Computational Chemistry Modeling of Photoswitchable Liquid Crystal Alignment Materials

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Abstract

The optical switching properties of spirooxazine in photoalignment command surfaces, used to control the molecular orientation of liquid crystals (LC), were modeled using density functional theory in order to identify the optimal molecular structure for a rewritable, photoswitchable LC beam shaper for high-peak-power lasers such as OMEGA EP. This photoswitchable device would replace existing laser beam-shaper technology, which is limited in its application scope by a low 1054-nm laser damage threshold. This work examined the effect of molecular structure on bistability (switching state lifetime) by modeling different functional groups attached to the spirooxazine chromophore, along with alkyl tethers ranging in length from 3 to 9 carbons to link the chromophore to a methacrylate polymer backbone, to find an ideal combination possessing high bistability. The most promising molecule that was modeled, a spirooxazine with a 1-(4-pyridyl)piperazine functional group and tether length of 4, exhibited the smallest isomerization-state energy difference and moderately high activation energy, and its larger functional group should prove effective at redirecting the orientation of the LC materials.

1. Introduction

Spirooxazine chromophores are under computational investigation in order to model their optical switching properties, which make them potential candidates for rewritable photoalignment materials for use in an all-optical liquid crystal (LC) beam shaper. The application of existing beam shaper technologies, for example metal-mask beam shapers and LC electro-optical spatial light modulators, is severely limited by a poor 1054-nm laser damage threshold of approximately 200 to 700 mJ/cm^2 [1]. A photoswitchable device (Fig. 1), currently in design at the Laboratory for Laser Energetics, presents a potential solution to this issue.

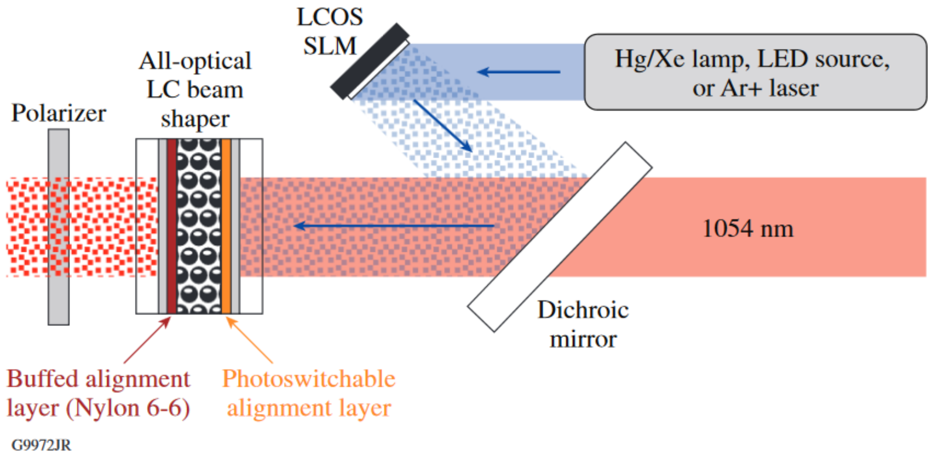


Fig. 1: Schematic of a photoswitchable device [1]. The 1054 nm laser beam is shaped using the all-optical photoswitchable device proposed. The all-optical LC beam shaper consists of a glass substrate, a photoswitchable alignment layer, liquid crystals (represented by the dotted pattern), and a buffed alignment layer, and is capped by a second glass substrate.

The schematic in Fig. 1 demonstrates how such a device would function. Here, the liquid-crystal-on-silicon spatial light modulator (LCOS SLM) electrically generates a pattern, which is reflected off the dichroic mirror and written onto the photoswitchable alignment layer, shown in orange. The molecules that make up the photoswitchable alignment layer generate the pattern in the LC layer (represented by the dotted pattern) by switching between the open and closed isomers upon exposure to light energy, and thereby physically redirecting the orientation of the liquid crystals. The buffed alignment layer produces a fixed LC orientation at its surface. Notably, unlike existing technology, this pattern will remain once the light source (provided by the Hg/Xe lamp, LED source, or Ar+ laser) is turned off.

