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Modulation of the Refractive Index by Photoisomerization of Diarylethenes: Theoretical Modeling

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Molecular polarizabilities of photochromic diarylethenes bearing different chemical groups as substituents have been calculated by density functional theory (DFT) simulations with the aim to obtain an estimate of the refractive index of a glassy matrix containing diarylethenes as active species. Simple models have been introduced in order to take into account the effects that occur in bulk materials. The results obtained show that the choice of suitable substituents enhances the modulation of the refractive index driven by the photochromic reaction; moreover, the trends predicted are consistent with the experimental data. This opens the way to use quantum chemical predictions on model molecules to foresee performances relative to the photoinduced modulation of the refractive index in bulk materials.

1. Introduction

Organic photochromic molecules are chemical species which present two (or more) stable states showing different colors. The reversible change between the states is induced, at least in one direction, by a suitable light stimulus (UV/visible light). The light-triggered change of relevant optical properties makes these molecules very attractive for their potential applications for the development of functional materials for signal processing.[1,2]

Photochromic materials can find real and practical use both as tunable optical elements and as optical switches, provided that several requirements, such as thermal stability, good conversion ratio, and fatigue resistance, are fulfilled.

On the other hand, since any technological application exploits the variation of a well-defined physical property (e.g., change in the absorption coefficient, change of refraction index, change of conductivity upon photochromic conversion), the knowledge of the specific chemical−physical properties of the active molecules in the two different forms plays a fundamental role in the optimization of the material. The discussion reported in this work is a contribution to this kind of investigations.

In the past two decades, 1,2-diarylethenes and particularly 1,2-dithienylperfluorocyclopentene derivatives have gained much attention as photochromic materials, in particular from the group of Irie[3] and from other groups.[4–9]

Among other properties, their relevant modulation of the refractive index in the near-IR and visible regions induced by photochromic conversion[10–12] has suggested possible applications of these molecules in photonic tools, such as rewritable wave guides,[13–15] and in linear and nonlinear optical devices (holographic gratings, wavelength tunable filters, holographic memories).[16–19]

In some previous papers,[20,21] the relationship between refractive index change (Δn) and chemical structure has been drawn for a series of different dithienylethenes. These works dealt with either photochromic molecules dispersed in glassy polymer matrix or dithienylethene polymers. The experimental data collected showed that the modulation of the refractive index Δn strongly changes depending on the type of chemical substituent attached to the 1,2-dithienylperfluorocyclopentene moiety.

On the basis of these results, we decided to carry out a theoretical analysis in order to rationalize the observed phenomenon and to provide guidelines leading to the synthesis of optimized compounds with enhanced Δn values. The aim of this work is to set up a model connecting the molecular parameters obtained through quantum chemical calculation on isolated molecules with the relevant optical properties of bulk photochromic material, focusing mainly on the prediction of photoinduced change of the refractive index Δn. Other photochromic properties such as absorption spectra, quantum yield (theoretically treated by other groups),[22–24] fatigue resistance, and conversion ratio will be neglected in this study.

Theoretical investigations are carried out using density functional theory (DFT) calculations with the B3LYP functional[25] and the 6-31G(d,p) basis set. This basis set is known to give a good description of systems containing conjugated π-electrons, a characteristic which is the source of the peculiar electronic and vibrational properties of the photochromic molecules under study. Moreover, the choice of the B3LYP functional is supported by our previous experience in predicting with success structural and optical properties of dithienylethenes;[26] nevertheless some calculations have been carried out making use of a different functional (namely BPW91[27]) which gives only modest differences. The calculation were carried out with the Gaussian 98 and Gaussian 03 software[28] on the HPSuperDome6400 at the Consorzio Interuniversitario Lombardo per la Elaborazione Automatica (CILEA).

2. DFT Prediction of Molecular Parameters

The link between molecular polarizability (α) and refractive index (n) can be made explicit based on the celebrated

