SYNTHESIS AND CHARACTERIZATION OF AZOBENZENE BASED COMPOUNDS FOR THEIR PHOTO-INDUCED EFFECTS

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Thesis submitted in fulfilment of the requirements
for the award of the degree of
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LIST OF EQUATION

LIST OF SYMBOLS

α	alpha
β	beta
δ	chemical shift
Cr	crystalline
^{o}C	degree centigrade
Equi	equivalence
υ	frequency
g	gram
Hz	hertz
H	hour
I	isotropic
K	kilo
L	litre
λ_{max}	maximum wavelength
MHz	mega hertz
µm	micrometre
mg	milligram
mL	millilitre
mmol	millimole
mW	milliwatt
mol	mole
mol L^{-1}	mole per litre
nm	nanometre
N	nematic
N	normality/normal
cm^{-1}	per centimetre
%	percentage
sec	second
cm^{2}	square of centimetre
λ	wavelength

LIST OF ABBREVIATIONS

Me_2CO	acetone
Ar	aromatic
^{13}C NMR	carbon nuclear magnetic resonance
$CHCl_3$	chloroform
CE	conversion efficiency
J	coupling constant
$(CD_3)_2CO$	deuterated acetone
$CDCl_3$	deuterated chloroform
DMSO-d6	deuterated dimethyl sulphoxide
CH_2Cl_2	dichloromethane
DCC	dicyclohexyl carbamide
DSC	differential scanning calorimetry
DMAP	dimethyl aminopyridine
d	doublet
dd	doublet of doublet
EtOH	ethanol
EtOAc	ethyl acetate
FAB+	fabrication plus
HCl	hydrochloric acid
H-bond	hydrogen bond
ITO	indium tin oxide
IR	infrared
MS	mass spectra
m/z	mass to charge ratio
MLC 6873-100	merck liquid crystal-commercial
MeOH	methanol
M^+	molecular ion
m	multiplet
pet	petroleum
POM	polarizing optical microscope
KBr	potassium bromide

pH	power of hydrogen
^{1}H NMR	proton nuclear magnetic resonance
R_f	retention factor
SiO_2	silica gel
s	singlet
NaOH	sodium hydroxide
TLC	thin layer chromatography
t	triplet
UV	ultraviolet
Vis	visible
XRD	X-ray diffraction

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ABSTRACT

Photonics, in which photo-induced effect can be controlled by light as stimulus has attracted a lot of attentions due to their variety of applications ranging from photonic industries to electronic computer technologies. Among them, optical storage system is a unique subject in which light illumination can alter the molecular structure drastically. These tuning structural property relations are extremely important to fabricate the optical storage devices. Although various light sensitive azobenzene derivatives are available in literature, no detail investigation has been carried out in terms of their controllable photo-induced effects with respect to structure-property relationship. Organic synthesis is a perfect tool, which can manipulate the molecular structure easily to get the desired compounds of azobenzene derivatives by incorporating several functional groups in the molecular architecture. This study gives an idea about the molecular structure and functional groups in azobenzene compounds to vary the time duration of photo-induced effects. Then, evaluated the photo-induced effects and liquid crystalline properties of the synthesized azobenzene compounds such as amides, aliphatic/aromatic spacers, phenol/anisol, fluorine with esters, isoflavones, halogens and siloxanes. The variation observed in the photo-induced effects of the respective compounds in terms of physical and chemical properties such as hydrogen bonding , electron withdrawing effect, hyper conjugation, flexibility, polarity, molecular symmetry, asymmetric effect, photo-crosslinking and electropositive nature. Particularly, amides, aliphatic/aromatic spacers, phenol/anisol, fluorine substituted esters, halogens and siloxane substituted azobenzene derivatives showed long duration of thermal back relaxation due to the action of hydrogen bonding effect, flexibility, polarity, molecular symmetry, photo-crosslinking and electropositive nature. These compounds with long duration of thermal back relaxation are suitable for optical storage technology. On the other hand, isoflavone based azobenzene compounds showed fast photo-response, due to the presence of asymmetric effect in the molecular system. Hence, these isoflavone based azobenzene derivatives are useful to fabricate molecular switches. However, other light sensitive compounds such as, chalcones, stilbenes and imines exhibited lack of photo-induced effects compare to azobenzene compounds. Tacitly, chalcones, stilbenes and imine did not show interesting photo-induced effects as compared to azobenzene compounds. Thus, azobenzene derivatives with various molecular structures and functional groups are suitable to evaluate the photo-induced effects. Also, azobenzene compounds are suitable for optical storage device fabrication. Nevertheless, amides, aliphatic/aromatic spacers, fluorine substituted esters and halogens substituted azobenzene derivatives were liquid crystals. Particularly, these compounds showed nematic and smectic liquid crystal phases. But, chalcones, stilbenes and imine derivatives did not showed liquid crystallinity. The optical storage device was fabricated using **20a,** azobenzene compound substituted by olefinic group. The resolution and sharp edges of the letters and pattern, which are stored in the fabricated optical storage device, are showing the novelty of this work. Thus, azobenzene derivatives can be extensively useful for photo-induced optical storage technology.

