvious that the intensity depends on the substituents in the other spectral ranges. For daeome, the intensity ratio between open and closed forms is large (1.58). In addition, also the absolute values of intensities are larger (4600 and 7250 km/mol for open and closed forms). For daecn, the ratio is very small, even smaller than for daeph, which has no side groups. This indicates that the presence of an acceptor does not help, but even hinders, the effort to increase the infrared intensities in this kind of system.

To better understand the reason for these changes and where they take place, we extracted the changes in dipole moment $d\mu/dR$ (dipole strength in infrared, related to the dipole transition moments) by changing any internal degree of freedom and in particular the stretching. These quantities are the ingredients of the infrared absorption intensity arising from the normal modes.

The results for the calculated modulus of $d\mu/dR$ are reported in Table 3. In the open form, focusing on the bonds of the phenyl ring (1−6), the effect of the substituents is evident when compared to the daeph molecule (no substituents). Both the withdrawing (−CN) and donor ($-O-CH_3$) groups increase the polarization of the bonds of the phenyl ring. This explains the small intensity of the 1660 cm^{-1} band of daeph when compared to the other two molecules (Figure 4). As for the diarylethene unit (bonds 7−16) it is less affected because of the presence of the substituents since the conjugation is reduced by the torsional angle between the two rings and the arrangement of the double bonds.

The situation changes quite dramatically along the entire molecule in the closed form. Figure 6 shows the bar plot of the difference between open and closed form for the bonds listed in Table 3. Taking into account bonds 1−6, the daeome turns out to show a large increment and the daeph shows a small increment, whereas for the daecn, the values of $d\mu/dR$ decrease. It is interesting to focus attention on the inter ring bond (bond 7), which behaves like the bonds of the phenyl ring, but with larger differences (+0.7 au for daeome, −0.4 au for daecn). This result is relevant since the inter ring bond is most sensitive to delocalization. As for the bonds of the thiophene ring (8−12) and the other bonds of the perfluorocyclopentene (13−16), the changes are large for all three molecules because of the rearrangement of the double bonds occurring during the cyclization reaction. The values for bonds 11, 12, and 16 decrease, while for bonds 8, 9, and 10 the values increases substantially (along the conjugation path). Again, daeome has the larger increments as expected from the intensity in the IR spectrum.

These results can be interpreted in terms of the different nature of the substituents. When the molecule switches from the open to the closed form, the electric withdrawing (A) perfluorocyclopentene unit and the side group set up a bridge through the conjugated double bonds. With the −CN the result is a decrease of the electronic density in the benzene ring and in the inter ring bond since −CN tends to withdraw electrons. It follows that the actual delocalization does not increase, regardless of the fact that the torsional angle between the two rings is smaller than in the open form. In contrast, the $-O-CH_3$ group, which is able to donate electrons (D), generates an increase of the actual conjugation and of the charge flux along the path between the donor and withdrawing groups. The schemes of the molecules can be thought as A−A−A for the daecn and D−A−D for the daeome. The daeph molecule lies in the middle because it has neither donating nor withdrawing chemical groups and it represents an unperturbed situation.

3. Experimental Memory Results

From these theoretical results, daeome was chosen as the material to make optical memories. An experimental setup was built as schematically represented in Figure 7. It consists of a Globar IR source, a low-pass filter (cutoff wavenumber = 2000 cm^{-1}), a sample holder, and an infrared camera (Merlin Camera 12 bit, multi bolometer 320 × 240, spectral range 3000−800 cm^{-1}). The actual measurement range is upper-limited by the lens transmission at approximately 2000 cm^{-1}. The infrared camera works at room temperature, therefore, it does not need cooling with liquid N_2 (as for MCT camera), which is appealing for widespread technological applications.

A layer of poly(tetrafluoroethylene) (PTFE, 100 μm thick) was used as the memory substrate. In addition, the PFTE film acts as a filter due to the very strong band at 1200 cm^{-1} that, combined with the IR filter, leaves a transmission window between 2000 and 1300 cm^{-1}. This range contains

Table 2. Infrared Intensity (km/mol) and the Ratio between the Closed and the Open Form in Different Spectral Regions[a]

	daeome			daecn			daeph		
	open	closed	ratio	open	closed	ratio	open	closed	ratio
total	4600	7250	1.58	2620	2920	1.12	2270	2920	1.29
tot-CH	4150	6790	1.64	2510	2850	1.13	2060	2740	1.33
800−2500	3870	6520	1.69	2260	2650	1.17	1750	2470	1.42
CH str.	450	463		105	72		212	182	

[a]Total: entire spectral range. Tot-CH: total except the contribution of CH stretching. 800−2500: from 800 to 2500 cm^{-1}. CH str.: only the CH stretching.