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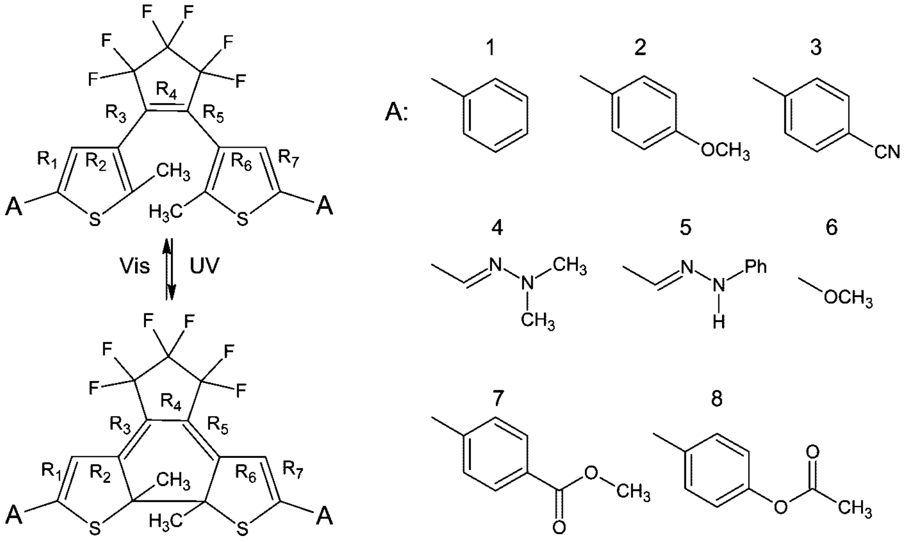

Figure 1. Chemical structure of 1,2-dithienylperfluorocyclopentene in its "open" and "closed" forms. The sequence of CC bonds labeled in the sketch defines a "conjugation path" for π electrons. The chemical substituents (A: **1**−**8**) characteristic of the molecules investigated are also reported.

Lorentz−Lorentz theoretical model,[29] which provides the well-known relationship:

$$(n^2 - 1)/(n^2 + 2) = (4\pi/3)(N_A/V)\alpha \qquad (1)$$

where N_A is the Avogadro number and V is the molar volume.

This relationship is at the basis of several theoretical studies dealing with predictions of the refractive index in organic and polymeric materials.[30−34] As will be discussed in section 3, eq 1 can be modified in order to describe the systems under investigation, consisting of active photochromic molecules dispersed (at a given concentration) in a glassy matrix of poly(methyl methacrylate) (PMMA).

From eq 1, it is clear that the basic molecular parameter essential for our investigation is the electronic polarizability of the photochromic molecules, and in particular the change of molecular polarizability which results from the light-induced isomerization. These quantities can be routinely obtained from the standard output of a DFT calculation. Moreover, in order to test the reliability of the level of theory adopted and to develop useful structure/property relationships, several other data obtained from the same DFT simulation will be compared with the experimentally available data.

The theoretical results concerning molecular structures and the associated energies as well as spectroscopic predictions are presented and discussed in sections 2.1, 2.2, 2.3, and 2.5.

Section 2.4 is devoted to the analysis of the theoretically derived molecular polarizabilities; in section 3 the models and the results obtained for the prediction of n and Δn values are illustrated and discussed.

2.1. Stabilization Energies. In Figure 1 the eight molecules considered in this work are reported. A sketch of the open and closed structures of the parent photochromic unit (common to all molecules investigated here) is also reported showing a sequence of (ideally) alternating double and single bonds (R_1−R_7) forming a "conjugation path" for π electrons arising as a consequence of the cyclization. While the closed form shows a unique molecular equilibrium conformation, the open one presents two different conformational isomers, which differ in the relative position in space of the two thiophene rings. The two different structures[35] correspond to different choices of the torsional angles around the CC bonds which join the perfluorocyclopentene units and the thiophene rings. Depending on the values of the torsional angles, the two thiophene rings can face either "edge to edge" (C_2 local symmetry, namely antisymmetric conformation) or "face to face" (C_s local symmetry, symmetric conformation).

Due to symmetry requirements for the excited electronic state involved in the photoisomerization reaction, the photoinduced isomerization to the closed form takes place starting only from the C_2 conformer.[3] This fact explains why the quantum yield experimentally determined does not usually exceed 50%.[3]

According to our calculations for the whole set of molecules analyzed, the lowest energy isomer corresponds to the open antisymmetric structure. The symmetric open conformer shows indeed an increase of the stabilization energy of approximately 1 kcal/mol. As their energy difference is relatively low, the two conformers at room temperature are constantly interchanging.

The energy of the closed form, for any molecule investigated, was found to be considerably higher than that of the open one. The energy difference is between 10 and 14 kcal/mol (with the exception of molecule **6** showing an energy gap of 5.2 kcal/mol).

Lehn and co-workers demonstrate with experiments that a substitution with an electron-withdrawing group destabilizes the closed form leading to shorter decay times.[36] In agreement with this observation, we found that the molecules with electron-withdrawing substituents, such as **3** and **7**, show the highest energy gap between the ground states of the open forms and of the closed forms. By contrast, electron-donor substituents (**2**, **4**, **5**, **8**) give lower energy gaps, while the value of the energy gap for molecule **1** is found to be intermediate.