ABSTRAK

Fotonik, merupakan photo-induced yang dapat dikawal dengan menggunakan rangsangan daripada cahaya telah menarik banyak perhatian kerana aplikasinya yang sangat meluas dalam industri fotonik hinggalah kepada teknologi komputer. Peranti simpanan optikal merupakan sistem yang sangat unik dimana pencahayaan iluminasi boleh mengubah struktur molekul secara drastik. Sifat pengubahsuaian ciri-ciri struktur adalah sangat penting untuk menghasilkan peranti simpanan optik. Walaupun banyak derivatif azobenzena yang sensitif terhadap cahaya telah dilaporkan, tetapi tiada kajian yang terperinci dijalankan dari segi kebolehan mengawal kesan photo-induced berkenaan dengan hubungan sifat struktur. Sintesis organik adalah cara yang terbaik dimana cara ini dapat memanipulasi struktur molekular dengan mudah untuk mendapatkan produk derivatif azobenzena yang diingini dengan menggabungkan beberapa kumpulan berfungsi.Kajian ini memberikan idea mengenai struktur molekular dan kumpulan berfungsi di dalam sebatian azobenzena untuk mengubah tempoh masa kesan photo-induced. Kemudian penilaian kesan photo-induced dan sifat-sifat kristal cecair telah dibuat terhadap sebatian azobenzena yang telah disintesis seperti amida, spacer aromatik/alifatik, fenol/anisol, florin dengan ester, isoflavon, halogen dan siloksan. Kepelbagaian yang diperhatikan pada kesan photo-induced diterangkan dengan ciri-ciri fizikal dan kimia pada setiap sebatian. Sifat-sifat fizikal dan kimia tersebut adalah kesan daripada ikatan hidrogen, kesan elektron penarik balik, hyper conjugation, fleksibiliti, kepolaran, molekular simetri, kesan asimetrik, photo-crosslinking dan sifat elektropositif. Terutamanya bagi amida, spacer alifatik/aromatik, fenol/anisol, florin pengganti ester, halogen dan siloksan pengganti derivatif azobenzena menunjukkan jangka masa yang lama untuk keadaan terma rehat berbalik disebabkan oleh kesan ikatan hidrogen, fleksibiliti, kepolaran, molekular simetri, photo-crosslinking dan sifat elektropositif. Sebatian dengan keadaan terma rehat berbalik yang panjang sesuai untuk teknologi simpanan optik. Sebaliknya, isoflavon berasaskan sebatian azobenzena menunjukkan tindak balas cahaya yang cepat disebabkan kehadiran kesan asimetrik di dalam sistem molekular. Oleh itu, isoflavon berasaskan derivatif azobenzena adalah berguna untuk menyediakan molecular switches. Bagaimanapun, sebatian lain yang sensitif terhadap cahaya seperti calkon, stilben dan imina disintesis untuk membandingkan kesan photo-induced dengan sebatian azobenzena. Jelas dilihat calkon, stilben dan dan imina tidak menunjukkan kesan photo-induced yang menarik jika dibandingkan dengan sebatian azobenzena. Oleh itu, derivatif azobenzena dengan pelbagai struktur molekular dan kumpulan berfungsi adalah sesuai untuk menilai kesan photo-induced. Selain itu sebatian azobenzena adalah sesuai untuk menghasilkan peranti simpanan optik. Namun, amida, spacer alifatik/aromatik florin pengganti ester dan halogen menunjukkan fasa kristal cecair nematik dan smektik. Tetapi calkon, stilben dan imina tidak menunjukkan kristal cecair. Peranti simpanan optik dihasil menggunakan sebatian azobenzena **20a,** diganti dengan kumpulan olefin. Resolusi dan sisi yang tajam pada huruf dan corak yang mana disimpan dalam peranti simpanan optik yang dihasil menunjukkan keaslian pada kajian ini. Kesimpulannya, derivatif azobenzena boleh digunakan secara meluas untuk teknologi photo-induced simpanan optikal.

REFERENCES

Abdel-Halim, S. T., Abdel-Kader, M. H., and Steiner, YU. E. 1988. Thermal cis-trans isomerization of solvatochromic merocyanines: linear correlations between solvent polarity and adiabatic and diabatic transition energies. *The Journal of Physical Chemistry*, **92**(19): 4324-4328.

Aliaga, C., Park, J. ., amada, ., Lee, H. S., Tsung, C., ang, P., and Somorjai, G. A. 2009. Capping Agents from Pt Nanoparticles by UV-Ozone Treatment. *Jouranl of Physical Chemistry*, **113**: 6150-6155.

Altoè, P., Bernardi, F., Conti, I., Garavelli, M., Negri, F., and Orlandi, G. 2007. Light driven molecular switches: Exploring and tuning their photophysical and photochemical properties. *Theoretical Chemistry Accounts*, **117**(5-6): 1041-1059.

Amaranatha Reddy, R., Baumeister, YU., Keith, C., Hahn, H., Lang, H., and Tschierske, C. 2007. Influence of the core structure on the development of polar order and superstructural chirality in liquid crystalline phases formed by silylated bent-core molecules: lateral substituents. *Journal Material Chemistry*, **17**(5): 62-75.

Aneela, R., Praveen, P. L., and Ojha, D. P. 2012. Role of configurational entropy on ordering and phase organization of nematic liquid crystals-A molecular model. *Journal of Molecular Liquids*, **166**: 70-75.

Apeloig, . 2004. Theoretical Aspects of Organosilicon Compounds. In Organic Silicon Compounds. *John Wiley and Sons Limited*, **1-2**(1989): 57-225.

Asano, T., Okada, T., Shinkai, S., Shigematsu, K., Kusano, ., and Manabe, O. 1981. Temperature and Pressure Dependences of Thermal Cis-Trans Isomerization of Azobenzenes Which Evidence an Inversion Mechanism. *Journal of the American Chemical Society*, **103**(19): 5161-5165.

Asano, T., ano, T., and Okada, T. 1982. Mechanistic study of thermal Z-E isomerization of azobenzenes by high-pressure kinetics. *Journal of the American Chemical Society*, **104**(18): 4900-4904.

Balamurugan, S., Yeap, G. ., Mahmood, W. A. K., Tan, P. L., and Cheong, K. . 2014. Thermal and photo reversible gel-sol transition of azobenzene based liquid crystalline organogel. *Journal of Photochemistry and Photobiology A: Chemistry*, **278**: 19-24.

Bandara, H. M. D., and Burdette, S. C. 2012. Photoisomerization in different classes of azobenzene. *Chemical Society Reviews*, **41**(5): 1809-1825.

Bandara, H. M. D., Friss, T. R., Enriquez, M. M., Isley, W., Incarvito, C., Frank, H., and Burdette, S. C. 2010. Proof for the concerted inversion mechanism in the trans-cis Isomerization of azobenzene using hydrogen bonding to induce isomer locking. *Journal of Organic Chemistry*, **75**: 4817-4827.