In order for such a device to be useful, the photoalignment layer must have a significantly higher laser damage threshold than that of existing beam-shaper technologies. Spirooxazine chromophores were therefore chosen for examination in this work for their similarity to spiropyran (Fig. 2), which was recently shown to have a 1-on-1 laser damage threshold (found by irradiating separate sites of a material with increasing intensity, therefore giving information only on the peak of damage resistance for single shot operation) of 91.30 ± 6.87 J/cm^2 and an N-on-1 laser damage threshold (found by irradiating a single site with multiple shots of increasing intensity, giving a more complete picture of a material's survivability and operational lifetime) of 100.84 ± 5.51 J/cm^2 [2].

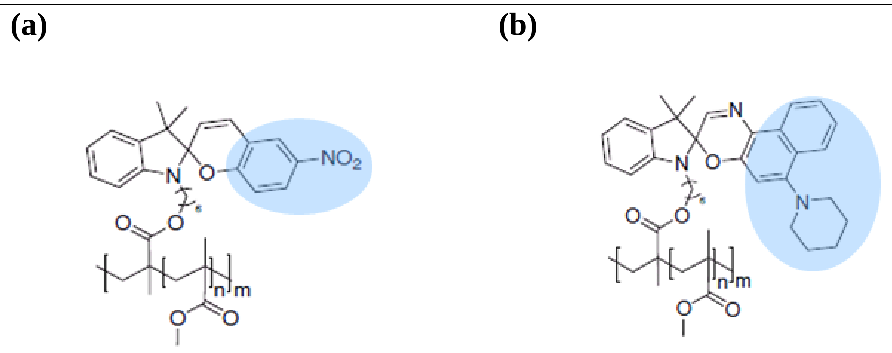


Fig. 2: Comparison of spiropyran (a) and spirooxazine (b) with methacrylate backbones. The only structural differences between spiropyran and spirooxazine are pointed out by the blue shaded areas.

The similarity of spirooxazine and spiropyran, as seen in Fig. 2, allows spirooxazine to be modeled under the assumption that it would have a laser-damage threshold superior to existing technologies.