2.2. Equilibrium Geometries. Starting from an input geometry characterized by the C_2 point group symmetry for both the open and closed forms, we carried out geometry optimization without any symmetry constraints. In spite of the symmetry of the chemical structure of the molecules, slight shifts toward C_1 conformation were detected for all molecules investigated. The reason for such symmetry breaking can be ascribed to the fact that the perfluorinated cycle cannot take up a planar structure, as already discussed by Perrier et al.[37]

Relevant structural parameters which are related to the color change upon photoisomerization are the lengths of the CC bonds

TABLE 1: Average Bond Length Alternation (BLA) and Torsional Angle (around the CC Bond Linking the Thiophene Ring and the Chemical Substituent A) As Calculated (DFT) for the Eight Molecules under Study, in Their Open and Closed Forms[a]

	BLA (pm)			torsional angle (deg)		
molecule	open form	closed form	Δ(BLA)	open form	closed form	Δ(angle)
1	8.56	6.71	1.85	26.4	19.4	7
2	8.56	6.48	2.08	26.5	14.4	12.1
3	8.43	6.53	1.9	22.9	18.1	4.8
4	8.39	5.90	2.49	0.2	2.4	−2.2
5	8.29	5.56	2.73	2.2	1.6	0.6
6	9.34	7.26	2.08	16.8	5.1	11.7
7	8.45	6.45	2	23.6	16.8	6.8
8	8.56	6.55	2.01	26.6	16.1	10.5

[a] The definition of BLA follows the numbering of CC bonds sequence as shown in Figure 1: BLA(open) = $(R_2 + R_3 + R_5 + R_6)/4 - (R_1 + R_4 + R_7)/3$; BLA(closed) = $(R_2 + R_4 + R_6)/3 - (R_1 + R_3 + R_5 + R_7)/4$.

TABLE 2: Electrical Dipole Moments As Calculated (DFT) for the Eight Molecules under Study, in Their Open and Closed Forms

	dipole moment (DM) (e bohr)		
molecule	open form	closed form	Δ(DM)
1	1.50	1.65	0.15
2	0.81	1.21	0.40
3	0.32	0.07	−0.25
4	2.10	2.72	0.62
5	2.46	2.63	0.17
6	2.27	3.11	0.84
7	0.08	0.33	0.25
8	0.63	1.12	0.49

from R_1 to R_7 defining the sequence forming the “conjugation path”.[37,38] The formation of such a sequence of (at least ideally) alternating single and double CC bonds is related to the loss of aromaticity of the thiophene rings in the closed form. It is worth noticing that the displacement of a double bond from a CC belonging to the thiophene ring to the CC linking the thiophene ring to the perfluorocyclopentene unit gives rise to a sequence of seven alternating CC bonds (from R_1 to R_7) along the dithienylethene moiety and a planarization of the molecular structure. This is the reason why the absorption spectra change, showing a relevant red shift of the HOMO−LUMO transition and an easily observed change of color. In terms of structural data, the enhancement of the conjugation, i.e., the occurrence of a more delocalized π electron system, results in a decrease of the degree of bond length alternation (BLA), namely in a larger “equalization” of the equilibrium bond length of the CC bonds involved in the conjugated sequence.

On the other hand, the introduction of chemical groups which donate electrons to or withdraw electrons from the π system, as well as the presence of chemical moieties which allow extending the conjugation path (e.g., an aromatic group), are expected to have a relevant effect especially regarding the structural changes induced by the closure reaction. There are two ways to quantify (through structural data) the change of conjugation upon the closure reaction: (i) analysis of the length of CC bonds along the conjugated path in the dithienylethene group (from R_1 to R_7, Figure 1); (ii) analysis of the value of the dihedral angle between the thiophene ring and the substituent group A.

As for point i, we calculated the BLA as the difference between the average length of the single C−C bonds and the average length of the double ones (see Table 1). As expected, the open form has a larger BLA than the closed form for all the molecules studied, showing values in a narrow range (8.3−8.6 pm) with the only exception of molecule **6** characterized by the largest (9.3 pm) BLA value. This deviation is simply explained considering that, except for molecule **6**, all A groups illustrated in Figure 1 are able to extend the conjugation path of thiophene ring along the additional aromatic ring or double bond; by contrast, the A group of molecule **6** (A = $-OCH_3$) does not have π electrons to share with the conjugated π system of the thiophene units.

BLA values in the closed form are generally lower, thus proving that π electrons are much more delocalized. However, the values of BLA of the closed isomers show a nonnegligible spread in values (ranging from 5.6 to 6.7 pm, reaching a maximum value of 7.26 in the case of **6**).