Bang, C. YU., Shishido, A., and Ikeda, T. 2007. Azobenzene Liquid Crystalline Polymer for Optical Switching of Grating Waveguide Couplers with a Flat Surface. *Macromolecular Rapid Communications*, **28**(9): 1040-1044.

Banghart, M. R., Mourot, A., Fortin, D. L., ao, J. Z., Kramer, R. H., and Trauner, D. 2009. Photochromic Blockers of Voltage-Gated Potassium Channels. *Angewandte Chemie International Edition*, **48**(48): 9097-9101.

Banghart, M., Borges, K., Isacoff, E., Trauner, D., and Kramer, R. H. 2004. Light-activated ion channels for remote control of neuronal firing. *Nature Neuroscience*, **7**(12): 1381-1386.

Barbero, G., Evangelista, L. R., and Komitov, L. 2002. Photomanipulation of the anchoring strength of a photochromic nematic liquid crystal. *Physical Review E*, **65**(4): 41719-41726.

Bartels, E., Wassermann, N. H., and Erlanger, B. F. 1971. Photochromic activators of the acetylcholine receptor. *Proceedings of the National Academy of Sciences of the United States of America*, **68**(8): 1820-1823.

Basch, H. 1967. Electronic States of the Amide Group. *The Journal of Chemical Physics*, **47**(4): 1201-1206.

Bautista, A. D., Appelbaum, J. S., Craig, C. J., Michel, J., and Schepartz, A. 2010. Bridged beta 3-Peptide Inhibitors of P53-HDM2 complexation: Correlation between affinity and cell permeability. *Journal of the American Chemical Society*, **132**(9): 2904-2906.

Beharry, A. A., and Woolley, G. A. 2011. Azobenzene photoswitches for biomolecules. *Chemical Society Reviews*, **40**(8): 4422-4437.

Benniston, A. C., Harriman, A., and McAvoy, C. 1998. Effect of resonance polarity on the rate of isomerization of merocyanine dyes. *Journal of the Chemical Society, Faraday Transactions*, **94**(4): 519-525.

Besharati-Seidani, T., and Mahmoodi, N. O. 2013. Synthesis of new bicyclic aziridines containing chalcone analogs and investigation of their photochromic properties. *Bull Korean Chemical Society*, **34**: 875-883.

Bhagavath, P., Mahabaleshwara, S., Bhat, S. G., Potukuchi, D. M., Chalapathi, P. V., and Srinivasulu, M. 2013. Mesomorphic thermal stabilities in supramolecular liquid crystals: Influence of the size and position of a substituent. *Journal of Molecular Liquids*, **186**: 56-62.

Binzet, G., Flörke, YU., Külcü, N., and Arslan, H. 2009. 4-Bromo-N-(diethyl-carbamothio-yl)-benzamide. *Acta Crystallographica Section E: Structure Reports Online*, **65**: 427-428.

Biswas, N., and Umapathy, S. 1995. Spectrum and resonance Raman excitation profiles. *Chemical Physics Letters*, **261**(4): 3-8.

Böckmann, M., Doltsinis, N. L., and Marx, D. 2010. Nonadiabatic hybrid quantum and molecular mechanic simulations of azobenzene photoswitching in bulk liquid environment. *Journal of Physical Chemistry A*, **114**(2), 745-754.

Bockmann, M., Marx, D., Peter, C., Site, L. D., Kremer, K., and Doltsinis, N. L. 2011. Multiscale modelling of mesoscopic phenomena triggered by quantum events: light-driven azo-materials and beyond. *Physical Chemistry Chemical Physics*, **13**(17): 7604-7621.

Bortolus, P., and Monti, S. 1979. Cis-trans photoisomerization of azobenzene. Solvent and triplet donors effects. *Journal of Physical Chemistry*, **83**(6): 648-652.

Brode, W., Gould, J., and Wyman, G. 1952. The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. Phototropism and cis-trans Isomerism in Aromatic Azo Compounds1. *Journal of the American Chemical Society*, **74**(9): 4641-4646.

Brown, C. J. 1966. A refinement of the crystal structure of azobenzene. *Acta Crystallographica*, **21**(1): 146-152.

Brzozowski, L. 2001. Azobenzenes for photonic network applications: Third-order nonlinear optical properties. *Journal of Materials Science: Materials in Electronics*, **12**: 483-489.

Bushuyev, O. S., Tomberg, A., Friščić, T., and Barrett, C. J. 2013. Shaping crystals with light: Crystal-to-crystal isomerization and photomechanical effect in fluorinated azobenzenes. *Journal of the American Chemical Society*, **135**(34): 12556-12559.

Butcher, R. J., athirajan, H. S., Sarojini, B. K., Narayana, B., and Vijaya Raj, K. K. 2006. 1, 5-Bis (4-chlorophenyl) penta-1, 4-dien-3-one. *Acta Crystallographica Section E: Structure Reports Online*, **62**(5): o1973-o1975.

Cabaleiro-Lago, E. M., Peña-Gallego, Á., and Rodríguez-Otero, J. 2008. Study of the interaction in clusters formed by phenol and CH3X (X = CN, F, Cl) molecules. *The Journal of Chemical Physics*, **128**(19): 194311-194318.

Cattaneo, P., and Persico, M. 1999. An abinitio study of the photochemistry of azobenzene. *Physical Chemistry Chemical Physics*, **1**(20), 4739-4743.

Cembran, A., Bernardi, F., Garavelli, M., Gagliardi, L., and Orlandi, G. 2004. On the Mechanism of the cis-trans Isomerization in the Lowest Electronic States of Azobenzene : S_0 , S_1 , and T_1. *Journal of the American Chemical Society*, **126**(8), 3234-3243.

Chang, C. W., Lu, . C., Wang, T. Te, and Diau, E. W. G. 2004. Photoisomerization dynamics of azobenzene in solution with S1 excitation: A femtosecond fluorescence anisotropy study. *Journal of the American Chemical Society*, **126**(29): 10109-10118.

Chowdary, P. D., and Umapathy, S. 2008. Ultrafast dynamics and photochemistry of π→π* excited trans-azobenzene: A comprehensive analysis of resonance Raman intensities. *Journal of Raman Spectroscopy*, **39**(11), 1538-1555.