Table 3. Contributions dμ/dR (a.u.) for the Different Bonds in the Open and Closed Form and the Difference (Δ)

	daeome			daecn			daeph		
bond[a]	open	closed	Δ	open	closed	Δ	open	closed	Δ
1	0.303	0.478	0.175	0.248	0.201	−0.047	0.028	0.059	0.031
2	0.261	0.510	0.249	0.251	0.145	−0.106	0.033	0.110	0.077
3	0.273	0.510	0.237	0.183	0.157	−0.026	0.055	0.143	0.089
4	0.373	0.659	0.286	0.172	0.173	0.001	0.081	0.220	0.140
5	0.205	0.423	0.217	0.263	0.184	−0.079	0.089	0.054	−0.036
6	0.187	0.392	0.205	0.254	0.157	−0.097	0.061	0.091	0.030
7	0.095	0.760	0.665	0.392	0.037	−0.355	0.095	0.337	0.242
8	0.134	0.885	0.752	0.266	0.493	0.227	0.110	0.646	0.536
9	0.208	0.642	0.435	0.148	0.533	0.385	0.176	0.571	0.394
10	0.227	0.730	0.503	0.404	0.520	0.115	0.231	0.573	0.343
11	0.274	0.138	−0.136	0.154	0.198	0.044	0.265	0.132	−0.133
12	0.310	0.144	−0.166	0.344	0.096	−0.248	0.311	0.116	−0.196
13	0.295	0.606	0.311	0.283	0.462	0.179	0.298	0.500	0.202
14	0.218	0.406	0.188	0.204	0.371	0.167	0.191	0.367	0.175
15	0.029	0.080	0.051	0.063	0.126	0.063	0.010	0.106	0.096
16	0.254	0.142	−0.112	0.322	0.089	−0.233	0.262	0.121	−0.142

[a] The bond numbers are shown in the reference structure (Figure 1).

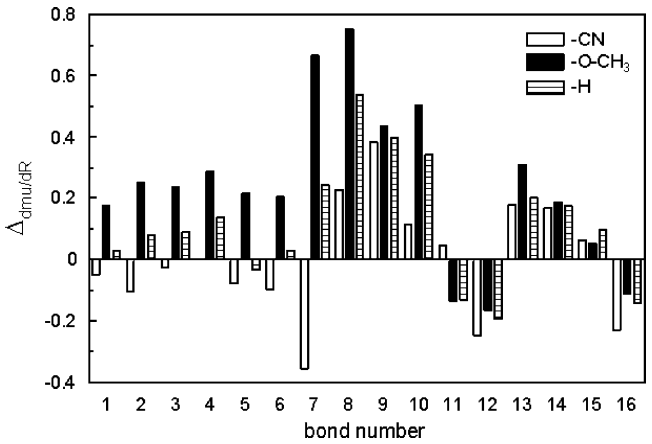

Figure 6. Bar plot of the difference between dμ/dR (a.u.) in the closed form and open form for the three different molecules, the bond numbers are the same as those in Figure 1.

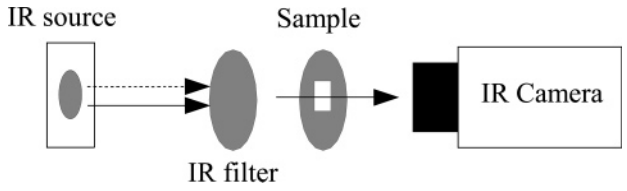

Figure 7. Scheme of the setup used to detect the change in chemical structure in the infrared spectral region. The source is a standard Globar, the filter coupled with the PFTE film selects a narrow transmission window.

the spectral region 1400−1500 cm^{-1} where daeome has strong changes in the infrared spectrum, as pointed out previously.

A film of a daeome and poly(methyl methacrylate) (PMMA) blend was cast on a PTFE layer from a $CHCl_3$ solution (14.8 mg of daeome + 20 mg of PMMA 560 000 M_W in 1 mL) with doctor blade technique. The thickness of this film was 12 μm measured using a confocal microscope (Zeiss LSM 510) by exploiting the fluorescence emission of the photochromic layer.

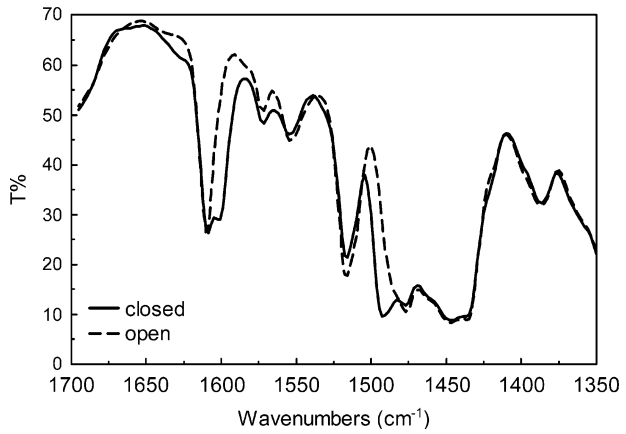

Figure 8. Infrared spectra of memory film in the two different isomers of daeome: open form (dotted line), closed form (solid line).