This last observation demonstrates that the effect of the A substituent on conjugation is much more relevant when an extended conjugation path is present. Moreover, a similar trend is revealed by the comparison between the experimental absorption maxima of the available molecules and the BLA values obtained from calculations.[20] This clearly proves that the model which has been adopted for the theoretical study is reliable. Moreover, when the conjugation increases, the atoms belonging to the conjugated sequence approach a planar geometry.

The effect of the ring closure on the torsional angle θ (point ii above) has been already discussed in ref 26 for molecules **1**, **2**, and **3**. It follows the same trend suggested by BLA values: the closed forms show systematically lower θ values with respect to the corresponding open forms. Moreover, the larger value of Δ(BLA) (molecule **2**) corresponds to the larger value of $\Delta\theta$.

A peculiar situation is found for molecules where the phenyl unit is absent (**4**) or not directly linked to the thiophene (**5**). Molecules **4** and **5** show nearly planar conformation in both the open and closed forms. Notice that these systems showed the highest values of Δ(BLA). These observations clearly demonstrate that even if the aromatic ring is able to extend the conjugation path, the effect of the steric hindrance between H atoms of the rings forces a nonnegligible deviation from planarity which necessarily prevents an efficient π-electrons delocalization. In other words, the equilibrium value of the angle θ can be described as the result of the balance of two opposite factors, namely the tendency to realize the largest conjugation between the dithienylene group and the phenyl ring and the repulsion from the closest nonbonded H atoms. As expected, it turns out that the first factor is more effective in the closed form than in the open one.

2.3. Molecular Dipole Moments. The electrical dipole moment is another observable affected by the transition from the open to the closed forms. The value of the dipole moment varies from molecule to molecule according to the extent of the electron-withdrawing/electron-donating capability of the substituent groups. Notice (see Table 2) that electron-withdrawing groups (molecules **3** and **7**) compete with the central perfluorinated cycle, thus reducing the electrical dipole moment. The opposite happens for molecules with electron donor groups, showing dipole moment values in the range 1−3 e bohr.

According to our predictions the dipole increases upon closure. The enhancement ranges from 0.15 to 0.84 e bohr. The only exception is molecule **3**, characterized by a very low dipole moment in the open form (0.32) and showing an even smaller (0.07) dipole after the closure reaction.

TABLE 3: Static Molecular Polarizabilities ($P = 1/3\ \mathrm{Tr}\ \alpha$) and Their Contribution per Electron (PPE = P/Z) As Calculated (DFT) for the Eight Molecules under Study, in Their Open and Closed Forms

	open form		closed form		Δ(polarizability)	
molecule	P (bohr^3)	PPE (bohr^3)	P (bohr^3)	PPE (bohr^3)	P (bohr^3)	PPE (bohr^3)
1	343	1.29	407	1.53	64	0.24
2	392	1.32	481	1.61	89	0.30
3	402	1.39	489	1.68	87	0.30
4	341	1.30	432	1.65	91	0.35
5	469	1.51	631	2.03	162	0.52
6	225	1.03	244	1.12	19	0.09
7	433	1.33	523	1.60	90	0.28
8	418	1.28	507	1.55	89	0.27

TABLE 4: Intensity Data from Simulations of the Infrared Spectra for the Eight Molecules under Study, in Their Open and Closed Forms[a]

	infrared intensities (km/mol)		
molecule	open form	closed form	ΔI^{IR}
1	2267	2922	655
2	4602	7342	2739
3	2270	2920	650
4	4663	8133	3470
5	6293	11253	4960
6	3520	5194	1674
7	5915	8434	2519
8	5896	7123	1228

[a] The data reported are obtained as a sum of the infrared intensities over the whole active transitions.

The presence of relevant dipoles may greatly affect the solute–solvent interactions in polar solvents. This means that the behavior of the photochromic molecules in a surrounding medium will be different from the isolated one, depending on its structure.

2.4. Molecular Polarizability. It is well-known that molecules containing aromatic rings and/or sequences of conjugated double bonds show, among the organic compounds, the highest values of polarizability.

Gussoni et al.,[39] based on experimental data on many small molecules, have shown that the electronic contribution to the polarizability of an isolated molecule is nearly proportional to the number of its electrons. However, conjugated molecules are outside this trend, showing a higher average contribution per electron. This can be intuitively explained considering that delocalized π electrons are most loosely fastened to the nuclei with respect to σ electrons and then they provide the molecule with a much more polarizable charge cloud.

The photochromic molecules under study show relatively high values of molecular polarizabilities. Moreover, in the closed form, polarizabilities are always larger than in the open form; this is expected as a consequence of the increase of the delocalization path for π electrons after photoisomerization.