Ciccone, S., and Halpern, J. 1959. Catalysis of the cis-trans isomerization of Azobenzehte by acids and Cupric salts. *Journal of Chemistry*, **37**: 1903-1910.

Ciminelli, C., Granucci, G., and Persico, M. 2004. The Photoisomerization Mechanism of Azobenzene: A Semiclassical Simulation of Nonadiabatic Dynamics. *Chemistry An European Journal*, **10**(9): 2327-2341.

Coelho, P. J., Castro, M. C. R., Fonseca, M. C., and Raposo, M. M. M. 2012. Photoswitching in azo dyes bearing thienylpyrrole and benzothiazole heterocyclic systems. *Dyes and Pigments*, **92**(1): 745-748.

Conti, I., Conti, I., Garavelli, M., Garavelli, M., Orlandi, G., and Orlandi, G. 2008. The Different Photoisomerization Efficiency of Azobenzene in the Lowest n→π*and π→π* singlets: The orle of a Phantom State. *Journal of the American Chemical Society*, **130**(16): 5216-5230.

Cook, A. G., Wardell, J. L., Brooks, N. J., Seddon, J. M., Martínez-Felipe, A., and Imrie, C. T. 2012. Non-symmetric liquid crystal dimer containing a carbohydrate-based moiety. *Carbohydrate Research*, **360**: 78-83.

Crecca, C. R., and Roitberg, A. E. 2006. Theoretical study of the isomerization mechanism of azobenzene and disubstituted azobenzene derivatives. *Journal of Physical Chemistry A*, **110**: 8188-8203.

Curtin, D. ., Grubbs, E. J., and Mccarty, C. G. 1966. Uncatalysed *syn-anti* Isomerization of Imines, Oxime Ethers and Haloimines. *Journal of the American Chemical Society*, **18**(12): 2775-2786.

Dandapat, M., and Mandal, D. 2015. Photoisomerization and reorientational dynamics of DTDCI in AOT/alkane reverse micelles containing non-aqueous polar liquids. Photochemical and Photobiological Science, **14**(2): 378-386.

Demus, D., Goto, ., Sawada, S., Nakagawa, E., Saito, H., and Tarao, R. 1995. Trifluorinated Liquid Crystals for TFT Displays. *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, **260**(1): 1-21.

Diau, E. W. G. 2004. A New Trans to Cis Photoisomerization Mechanism of Azobenzene on the S_1 Surface. *Journal of Physical Chemistry A*, **108**(6): 950-956.

Dickey, J. B., Towne, E. B., Bloom, M. S., Taylor, G. J., Hill, H. M., Corbitt, R. A., and Hedberg, D. G. 1953. Effect of fluorine substitution on color and fastness of monoazo dyes. *Industrial and Engineering Chemistry*, **45**(8): 1730-1734.

Dong, R., Zhu, B., Zhou, ., an, D., and Zhu, X. 2013. Reversible photoisomerization of azobenzene-containing polymeric systems driven by visible light. *Polymer Chemistry*, **4**(4): 912-915.

Dou, ., Hu, ., Yuan, S., Wu, W., and Tang, H. 2009. Photoisomerization of Azobenzene Studied By Semiclassical Dynamics Simulation. *Molecular Physics*, **107**(2): 181-190.

Dürr, H., and Bouas-Laurent, H. 2003. Photochromism: Molecules and Systems: Molecules and Systems. *Gulf Professional Publishing*, **265**(1): 231-232.

Dyck, R. H., and McClure, D. S. 1962. Ultraviolet Spectra of Stilbene, Monohalogen Stilbenes, and Azobenzene and the trans to cis Photoisomerization Process. *The Journal of Chemical Physics*, **36**(9): 2326-2345.

Eremin, A., and Jákli, A. 2013. Polar bent-shape liquid crystals-from molecular bend to layer splay and chirality. *Soft Matter*, **9**(3): 615-637.

Escudero, D., Trupp, S., Bussemer, B., Mohr, G. J., and González, L. 2011. Spectroscopic properties of azobenzene-based pH indicator dyes: A quantum

chemical and experimental study. *Journal of Chemical Theory and Computation*, **7**: 1062-1072.

Evangelio, E., Saiz-Poseu, J., Maspoch, D., Wurst, K., Busque, F., and Ruiz-Molina, D. 2008. Synthesis, X-ray Structure and Reactivity of a Sterically Protected Azobisphenol Ligand: On the Quest for New Multifunctional Active Ligands. *European Journal of Inorganic Chemistry*, **2008**(14): 2278-2285.

Fattal, E., Rojas, J., Roblot-Treupel, L., Andremont, a., and Couvreur, P. 1991. Antimicrobial Activity. *Journal of Microencapsulation*, **8**(1): 29-36.

Fernández, R., Mondragon, I., Sanfelice, R. C., Pavinatto, F. J., Oliveira, O. N., Oyanguren, P., and Galante, M. J. 2013. Optical storage in azobenzene-containing epoxy polymers processed as Langmuir Blodgett films. *Materials Science and Engineering C*, **33**(3): 1403-1408.

Ferri, V., Elbing, M., Pace, G., Dickey, M. D., Zharnikov, M., Samorì, P., and Rampi, M. A. 2008. Light-Powered Electrical Switch Based on Cargo-Lifting Azobenzene Monolayers. *Angewandte Chemie International Edition*, **47**(18): 3407-3409.

Fischer, E. 1960. Temperature Dependence of Photoisomerization Equilibria Part I and the Azonaphthalenes. *Journal of the American Chemical Society*, **82**(6): 3249-3252.

Forber, C. L., Kelusky, E. C., Bunce, N. J., and Zerner, M. C. 1985. Electronic Spectra of cis- and trans-Azobenzenes: Consequences of Ortho Substitution. *Journal of the American Chemical Society*, **107**(15): 5884-5890.

Franz, A. K., and Wilson, S. O. 2013. Organosilicon Molecules with Medicinal Applications. *Journal of Medicinal Chemistry*, **56**(2): 388-405.