The IR spectra of the memory film in the open and closed form were collected with a FT-IR spectrometer (Figure 8). Despite the presence of the polymer matrix, the bands of which are necessarily superimposed on those of the active molecule, it can be observed that the difference in intensity over the entire spectral range considered is not negligible (11%).

To show the memory effect and to prove the reliability of the setup we followed specific experimental steps. First, the memory layer was illuminated with UV light (Hg(Ar) lamp), filtering the wavelengths below 300 nm to avoid dangerous side reactions. At this stage, the photochromic material has switched to the colored closed form. Next, the film was positioned on the sample holder. Because the IR illumination

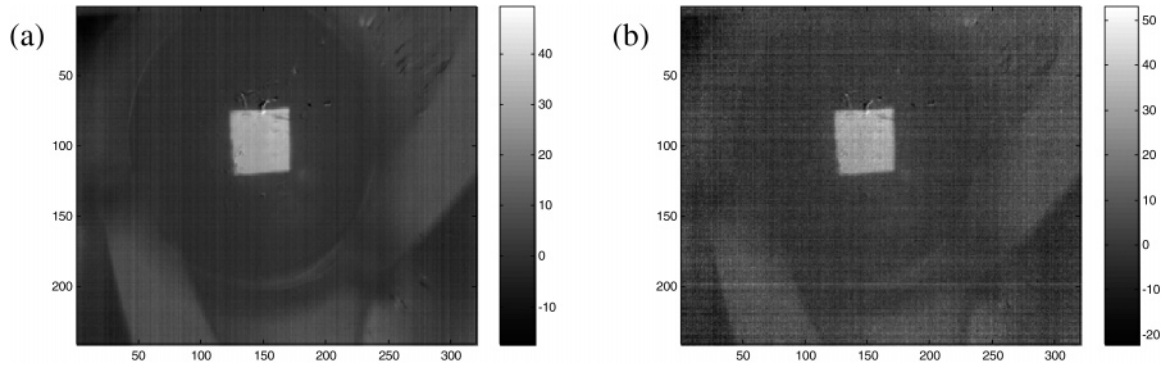

Figure 9. FPA images in the filtered range (1300−2000 cm^{-1}) of the squared pattern written on a memory layer: (a) average of 50 frames, (b) single frame.

from the Globar was not uniform on the focal plane array, a reference image was needed. A set of frames was collected with the camera (50 frames in 6 s, the integration time was 45 ms), which became the reference for our memory. A square pattern was then written on the memory layer by using a mask and a 532-nm laser. The same number of frames was collected with the same conditions without moving the sample, resulting in the memory image.

The IR images are shown in Figure 9. The square-shaped pattern is clearly visible and the count difference between the reference and the memory images is roughly 30 on a total of 1500. It is also detected in the single frame image although the contrast is lower than in the averaged image since the background noise is higher. This is an important result because it means that the difference in absorption is large enough to use a single frame to read the information. Because it takes only 45 ms to read the information, this kind of memory can be considered fast.

The results obtained show that the difference in intensity in the IR spectra is large and it is easily detected. It follows that it is not mandatory to use an infrared light source that matches exactly the wavenumber of the infrared band, but that a source with a quite large emission spectrum can be used (e.g., an infrared LED). This is an important advantage for the technological application because, at present, it is not easy to have an IR laser with a well-defined emission line matching the band of the photochromic memory. Moreover, the transmitted spectral range could be narrowed using a different filter (for example with a cutoff at 1700 cm^{-1}), which would improve the image contrast, ultimately resulting in fewer constraints, thus requiring fewer constraints in terms of film thickness and active molecules concentration.

4. Conclusion

A theoretical study was performed to rationalize the relationship between chemical structure and infrared spectrum of diarylethenes with electroactive substituents. The reliability of the model used was revealed by the comparison between experimental and theoretical IR spectra. It allowed understanding the strong influence of electron donor or electron acceptor side groups on the intensity of particular normal modes involving the CC stretching of the rings. In the case of daeome, it was determined that the donating group increases the IR intensity of some specific normal modes especially in the closed form where the conjugation is larger. Consequently, the charge flux along this path becomes enhanced. This molecular system can be assimilated to a donor−acceptor−donor structure, namely push−pull−push. In contrast, if the substituent is a withdrawing group, as in daecn, the system becomes acceptor−acceptor−acceptor in the closed form and the conjugation is small through the flux channel. The result is a small difference in intensity between open and closed form and consequently a small memory effect.

Our results show that diarylethenes tailored for memory application can be designed by increasing the strength of the side donor groups. Such molecules would allow the use of thinner photochromic films or smaller concentration of active molecules in the polymer matrix.

A versatile setup was built to demonstrate the memory effect and the reading procedure using infrared light. The information written on the memory layer was easily read using a large spectral range (2000−1300 cm^{-1}), although only the intensity of two bands (roughly 20 cm^{-1} their bandwidth) changes. The readout is fast (45 ms) and it could be made faster by using a narrower transparent window or a smaller spectral range source.

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