Calculated values of static molecular polarizabilities (average molecular polarizability expressed in terms of the trace of the polarizability tensor, namely $P = 1/3\ \mathrm{Tr}\ \alpha$), and of polarizabilities per electron (PPE = $(1/3\ \mathrm{Tr}\ \alpha)/Z$; Z = total number of electrons in the molecule) are reported in Table 3.

The results in Table 3 can be rationalized as follows:

(1) The presence of electron-donating or electro-withdrawing side groups usually raises the molecular polarizability (especially in the closed form). The larger the capability to donate/withdraw electrons, the larger the effect on the polarizability. This is the case for hydrazones (—C=N—N—), which are strong donor groups.

(2) The longer the conjugation path, the greater the PPE value. Notice that the addition of a phenyl group is effective in extending the conjugation path.

Examples supporting these statements are the following:

(1) Molecule **6** has the shortest conjugated path and the lowest PPE, both in the open form and in the closed form; moreover the change in PPE (Δ(PPE)) after ring closure is the lowest obtained (0.09 bohr^3, compared with value of 0.3 bohr^3 for the corresponding diarylethene **2** with the additional phenyl rings).

(2) The introduction of an electron-donating (or -withdrawing) group in molecules **2** and **3** enhances PPE with respect to molecule **1**; notice that the increase is the same independent of the fact that the end group donates (methoxy) or withdraws (cyano) electrons, as indeed happens also for molecules **7** and **8**.

(3) Molecule **4** does not bear any phenyl or other aryl group, and consequently, has a relatively low number of π electrons: in spite of that it shows large ΔP and Δ(PPE) values, thus highlighting the strong effect of the hydrazone group (the fully coplanar —C=N—N— moiety).

(4) We find for molecule **5** (which shows the longer conjugation path) the highest PPE value and the highest Δ(PPE); the result is not surprising if we consider that molecule **5** bears the hydrazone moiety (an efficient donor group) together with the phenyl ring, both allowing a further extension of the conjugation path.

Assuming that the change in the refraction index follows the same trend indicated by ΔP, one must conclude that the efficiency in raising the refraction index through cyclization should follow the trend **6** < **1** < **3** < **2** = **8** < **7** < **4** < **5**.

The experimental data relative to Δn of molecules **1**–**5**[20] gives the following trend: **1** < **3** < **2** < **4** < **5**.

This preliminary comparison shows that the theoretically predicted changes of polarizabilities ΔP show a trend which mainly parallels that derived from the experimental Δn values.

The analysis of the trend resulting from the comparison of the Δ(PPE) values provides an indication of the intrinsic efficiency of the various chemical substituents to contribute to the enhancement of Δn (i.e., it clearly shows the relevant effect of specific strong electron-donating groups).

In section 3 we will discuss models for the prediction of the refractive index of the material going from the molecular to the bulk properties. At least in principle this approach should provide values to be directly compared to those experimentally obtained.

2.5. Infrared Spectra. Vibrational spectra provide information about the chemical structure of molecules; moreover, the effect of the introduction of different chemical groups as substituents can be monitored following the changes in band intensities and frequency shifts. In refs 40–42 it has been experimentally shown that the closed form shows a general enhancement of the infrared spectrum with respect to the open form. This enhancement is modulated by the presence of electron donor or acceptor groups.

This effect is clearly illustrated in Table 4, where the sum of the absorption intensities (over the whole infrared spectrum) is reported, as obtained from DFT calculations on open and closed forms. Differences of the total intensity (ΔI^{IR}) are also reported in Table 4. A look at this quantity allows the realization that generally the lengthening of the conjugation path obtained through photoisomerization results also in a larger mobility of π electrons belonging to CC bonds of the conjugated bridge. Large charge fluxes during the stretching of CC bonds are indeed responsible for large band intensities for CC stretching vibrations.[43] Notice that these vibrations are mainly responsible for ΔI^{IR}.