Fujino, T., and Tahara, T. 2000. Picosecond Time-Resolved Raman Study of trans-Azobenzene. *The Journal of Physical Chemistry A*, **104**(18): 4203-4210.

Fujino, T., Arzhantsev, S. ., and Tahara, T. 2001. Femtosecond Time-Resolved Fluorescence Study of Photoisomerization of trans -Azobenzene. *Journal of Physical Chemistry A*, **105**(35): 8123-8129.

Fujino, T., Arzhantsev, S. ., and Tahara, T. 2002. Femtosecond/Picosecond Time-Resolved Spectroscopy of trans-Azobenzene: Isomerization Mechanism Following S_2-S_0 Photoexcitation. *Bulletin of the Chemical Society of Japan*, **75**(5): 1031-1040.

Gagliardi, L., Orlandi, G., Bernardi, F., Cembran, A., and Garavelli, M. 2004. A theoretical study of the lowest electronic states of azobenzene: the role of torsion coordinate in the cis-trans photoisomerization. *Theoretical Chemistry Accounts: Theory, Computation and Modeling-Theoretica Chimica Acta*, **111**: 363-372.

Garavelli, M., Bernardi, F., Robb, M. a., and Olivucci, M. 1999. The short-chain acroleiniminium and pentadieniminium cations: Towards a model for retinal photoisomerization. *Journal of Molecular Structure: Theochemistry*, **463**: 59-64.

Garcia-Amorós, J., Finkelmann, H., and Velasco, D. 2011. Increasing the Isomerisation Kinetics of Azo Dyes by Chemical Bonding to Liquid-Crystalline Polymers. *Chemistry-A European Journal*, **17**(23): 6518-6523.

Garcia-Iriepa, C., Marazzi, M., Frutos, L. M., and Sampedro, D. 2013. E/Z Photochemical switches: syntheses, properties and applications. *RSC Advances*, **3**(18): 6241-6266.

Gegiou, D., Muszkat, K. a, and Fischer, E. 1968. Temperature dependence of photoisomerization. VI. Viscosity effect. *Journal of the American Chemical Society*, **90**(5): 12-18.

Geyer, M., Karlsson, O., Baus, J. A., Wellner, E., and Tacke, R. 2015. Si- and C-Functional Organosilicon Building Blocks for Synthesis Based on 4-Silacyclohexan-1-ones Containing the Silicon Protecting Groups MOP (4-Methoxyphenyl), DMOP (2,6-Dimethoxyphenyl), or TMOP (2,4,6-Trimethoxyphenyl). *The Journal of Organic Chemistry*, **80**(11): 5804-5811.

Gimarc, B. M. 1970. Shapes of simple polyatomic molecules and ions. I. Series HAAH and BAAB. *Journal of the American Chemical Society*, **92**(2): 266-275.

Goodby, J. W., Gortz, V., Cowling, S. J., Mackenzie, G., Martin, P., Plusquellec, D., and Fitremann, J. 2007. Thermotropic liquid crystalline glycolipids. *Chemical Society Reviews*, **36**(12): 1971-2032.

Gorostiza, P., and Isacoff, E. . 2008. Optical switches for remote and noninvasive control of cell signaling. *Science*, **322**(5900): 395-399.

Goswami, D., Sinha, D., Debnath, A., Mandal, P. K., Gupta, S. K., Haase, W., and Dabrowski, R. 2013. Molecular and dynamical properties of a per fl uorinated liquid crystal with direct transition from ferroelectric SmC phase to isotropic phase. *Journal of Molecular Liquids*, **182**: 95-101.

Gowda, B. T., Foro, S., and Fuess, H. 2008. 2-Chloro-N-(2,3-dichlorophenyl)acetamide. *Acta Crystallographica Section E: Structure Reports Online*, **64**(1): 419-428.

Granucci, G., and Persico, M. 2007. Excited state dynamics with the direct trajectory surface hopping method: Azobenzene and its derivatives as a case study. *Theoretical Chemistry Accounts*, **117**: 1131-1143.

Haberfield, P., and Lux, M. S. 1975. Enthalpies of Solvent Transfer of the Transition States in the Cis-Trans Isomerization of Azo Compounds. The Rotation Vs the Nitrogen Inversion Mechanism. *Journal of the American Chemical Society*, **97**(20): 5804-5806.

Hagen, R., and Bieringer, T. 2001. Photoaddressable Polymers for Optical Data Storage. *Advanced Materials*, **13**(23): 1805-1810.

Hamm, P., Ohline, S. M., and Zinth, W. 1997. Vibrational cooling after ultrafast photoisomerization of azobenzene measured by femtosecond infrared spectroscopy. *The Journal of Chemical Physics*, **106**(2): 519-529.

Harrison, W. T. A., Sarojini, B. K., Vijaya Raj, K. K., athirajan, H. S., and Narayana, B. 2006. A redetermination of 1, 5-bis (4-methoxyphenyl) penta-1, 4-dien-3-one at

120 K. *Acta Crystallographica Section E: Structure Reports Online*, **62**(4): o1522-o1523.

Hartley, G. S. 1937. The cis-form of azobenzene. *Nature*, **140**: 281-288.

He, T., Cheng, ., Du, ., and Mo, . 2007. Z-scan determination of third-order nonlinear optical nonlinearity of three azobenzenes doped polymer films. *Optics Communications*, **275**: 240-244.

Hegde, G., Alla, R. A., Matharu, A., and Komitov, L. 2013. Azo containing thiophene based prop-2-enoates for photoalignment of a nematic liquid crystal. *Journal of Materials Chemistry C*, **1**(22): 3600-3605.

Hegde, G., Kozenkov, V. M., Chigrinov, V. G., and Kwok, H. S. 2009. Photoisomerization in Photoaligned Azo Dyes Exhibiting Photostability. *Molecular Crystals and Liquid Crystals*, **507**(1): 1542-1406.

Henzl, J., Mehlhorn, M., Gawronski, H., Rieder, K. H., and Morgenstern, K. 2006. Reversible cis-trans Isomerization of a Single Azobenzene Molecule. *Angewandte Chemie International Edition*, **45**(4): 603-606.