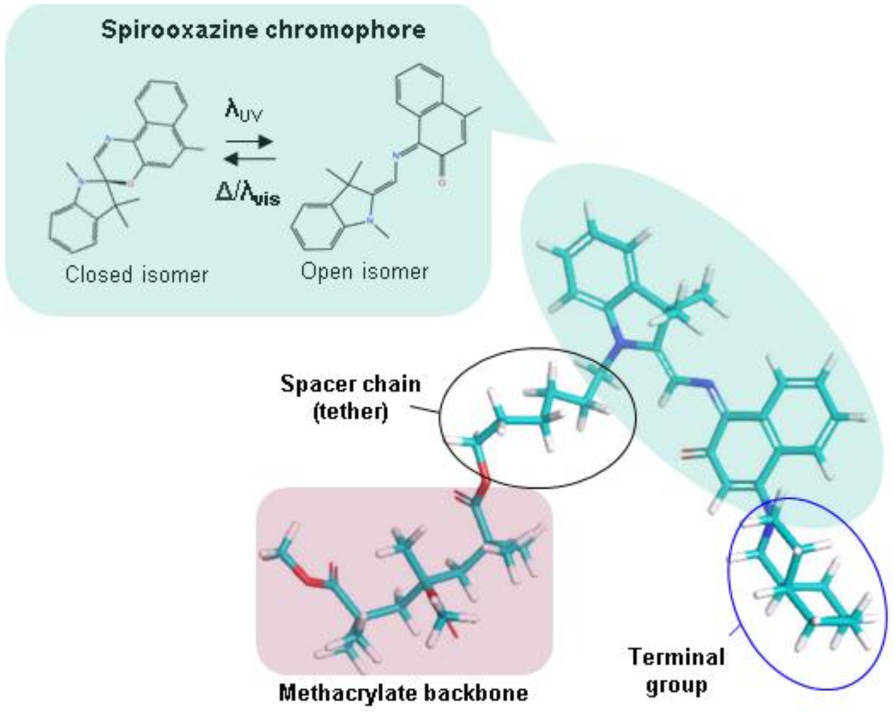


Fig. 3: Example of a spirooxazine molecule as displayed in computational models. The spirooxazine molecules modeled consist of four parts: the methacrylate backbone, carbon tether, spirooxazine chromophore (the component responsible for the actual mechanism that switches the molecule between the open and closed isomers upon exposure to light or heat energy), and terminal group, also known as functional group.

In the proposed device, spirooxazine molecules such as the one shown in Fig. 3 are found in the photoalignment layer of the command surface, pictured in orange in Fig. 1. The spirooxazine chromophore is photoswitchable, so exposure to UV light prompts the molecule to open and likewise exposure to visible light reverses the isomerization. In the photoalignment layer, this chromophore switching of spirooxazine would act as a mechanism to redirect the orientation of the LC materials and shape the laser beam. Fig. 4 shows a magnified view of the command surface, which consists of a glass substrate, the spirooxazine molecule – tethered to the command surface by its methacrylate backbone – and the LC molecules above [3]. This command surface would be capped by a buffed alignment layer and a second glass substrate, as shown in Fig. 1.

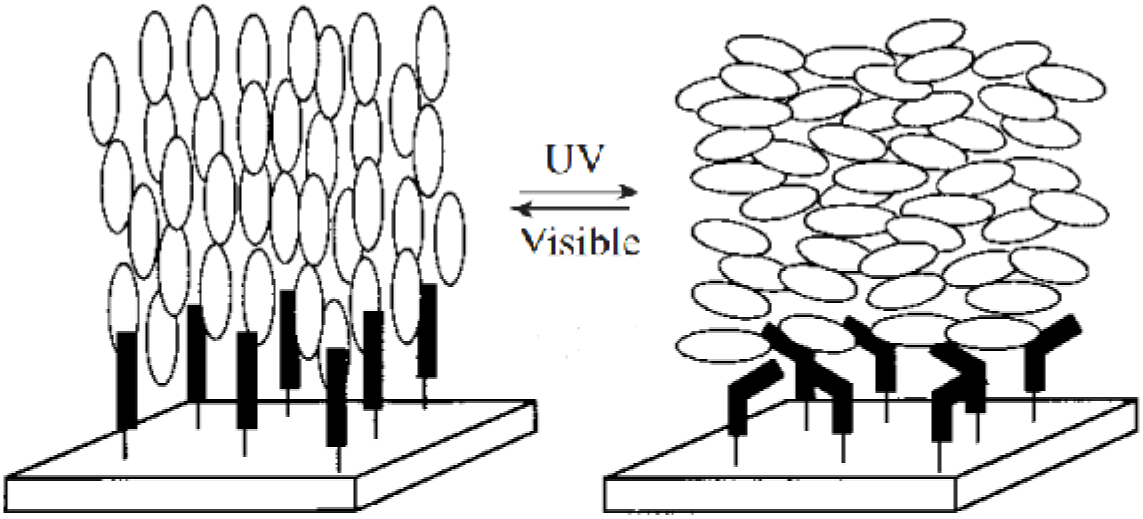


Fig. 4: Command surface diagram. The command surface in a photoswitchable device (referred to as the all-optical LC beam shaper in Fig. 1) is shown here in greater detail. The black rectangles are representative of the photoswitchable molecules, anchored to the glass substrate by the molecule's backbone, and the ellipses represent the LC materials [3]. Note that this diagram is specific to trans/cis azobenzene chromophores; however, the idea holds for spirooxazine chromophores as well.