The largest infrared intensities are indeed reached when mobile electrons are present (i.e., for long conjugation paths, as for instance in case **5**). On the other hand, end groups able to induce the polarization of the π electron system greatly contribute to the intensity enhancement upon the closure reaction (compare molecule **1**, without polar end groups, and molecule **6**, where the presence of an electron donor ($-OCH_3$) group is much more effective in enhancing ΔI^{IR}). An interesting case is that of molecule **2** where, in spite of the presence of mobile electrons in the phenyl group, polarized by the $-CN$ unit, the infrared intensities are relatively low in both isomers. This fact can be related to the very small permanent molecular dipole, already discussed in section 2.3. The competitive effect of the two electron-withdrawing units (i.e., perfluorocyclopentene and $-CN$ group) results in a modest polarization of the π electron system, which in turn gives rise to a small net charge flux during CC bond oscillations and then to relatively low infrared intensities of the CC stretching bands. In other words, the different effects on the infrared spectrum found when comparing electron-donating and electron-withdrawing end groups can be related to the existence of a conjugated bridge between push and pull end groups in the former case, while in the latter the molecule can be described as formed by a push$-\pi-$push system. It is indeed well recognized that the effect of infrared intensity enhancement of CC stretchings is largely determined by the presence of polarized π electrons in a push$-\pi-$pull molecular structure.[43]

In the case of Raman intensities, the effect of the closure reaction always results in an increase of the total Raman intensity. However, the effect in the Raman spectra is much more marked: for the whole set of molecules the enhancement is about 1 order of magnitude. This peculiar feature, which is a direct consequence of the enhanced degree of conjugation, has been already discussed in ref 19 in connection with the nonlinear optical behavior of such molecules.

3. Prediction of Δn

A relevant issue of this study is the choice of the models suitable for obtaining a theoretical estimate of the physical macroscopic property (refractive index) from molecular parameters (as obtained by DFT calculations).

The calculation provides the electronic molecular polarizability tensor α for an isolated molecule in a static electric field. Our aim is to estimate the macroscopic refractive index at a given wavelength in the near-infrared. Several effects have to be taken into account which can be described as (i) effects which directly affect the molecular polarizability and (ii) effects which determine the link between molecular polarizability and the macroscopic refractive index of the bulk material.

(i) The corrections to molecular polarizability must account for the following effects:

(a) The dispersion effect, namely the polarizability as a function of the frequency of the electromagnetic field must be accounted for. Indeed, in order to make a comparison with the experimental data available, we have to evaluate molecular polarizabilities at optical wavelengths (usually in the near-infrared), while the available theoretical data are obtained in the static electric field limit.

TABLE 5: Values of P at Static Field and at 1.5 μm for the First Five Molecules

	open form		closed form	
molecule	P (bohr^3)	P at 1.5 μm (bohr^3)	P (bohr^3)	P at 1.5 μm (bohr^3)
1	343	355	407	480
2	392	408	481	570
3	402	421	489	584
4	341	357	432	522
5	469	497	631	778

(b) The solute$-$solvent (matrix) and possibility solute$-$solute interactions must also be accounted for. Since the α values from calculations refer to the molecule in vacuo, it is necessary to estimate the change of α in the presence of other surrounding molecules, i.e., solvent molecules or even molecules of the same species.

(ii) Models for the calculation of the refractive index have to describe the following effects:

(a) They must describe the local field effect: the external electromagnetic field applied to the material is different from the field felt by the molecule inside the material. This can be taken into account following the Lorentz$-$Lorentz model (eq 1).

(b) The models must also describe the effect of the mixing of active photochromic molecules and molecules of the solvent (in our case a PMMA matrix) on the refractive index of the bulk. Clearly the important parameter is the concentration of the active molecules that are responsible for the change in the refractive index, Δn, upon photoisomerization.

Let us describe in detail how the "corrections" listed at points i and ii have been dealt with.

(1a) We are interested in the refractive index in the near-infrared spectral region where the photochromic materials are transparent. In this spectral range only the electronic component of the polarizability is active. A possible way to obtain frequency-dependent α values (in a nonabsorbing region) from the static ones is to use a single resonance Lorentz model:

$$\alpha(\lambda) = \alpha(0)\lambda^2/(\lambda^2 - \lambda_0^2) \quad (2)$$

The energy gap between the ground state and the "relevant" electronic excited state is expressed in terms of the wavelength of the absorption maximum (λ_0) and has been obtained from the UV$-$vis spectra of photochromic molecules in chloroform solution.[20] All α values are considered at the wavelength of 1.5 μm (Table 5), which is taken as reference for its relevance in the field of telecommunication. The dispersion effect is always much more marked for the closed form: this is expected as a consequence of the decrease of the energy gap of the molecule after photocyclization. Moreover, the longer λ_0 is (from 585 nm of **1** to 650 nm of **5**, 2.12$-$1.91 eV), the stronger is the enhancement of $\alpha(\lambda)$. Anyhow, the trend of ΔP at 1.5 μm remains similar to that of the static polarizability ΔP (see Table 3) and no reversal of trend occurs when the functional groups A of the diarylethene are changed.