Hicks, J. M., Vandersall, M. T., Sitzmann, E. V, and Eisenthal, K. B. 1987. Polarity-Dependent Babriers and the Photoisomerization Dynamics of Molecules in Solution. *Chemical Physics Letters*, **135**(4): 413-420.

Hikmet, R. A. M., Lub, J., and Maassen van der Brink, P. 1992. Structure and mobility within anisotropic networks obtained by photopolymerization of liquid crystal molecules. *Macromolecules*, **25**(16): 4194-4199.

Hochstrasser, R. M. 1962. Absorption Spectrum of Phenazine Single Crystals at 77° and 4.2° K in the Region of the n→π* Transition. *The Journal of Chemical Physics*, **36**(7): 3505-3506.

Howell, J. M. 1976. Charge Distributions and Isomer Stability of the Fluoro Derivatives of Methylenimide. *Journal of the American Chemical Society*, **98**(4): 886-887.

Ichimura, K., Oh, S. K., and Nakagawa, M. 2000. Light-driven motion of liquids on a photoresponsive surface. *Science*, **288**(5): 1624-1626.

Ikegami, T., Kurita, N., Sekino, H., and Ishikawa, . 2003. Mechanism of Cis to trans isomerization of azobenzene: Direct MD study. *Journal of Physical Chemistry A*, **107**(22): 4555-4562.

Imrie, C. T., and Henderson, P. a. 2002. Liquid crystal dimers and oligomers. *Current Opinion in Colloid and Interface Science*, **7**: 298-311.

Ishikawa, D., Ito, E., Han, M., and Hara, M. 2013. Effect of the steric molecular structure of azobenzene on the formation of self-assembled monolayers with a photoswitchable surface morphology. *Langmuir*, **29**: 4622-4631.

Ishitobi, H., Nakamura, I., Kobayashi, T., Hayazawa, N., Sekkat, Z., Kawata, S., and Inouye, . 2014. Nanomovement of Azo Polymers Induced by Longitudinal Fields. *ACS Photonics*, **1**(3): 190-197.

Itoh, M., Harada, K., Kamemaru, S., and atagai, T. 2004. Holographic Recording on Azo-benzene Functionalized Polymer Film. *Japanese Journal of Applied Physics*, **43**(7): 4968-4971.

Jaffé, H. H. 1953. A Reëxamination of the Hammett Equation. *Chemical Reviews*, **53**(2), 191-261.

Jaworska, J., Bartkiewicz, S., and Galewski, Z. 2013. Phase diagram of trans-Cis isomers for photoactive and mesogenic 4-hexyl-4^{1}-propoxyazobenzene. *Journal of Physical Chemistry C*, **117**(51): 27067-27072.

Jiang, X. L., Li, L., Kumar, J., Kim, D. ., and Tripathy, S. K. 1998. Unusual polarization dependent optical erasure of surface relief gratings on azobenzene polymer films. *Applied Physics Letters*, **72**(20): 2502-2504.

Joshi, N. K., Fuyuki, M., and Wada, A. 2014. Polarity controlled reaction path and kinetics of thermal cis-to-trans isomerization of 4-aminoazobenzene. *Journal of Physical Chemistry B*, **118**(7): 1891-1899.

Jung, B., and Theato, P. 2011. Chemical Strategies for the Synthesis of Protein-Polymer Conjugates. *Advances in Polymer Science*, **235**: 33-110.

Kakiage, K., amamura, M., Ido, E., Kyomen, T., Unno, M., and Hanaya, M. 2011. Reactivity of alkoxysilyl compounds: chemical surface modification of nano-porous alumina membrane using alkoxysilylazobenzenes. *Applied Organometallic Chemistry*, **25**(2): 98-104.

Kay, E. R., Leigh, D. A., and Zerbetto, F. 2007. Synthetic Molecular Motors and Mechanical Machines. *Angewandte Chemie International Edition*, **46**(1-2): 72-191.

Kearns, D. R. 1965. The Temperature Dependence of the cis—trans Photoisomerization of Azo Compounds: Theoretical Considerations. *The Journal of Physical Chemistry*, **69**(3): 1062-1065.

Khan, A., and Hecht, S. 2006. Towards Photocontrol over the Helix-Coil Transition in Foldamers: Synthesis and Photoresponsive Behavior of Azobenzene-Core Amphiphilic Oligo(meta-phenylene ethynylene)s. *Chemistry-An European Journal*, **12**(18): 4764-4774.

Kieffer, R., Prehm, M., Pelz, K., Baumeister, YU., Liu, F., Hahn, H., and Tschierske, C. 2009. Siloxanes and carbosilanes as new building blocks for T-shaped bolaamphiphilic LC molecules. *Soft Matter*, **5**(6): 1214-1227.

Kim, D. ., Tripathy, S. K., Li, L., and Kumar, J. 1995. Laser-induced holographic surface relief gratings on nonlinear optical polymer films. *Applied Physics Letters*, **66**(10): 1166-1173.

Kim, S. ., and Hong, J.-I. 2007. Chromogenic and Fluorescent Chemodosimeter for Detection of Fluoride in Aqueous Solution. *Organic Letters*, **9**(16): 3109-3112.

Kim, ., Phillips, J. a, Liu, H., Kang, H., and Tan, W. 2009. Using photons to manipulate enzyme inhibition by an azobenzene-modified nucleic acid probe. *Proceedings of the National Academy of Sciences of the United States of America*, **106**(23): 6489-6494.

Koshima, H., Ojima, N., and Uchimoto, H. 2009. Mechanical motion of azobenzene crystals upon photoirradiation. *Journal of the American Chemical Society*, **131**(20): 6890-6891.

Krishna prasad, S., Nair, G. G., Hegde, G., Sandhya, K. L., Shankar Rao, D. S., Lobo, C. V, and elamaggad, C. V. 2005. Photoinduced effects in nematic liquid crystals. *Phase Transitions*, **78**(6): 443-455.

Kropf, A., and Hubbard, R. 1958. The Mechanism of Bleaching Rhodopsin. *Annals of the New York Academy of Sciences*, **74**(2): 266-280.