In order to identify molecules well suited for these photoalignment layers, the effect of molecular structure on bistability (Fig. 5) was modeled by performing isomerization and transition-state calculations for spirooxazine molecules with different functional/terminal groups and alkyl tether lengths ranging from 3 to 9 carbons. Bistability is defined as switching state lifetime, meaning how stable the molecule's orientation is when it switches between isomers. A molecule that stays as an open isomer for a longer period of time after being exposed to the correct amount of light energy, for example, would be considered to have a higher bistability.

Bistability is affected by a combination of the molecule's isomerization-state energy difference and activation energy [1].

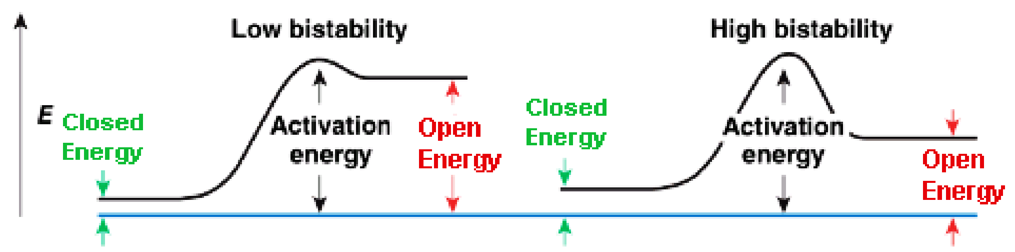


Fig. 5: Graph demonstrating bistability. Note that the energy barrier for the transition from the closed to open isomers is large in each case, but for the system with low bistability the reverse isomerization from the open to closed isomers has a low energy barrier. The graph of high bistability, on the other hand, shows a significant energy barrier for both directions of isomerization.

Molecules with high bistability are less likely to switch between isomers without deliberate interference, since, for example, environmental factors like heat are unlikely to prompt the molecule to switch back to the closed isomer [1]. The goal of this computational modeling was to identify candidate molecules for use in photoswitchable alignment layers by identifying those with the highest bistability. In order to identify such molecules, isomerization-state energy differences – the difference in potential energy between the open and closed isomers of a molecule – and activation energies necessary for the transition between isomers were calculated.

2. Previous Research

Previous research into molecules for potential use in photoswitchable alignment layers in an optically addressable LC device has largely focused on the use of computational modeling to predict the physical properties of molecules with azobenzene chromophores, thereby preserving time, labor, and money that would otherwise be spent on synthesis. The methods for such computational chemistry modeling can be categorized as follows: (1) *ab initio*, which employ only physical principles for calculations; (2) semi-empirical, whose calculations are based on existing data in the literature; and (3) density functional theory (DFT) and time-dependent density functional theory (TDDFT), more recent computational methods that use approximations of the Schrodinger equation to calculate electron density [1]. Hartree-Fock is the most basic *ab initio* method, and uses a many-electron wave function that assumes that all nuclei are motionless with respect to the electrons [4]. As such, the accuracy of the Hartree-Fock method decreases as molecular size increases, whereas DFT uses a 3D electron density function as pictured in Fig. 6, and is therefore more efficient for molecules of greater complexity.