(1b) The interaction between solute and solvent is certainly the most difficult effect to describe. Moreover, it is difficult a priori to determine its influence on the total polarizability. It arises from the interaction between the "active" molecule and the surrounding molecules (molecules of the solvent or other "active" molecules): the solute molecules induce polarization charges on the surrounding molecules that in their turn generate a reaction field that acts on the system. The result of this process is known as "solvent effect".

There are several different theoretical approaches, many of them based on quantum chemical models, which provide analytical results for the description of solvent effect.[44] The model adopted in this work is the semiclassical treatment developed by Agren.[45–47] The starting point is the Onsager model[48,49] (dipolar reaction field model) with an ellipsoidal cavity, which allows determination of the solvent effect on molecular polarizability and hyperpolarizabilities starting from single molecule properties. Since we deal with solid solutions and short wavelengths, we neglect the orientation effect of the dipole due to the applied electric field. To find the ellipsoid cavity, we used the calculated geometry.

From the calculation on photochromic molecules dispersed in PMMA, the change in polarizability due to the solvent effect turns out to be small (less than 5%) and it is similar for all the molecules. Based on this evidence, we neglected this effect.

(ii) As already mentioned, we have simply used the Lorentz–Lorenz model to describe the relationship between α and n. However, eq 1 must be modified in order to take into account that the material is made by two components, namely, the photochromic molecule (index 1) and the matrix (index 2). In the hypothesis that the two contributions are additive (weakly interacting species), the following equation is obtained:

$$(n^2 - 1)/(n^2 + 2) = (4\pi/3)(n_{v1}\alpha_1 + n_{v2}\alpha_2) \qquad (3)$$

The values of α_1 for the photochromic molecules are those obtained by DFT methods, suitably corrected according to the procedure illustrated at point i. As for the PMMA matrix α_2 is referred to the structural unit ($CH_2CCH_3COOCH_3$); its value has been obtained through eq 1 from the experimentally determined refractive index of a pure PMMA sample, $n = 1.48$. Notice that the molar density n_v (PMMA) can be simply obtained from the experimental value of the sample density ($\rho = 1.1$ g/cm^3).

The final expression for the refractive index is

$$n = [(3 + 8\pi(n_{v1}\alpha_1 + n_{v2}\alpha_2))/(3 - 4\pi(n_{v1}\alpha_1 + n_{v2}\alpha_2))]^{1/2} \qquad (4)$$

The values of molar densities n_{v1} and n_{v2} used in eq 4 have been obtained as follows: n_{v1} has been estimated from the molar concentration of the photochromic molecules (6 wt %/wt) dissolved in the PMMA matrix, assuming that the density of the blend is the same that of the pure PMMA. The value n_{v2} has been taken to be the same as that for a pure PMMA sample and determined from density data as illustrated above.

In Figure 2 we report a comparison between the refractive indexes theoretically predicted according to eq 4 and experimental n values for the molecules available from experiments (molecules **1**–**5** in a PMMA matrix) in both the open and closed forms.

From the data shown in Figure 2, we can observe that the theoretically predicted n values for the *closed* forms always exceed the experimental ones, while the discrepancy is smaller for the *open* forms. In the latter case, the contribution to the refractive index of the photochromic species is small, which means that the refractive index of PMMA is only moderately affected by the presence of the functional molecules in the blend.

According to the theoretical values of Δn, we find the following trend, which parallels the trend shown by Δ(PPE) obtained from the static theoretical $\Delta\alpha$ values (see section 2.4): $\mathbf{1} < \mathbf{2} \approx \mathbf{3} < \mathbf{4} < \mathbf{5}$.

This result is clearly illustrated by the plot of Figure 3, where theoretically predicted Δn values are shown to follow a good linear relationship with predicted ΔP (weighted on the molecular mass of the molecules).

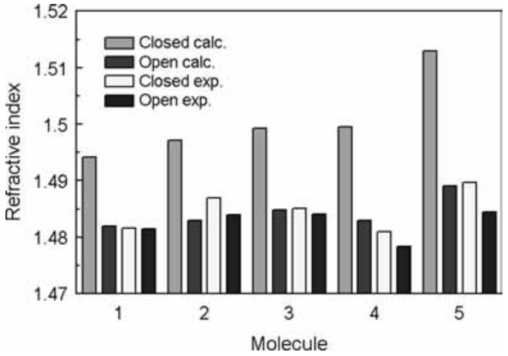

Figure 2. Comparison between the values of refractive indexes n predicted by theory (eq 4) and experimentally measured for molecules **1**–**5**, in PMMA matrix. For each molecule, the first pair of columns refers to the calculated values and the second pair to the experimental ones.