Kuciński, K., Pawluć, P., Marciniec, B., and Hreczycho, G. 2015. Highly Selective Hydrothiolation of Unsaturated Organosilicon Compounds Catalyzed by Scandium(III) Triflate. *Chemistry-A European Journal*, **21**(13): 4940-4943.

Kumar, G., and Neckers, D. 1989. Photochemistry of azobenzene-containing polymers. *Chemical Reviews*, **89**(48): 1915-1925.

Lava, K., Binnemans, K., and Cardinaels, T. 2009. Piperidinium, piperazinium and morpholinium ionic liquid crystals. *Journal of Physical Chemistry B*, **113**(28): 9506-9511.

Lednev, I. K., e, T. Q., Hester, R. E., and Moore, J. N. 1996. Femtosecond time-resolved UV-visible absorption spectroscopy of trans-azobenzene in solution. *Journal of Physical Chemistry*, **100**(96): 13338-13341.

Lednev, I. K., e, T. Q., Matousek, P., Towrie, M., Foggi, P., Neuwahl, F. V. R., and Moore, J. N. 1998. Femtosecond time-resolved UV-visible absorption spectroscopy of trans-azobenzene: dependence on excitation wavelength. *Chemical physics letters*, **290**: 68-74.

Leigh, W. J., Frendo, D. T., and Klawunn, P. J. 1985. Organic reactions in liquid crystalline solvents. 1. The thermal cis-trans isomerization of a bulky olefin in cholesteric liquid crystalline solvents. *Canadian Journal of Chemistry*, **63**(8): 2131-2138.

Leydet, ., Batat, P., Jonusauskas, G., Denisov, S., Lima, J. C., Parola, A. J., and Pina, F. 2013. Impact of water on the cis-trans photoisomerization of hydroxychalcones. *Journal of Physical Chemistry A,* **117**(20): 4167-4173.

Li, B., Williams, B. D., and Smith, A. B. 2015. A Mild, Diastereoselective Construction of Cyclic and Spirocyclic Ketals Employing a Tandem Photoisomerization/Cyclization Tactic. *Organic letters*, **17**(1): 2014-2016.

Li, Z., Zhang, D., Weng, J., Chen, B., and Liu, H. 2014. Synthesis and characterization of photochromic azobenzene cellulose ethers. *Carbohydrate Polymers*, **99**: 748-754.

Lin, S. H., Villaeys, A. A., and Fujimura, . 1986. Advances in Multi-Photon Processes and Spectroscopy. Singapore: *World Science publishing Company*, **22**: 1-72.

Lindberg, B., Hudson, C. S., Overend, W. G., Whistler, R. L., and Mittag, T. W. 1964. Classification of Alcohols by Nuclear Magnetic Resonance Spectroscopy. *Journal of the American Chemical Society*, **87**(18), 4219-4220.

Long, M. E., and Trotter, P. J. 1981. Vibrational Manifold Considerations for the Metal Indicator Dye 2-(2-Pyridylazo)-1-Naphthol. *Applied Spectroscopy*, **35**(3): 289-292.

Loudwig, S., and Bayley, H. 2006. Photoisomerization of an individual azobenzene molecule in water: An on-off switch triggered by light at a fixed wavelength. *Journal of the American Chemical Society*, **128**(38): 12404-12405.

Lu, . C., Diau, E. W. G., and Rau, H. 2005. Femtosecond fluorescence dynamics of rotation-restricted azobenzenophanes: New evidence on the mechanism of trans-cis photoisomerization of azobenzene. *Journal of Physical Chemistry A*, **109**(10): 2090-2099.

Luboch, E., Wagner-Wysiecka, E., and Rzymowski, T. 2009. 4-Hexylresorcinol-derived hydroxyazobenzocrown ethers as chromoionophores. *Tetrahedron*, **65**: 10671-10678.

Luboch, E., Wagner-Wysiecka, E., Poleska-Muchlado, Z., and Kravtsov, V. C. 2005. Synthesis and properties of azobenzocrown ethers with electron donor, or electron donor and electron acceptor groups on benzene rings. *Tetrahedron*, **61**: 10738-10747.

Lutfor, M. R., Hegde, G., Kumar, S., Tschierske, C., and Chigrinov, V. G. 2009. Synthesis and characterization of bent-shaped azobenzene monomers: Host-guest effects in liquid crystals with azo dyes for optical image storage devices. *Optical Materials*, **32**(1): 176-183.

Lutfor, M. R., Hegde, G., Kumar, S., Tschierske, C., and Chigrinov, V. G. 2009. Synthesis and characterization of bent-shaped azobenzene monomers: Host-guest effects in liquid crystals with azo dyes for optical image storage devices. *Optical Materials*, **32**(1): 176-183.

Lutfor, M. R., Hegde, G., Yusoff, M. M., Malek, F. M. N. A., Srinivasa, H. T., and Kumar, S. 2013. New pyrimidine-based photo-switchable bent-core liquid crystals. *New Journal of Chemistry*, **37**(8): 2460-2467.

Lutfor, M. R., Yusoff, M. M., Hegde, G., Fazli, M. N., Malek, A., Samah, N. A., and Srinivasa, H. T. 2013. Synthesis of Banana-Shaped Liquid Crystals for Photoswitching Properties. *Molecular Crystals and Liquid Crystals*, **587**(1): 41-53.

Lv, J., Wang, W., Xu, J., Ikeda, T., and Yu, . 2014. Photoinduced Bending Behavior of Cross-linked Azobenzene Liquid-Crystalline Polymer Films with a Poly(oxyethylene) Backbone. *Macromolecular Rapid Communications*, **35**(14): 1266-1272.

M. Boland, G., and M. X. Donnelly, D. 1998. Isoflavonoids and related compounds. *Natural Product Reports*, **15**(3): 241-260.

Macaulay, R., Burnelle, L. a., and Sandorfy, C. 1973. Theoretical investigation of the carbon nitrogen double bond. *Theoretica Chimica Acta*, **29**(1): 1-7.

Madani, A., Beeckmanc, J., and Neytsc, K. 2013. An experimental observation of a spatial optical soliton beam and self splitting of beam into two soliton beams in chiral nematic liquid crystal. *Optics Communications*, **298**: 222-226.