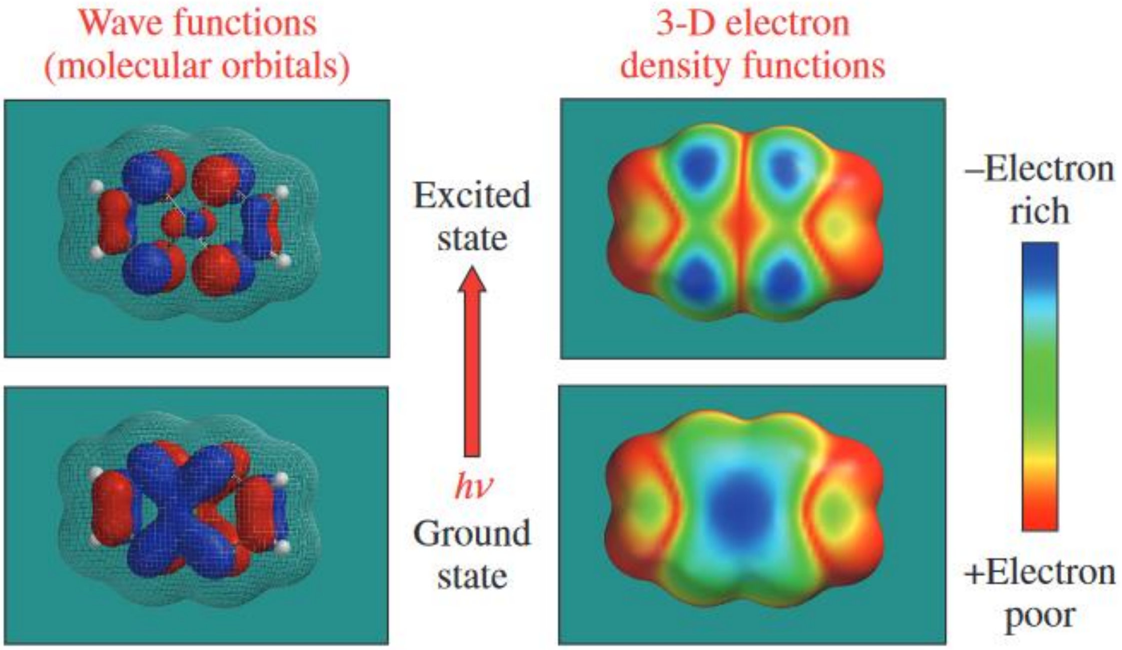


Fig. 6: A visualization of computed wave functions versus electron density functions for the same molecule [1].

Past work that used DFT as the chosen computational method for the investigation of azobenzenes for use in photoswitchable alignment layers has shown that a basis set of 6-31G**+

was the best compromise between efficiency and accuracy [2]. Note that a basis is a set of functions used to create the molecular orbitals in the computational model [5]. The notation ** indicates that all atoms, with the exception of transition metals, have polarization functions on them to describe additional electron orbitals, and the + places diffuse functions, which help to more accurately model electrons further from the nucleus, on all atoms excluding H and He [5].

3. Methodology

The optimal molecular structure for spirooxazine molecules was investigated by altering two factors: (1) the composition of the functional group, and (2) the length of the carbon tether attaching the spirooxazine chromophore to the methacrylate backbone. It was decided to vary the alkyl tether length between 3 and 9 carbons for relative ease of synthesis, as a tether length of less than 3 would be difficult to synthesize, while a tether longer than 9 carbons is expected to produce chain tangling and products with very low melting points that would be difficult to purify, and likely not well suited to use in photoalignment materials. Functional groups were initially chosen largely based on the work of Tan *et al* [6] in synthesis, characterization, and photochromic studies in spirooxazines containing heterocycle functional groups. These functional groups are depicted in Fig. 7 (a-c). However, extremely promising results from preliminary work with spirooxazines guided the modeling towards substituted piperazine functional groups, shown in Fig. 7 (d-e). It was theorized that like spirooxazine molecules with piperazine functional groups, the molecules with substituted groups would have relatively low isomerization-state energy differences, and that their larger size would make them more effective at redirecting the LC materials [7].