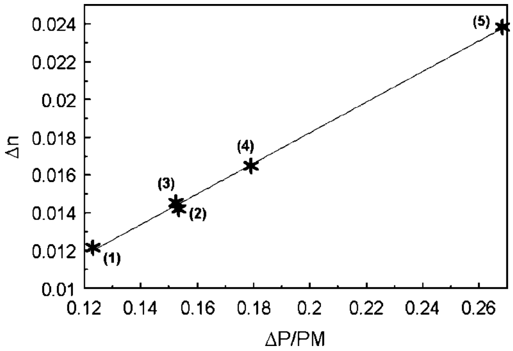

Figure 3. Plot of change of static polarizability (weighted on the molecular mass of the molecules, to make it comparable to the refractive index) vs calculated modulation of the refractive index.

As a consequence, the same weakness found in the use of $\Delta\alpha$ for predicting the experimental trend of Δn is found also when we explicitly estimate the theoretical Δn values through eq 4. In particular, if we consider the experimental trend, molecules **2** and **3** are misplaced according to our predictions. In conclusion, we are able to clearly distinguish between the two groups **1**–**3** and **4**, **5**, but we are still unable to reproduce the differences experimentally found for the materials with lower Δn values.

The fact that the theoretically predicted Δn largely exceeds the experimental values indicates that a quantitative prediction requires the explicit introduction in the model of other effects. For example, an important role can be played by the actual conversion in the photochromic process in the solid state, which so far has been assumed to be 100% for all molecules, but which might be slightly different in the different materials; indeed the experimental quantum yields of the studied molecules are close to 0.5 due to the C_s/C_2 conformational effect. It is easy to understand that the effect on Δn cannot be negligible.

4. Conclusions

This work opens the way for the use of quantum chemical prediction of molecular polarizabilities as a tool for a first cheap and quick screening of the most promising chemical modification of photochromic 1,2-dithienylethenes, through the introduction of suitable substituent A groups. The optimization of the chemical structure of the functional molecules is indeed required in order to obtain the largest modulation of the refractive index of the derived materials (e.g., blends with PMMA) upon photoisomerization of the active species.

The use of the parameters ΔP and Δ(PPE) obtained directly from the theoretically predicted (DFT method) molecular polarizabilities of the closed forms and of the open forms provides trends in good qualitative agreement with the experimentally determined Δn values at $\lambda = 1.5\ \mu$m.

In order to obtain a quantitative prediction of Δn, we proposed a classical model that allows linking the polarizability predicted in the case of isolated molecule to the bulk refractive index of the material. The analysis of the results obtained with this model leads to the following conclusions:

(1) The model is adequate to predict the effect of the different chemical substitutions. In fact, the hierarchy of the predicted Δn values for the materials analyzed copes with what is found experimentally.

(2) The predicted absolute values of the refractive index fit well the experimental results in the case of the open form, while for the closed form they are always overestimated.

(3) The overestimation of the refractive index of closed forms is somehow systematic and seems to indicate that a scale factor is affecting the predicted Δn values; this implies that the theoretical trends obtained looking at the different materials are still sufficiently reliable.

(4) This quantitative disagreement requires further investigation at least with respect to the following effects. (i) The first is the partial photoinduced conversion, which can be different depending on the chemical structure of the diarylethene. This leads to a decrease of the values of Δn, since the concentration of the active species is lower with respect to the *ideal* concentration (n_{v2}) introduced in our model. (ii) The effect of the interaction of the photochromic molecule with the surrounding must also be further investigated: in our work, this effect has been simulated by means of a continuous distribution of charges on an ideal boundary surface and may be an oversimplification responsible for the discrepancies between calculations and experimental findings.

The analysis of both the predicted Δ(PPE) and Δn and their correlation with structural parameters derived from DFT calculations allows rationalizion of the effect of the different chemical substitutions. In particular, we can state the following:

(1) The capability of the A group to inject or withdraw electrons is shown to play an important role in increasing Δn. This effect is enhanced when the conjugation path for π electrons is increased (this always happens in the closed forms and explains why differences in the α values among different molecules is enhanced after the closure reaction).

(2) A direct link of a phenyl ring to the thiophene ring always extends the conjugation and raises Δn. However, the steric hindrance prevents the coplanarity of the rings, thus limiting the electron delocalization and reducing the effect on the whole backbone of the active substituents placed in para position. This fact is confirmed by the results obtained when the phenyl ring is replaced by less bulky donor conjugated fragments (molecules **4** and **5**). The strong donor effect increases the delocalization of the π electrons along the conjugated dithienyl path. The effect is even larger when a "reservoir" of π electrons (benzene ring in molecule **5**) is provided. This turns into a stronger effect of modulation of the refractive index.

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