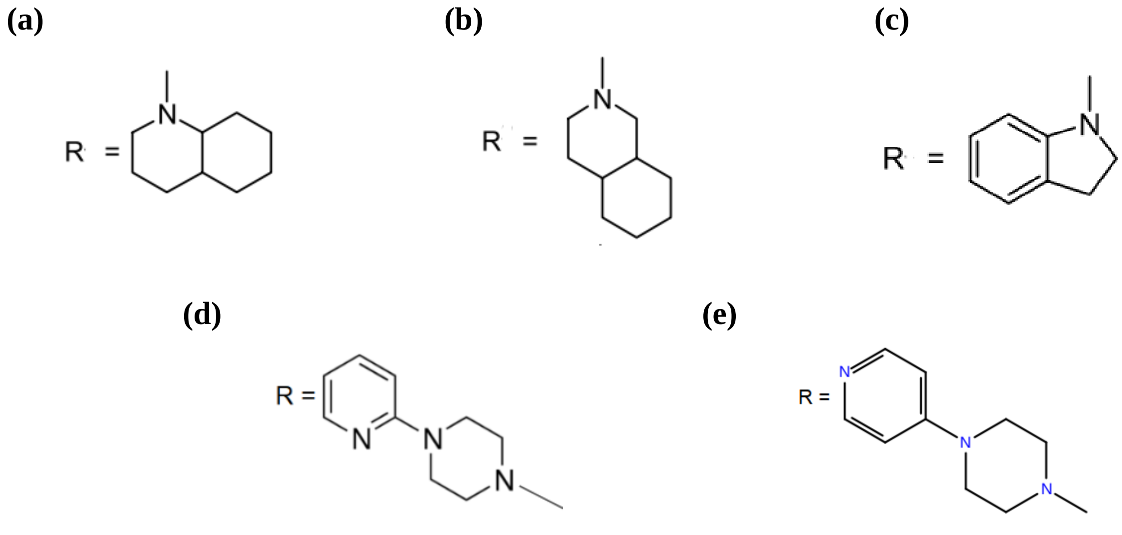


Fig. 7: Functional groups modeled. (a) through (e) are decahydroquinoline, decahydroisoquinoline, indoline, 1-(2-pyridyl)piperazine, and 1-(4-pyridyl)piperazine, respectively. Note that (d) and (e) are also referred to as substituted piperazine functional groups.

As with similar previous research, DFT was chosen in this work for optimization, single point energy, and transition state calculations to model the aforementioned different structures of spirooxazine molecules because of its combined efficiency and accuracy, since the models are highly computationally intensive. Geometry optimization of molecules for isomerization-state energy difference calculations, for example, takes approximately eight to sixteen hours, and transition state analysis averages a week (168 hours). Again based on previous research, this study selected the basis set 6-31G**+ for its efficiency and accuracy. In the interest of preserving computational resources, the length of the molecule was limited to contain only one tethered chromophore and four repeating units in the methacrylate backbone.

This work utilized the Schrodinger Materials Science Suite and the Maestro design and visualization interface for all calculations, more specifically employing Jaguar software for geometry optimizations, single point energy calculations, and transition state searches, and

Desmond for geometry minimizations [5]. These calculations were run on the Laboratory for Laser Energetics' supercomputing clusters.

With regards to transition state analysis, transition state searches were conducted only on molecules with isomerization-state energy differences of less than 5 kJ/mol, again in an effort to preserve time and computational resources. Transition state searches were run using linear synchronous transit (LST) along the lowest Hessian vector as recommended by the Schrodinger Materials Science Suite when input geometries are available [5]. In this case, the input geometries refer to the optimized open and closed isomers. Transition state searches were especially intensive computationally not only because they required the input for the open isomer to be manually built from the closed isomer in Maestro's 3D "drawer" in order to ensure that corresponding atoms in each isomer were properly numbered, but also because the resulting open isomer had to be minimized using Desmond and then re-optimized using Jaguar before the transition state search itself could proceed. Furthermore, vibrational frequencies were calculated for each transition state as a simple check on their accuracy, as transition states should have one vibrational frequency each.

4. Results and Discussions

Isomerization-state energy differences were calculated for spirooxazine molecules with five different functional groups for tether lengths 3 through 9, the most promising of which were then modeled in the transition state to gain further insight into the molecule's bistability. The five functional groups investigated in this work (Fig. 7) can be broadly categorized as nitrogen heterocycles or substituted piperazines. The isomerization-state energy differences for the spirooxazine molecules with the nitrogen heterocycle functional groups of Fig. 7(a-c) are shown in Fig. 8. These values were all relatively small, with only the molecule with a decahydroisoquinoline functional group and tether length of 8 yielding an energy difference between the open and closed isomers of greater than 25 kJ/mol.

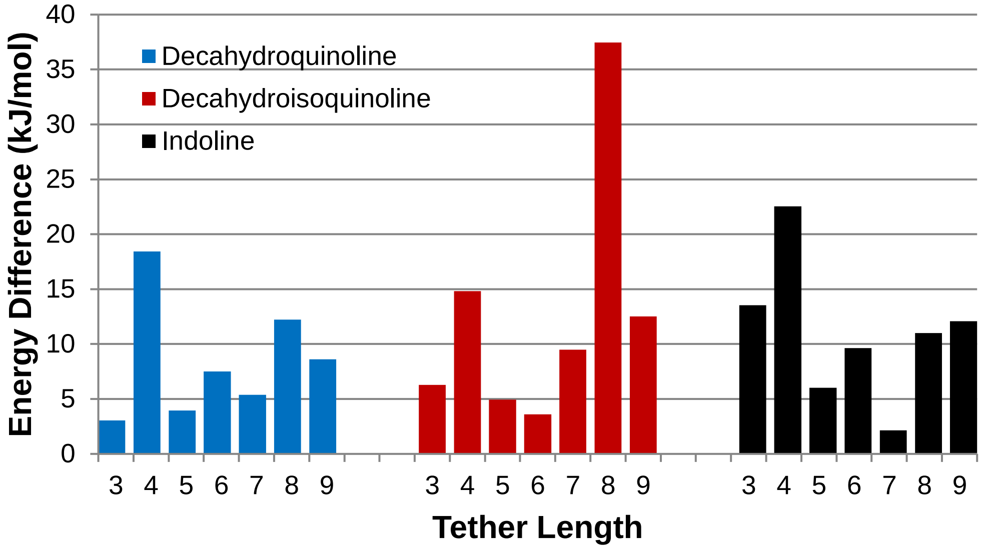


Fig. 8: Graph of isomerization-state energy differences for tether lengths 3 to 9 for three nitrogen heterocycle functional groups, depicted in Fig. 7(a-c). Note that a small isomerization-state energy difference is ideal, as it yields the highest bistability.

For spirooxazines with decahydroquinoline and indoline functional groups, an odd-even pattern is seen where the molecules with an even number of carbons making up its alkyl tether display a higher isomerization-state energy difference than that of the preceding odd tether length. This pattern has emerged in previous research with azobenzenes and is also a common phenomenon in LC materials, possibly due to steric effects caused by the folding of the alkyl chain [1].

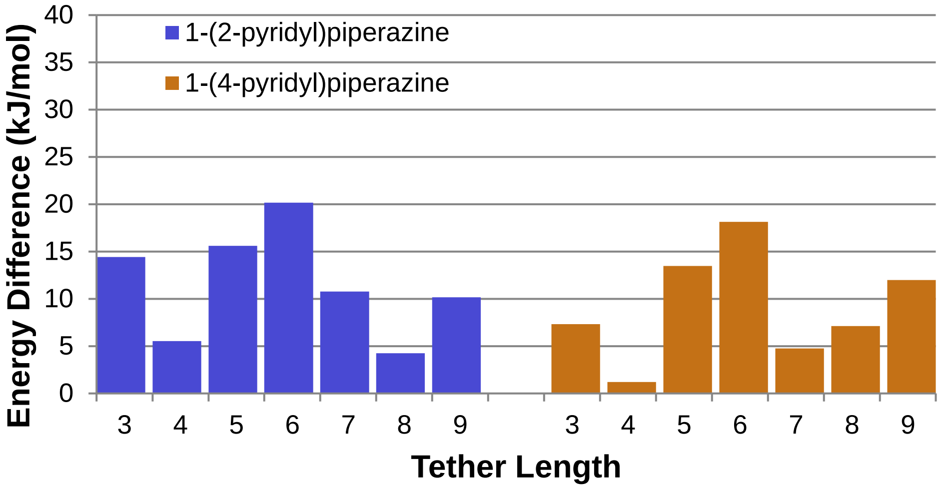


Fig. 9: Same as Fig. 8, but for substituted piperazine functional groups as depicted in Fig. 7(d-e).

The substituted piperazine functional groups of Fig. 7(d-e) also displayed promising isomerization-state energy differences, as seen in Fig. 9, although no similar odd-even pattern is evident. Notably, the spirooxazine molecule with a 1-(4-pyridyl)piperazine functional group and tether length of 4 yielded the smallest isomerization-state energy difference in this investigation of approximately 1.2 kJ/mol.

As previously described, transition state analysis was performed for molecules with an isomerization-state energy difference of less than 5 kJ/mole in order to gain further insight into the molecule's bistability by modeling the activation energy of the molecules' isomerization. These results are displayed in Table 1.

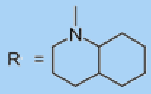
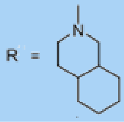
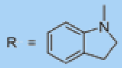
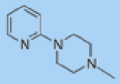
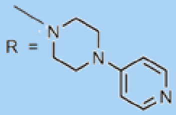
Terminal group	Tether length	Terminal group	Activation energy (kJ/mol)
Decahydroquinoline	3		**79.2**
Decahydroquinoline	5		**182.6**
Decahydroisoquinoline	5		**80.6**
Decahydroisoquinoline	6		**70.6**
Indoline	7		**68.8**
1-(2-pyridyl)piperazine	8		**85.9**
1-(4-pyridyl)piperazine	4		**78.0**
1-(4-pyridyl)piperazine	7		**57.7**

Table 1: Activation energies for selected molecules

In general, activation energies ranged from approximately 60 to 80 kJ/mol with the exception of the spirooxazine molecule with a decahydroquinoline terminal group and tether length of five, whose activation energy (183 kJ/mol) was unusually high. However, the transition state search for this molecule returned three imaginary vibrational frequencies, when the transition state should only have one. Although two of the frequencies were small relative to the other, different options are being explored in the transition state search, for example quadratic synchronous transit (QST), to further examine this result. However, QST requires one to make a “guess” at the transition state structure as input; in this case, the transition state structure is relatively unknown.

Other than this outlier, the results displayed in Table 1 helped to identify the most promising candidate molecule, the spirooxazine molecule with a 1-(4-pyridyl)piperazine functional group and tether length of 4, noted in the discussion of Fig. 9. Computational modeling of this molecule demonstrated both a low isomerization-state energy difference and significant activation energy, characteristics that combine for the high bistability necessary for molecules in a photoswitchable alignment layer. Although this molecule appears to be the most promising, many of the other molecules selected for transition state analysis display similar characteristics, and will be further examined experimentally for confirmation of their suitability.

5. Conclusions

Based on computational modeling, spirooxazine appears to be a highly promising chromophore for use in photoalignment materials. The vast majority of the molecules examined displayed isomerization-state energy differences of less than 25 kJ/mol, with several demonstrating extremely low isomerization-state energy differences of less than 5 kJ/mol. Furthermore, the molecules that qualified for transition state analysis also displayed significant activation energies, which, in combination with the low isomerization-state energy differences, are indicative of a high bistability as shown by Fig. 5. Of the molecules modeled, spirooxazine with a 1-(4-pyridyl)piperazine functional group and tether length of 4 appears to be the most promising. Not only did it display the lowest isomerization-state energy difference, but transition state analysis also yielded a significant activation energy; both of these characteristics yield high bistability, and the larger functional group should be able to more effectively redirect the orientation of the LC materials.

In the future, additional methods of transition state analysis, for example QST, will be explored to corroborate the abnormal result of spirooxazine with a decahydroquinoline functional group and tether length of 5. It is also hoped to explore other backbones in addition to methacrylate to examine the effect of the backbone on the molecule’s bistability. Potential backbone candidates for such research include acrylamide (which has been modeled extensively with azobenzenes) and siloxane.

The computational results described in this work are intended to guide the synthesis of molecules for use in photoalignment materials. In the future, experimental corroboration of this modeling is necessary before further development is done.

6. Acknowledgements

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