Magee, J. L., Shand, W., and Eyring, H. 1941. Non-adiabatic Reactions. Rotation about the Double Bond. *Journal of the American Chemical Society*, **63**(3): 677-688.

Malkin, S., and Fischer, E. 1962. Temperature Dependence of Photoisomerization. Part II. Quantum ields of Cis ⇆ Trans Isomerizations in Azo Compounds. *The Journal of Physical Chemistry*, **66**(7): 2482-2486.

Mathews, M., and Tamaoki, N. 2008. Planar chiral azobenzenophanes as chiroptic switches for photon mode reversible reflection color control in induced chiral nematic liquid crystals. *Journal of the American Chemical Society*, **130**(7): 11409-11416.

Misra, A. K., Tripathi, P. K., and Manohar, R. 2012. Reduction of optical response time for fluorescent dye doped ferroelectric liquid crystal. *Journal of Molecular Liquids*, **175**: 67-71.

Moore, W. M., Morgan, D. D., and Stermitz, F. R. 1963. The Photochemical Conversion of Stilbene to Phenanthrene. The Nature of the Intermediate. *Journal of the American Chemical Society*, **85**(6): 829-830.

Morgante, C. G., and Struve, W. S. 1979. $S_2 \rightarrow S_0$ fluorescence in trans-azobenzene. *Chemical Physics Letters*, **68**(2): 267-271.

Mostad, A., and Rømming, C. 1971. A refinement of the crystal structure of cis-azobenzene. *Acta Chemica Scandinavica*, **25**(10): 3561-3564.

Murakami, H., Kawabuchi, a., Kotoo, K., Kunitake, M., and Nakashima, N. 1997. A light-driven molecular shuttle based on a rotaxane. *Journal of the American Chemical Society*, **119**(10): 7605-7606.

Muraoka, T., Kinbara, K., and Aida, T. 2006. Mechanical twisting of a guest by a photoresponsive host. *Nature*, **440**(7083): 512-515.

Muszkat, K. A., and Fischer, E. 1967. Structure, spectra, photochemistry, and thermal reactions of the 4a,4b-dihydrophenanthrenes. *Journal of the Chemical Society B: Physical Organic*, **17**(1): 662-678.

Nägele, T., Hoche, R., Zinth, W., and Wachtveitl, J. 1997. Femtosecond photoisomerization of cis-azobenzene. *Chemical Physics Letters*, **272**(5-6): 489-495.

Nair, G. G., Hegde, G., Prasad, S. K., and Negi, . S. 2006. Investigations of the opto-dielectric effects in the vicinity of the smectic-A, smectic-C transition. *Journal of Physics: Condensed Matter*, **18**(41): 9415-9419.

Nair, G. G., Prasad, S. K., and Hegde, G. 2004. Influence of a long-chain alkane on the photoinduced nematic-isotropic transition. *Physical Review E*, **69**(2): 21708-21714.

Namazian, M., and Coote, M. L. 2009. Gas-phase acidity, bond dissociation energy and enthalpy of formation of fluorine-substituted benzenes: A theoretical study. *Journal of Fluorine Chemistry*, **130**: 621-628.

Natansohn, A., and Rochon, P. 2002. Photoinduced Motions in Azo-Containing Polymers. *Chemical Reviews*, **102**(11): 4139-4176.

Nicodem, D. E., and de M. G. Matos, J. A. 1981. Photoisomerization of chalcone: wavelength dependence. *Journal of Photochemistry*, **15**(3): 193-202.

Norikane, ., and Tamaoki, N. 2004. Light-driven molecular hinge: A new molecular machine showing a light-intensity-dependent photoresponse that utilizes the trans-cis isomerization of azobenzene. *Organic Letters*, **6**(4): 2595-2598.

Noyce, D. S., and Jorgenson, M. J. 1963. The Isomerization of Substituted cis-Chalcones in Sulfuric Acid. Consequences of the Two Mechanisms. *Journal of the American Chemical Society*, **85**(16): 2420-2426.

Ohtani, O., Furukawa, T., Sasai, R., Hayashi, E., Shichi, T., ui, T., and Takagi, K. 2004. Effect of fluorinated ammonium counterions upon the reversibility in E-Z

photoisomerization of azobenzene ion pair films. *Journal of Material Chemistry*, **14**(2): 196-200.

Padwa, A. 1977. Photochemistry of the carbon-nitrogen double bond. *Chemical Reviews*, **77**(1): 37-68.

Parker, R. M., Gates, J. C., Rogers, H. L., Smith, P. G. R., and Grossel, M. C. 2010. Using the photoinduced reversible refractive-index change of an azobenzene co-polymer to reconfigure an optical Bragg grating. *Journal of Material Chemistry*, **20**(41): 9118-9125.

Pelzl, G., Diele, S., and Weissflog, W. 1999. Banana-Shaped Compounds-A New Field of Liquid Crystals. *Advanced Materials*, **11**(9): 707-724.

Petrov, M., Katranchev, B., Rafailov, P. M., Naradikian, H., Dettlaff-Weglikowska, YU., and Keskinova, E. 2013. Smectic C liquid crystal growth and memory effect through surface orientation by carbon nanotubes. *Journal of Molecular Liquids*, **180**: 215-220.

Petrov, V., Stanimirov, S., Petrov, I. K., Fernandes, A., De Freitas, V., and Pina, F. 2013. Emptying the ??-cyclodextrin cavity by light: Photochemical removal of the trans -chalcone of 4, 7-dihydroxyflavylium. *Journal of Physical Chemistry A*, **117**(41): 10692-10701.

Phillips, J. a., Liu, H., O'Donoghue, M. B., Xiong, X., Wang, R., ou, M., and Tan, W. 2011. Using azobenzene incorporated DNA aptamers to probe molecular binding interactions. *Bioconjugate Chemistry*, **22**: 282-288.

Poloni, C., Szymański, W., Hou, L., Browne, W. R., and Feringa, B. L. 2014. A Fast, Visible-Light-Sensitive Azobenzene for Bioorthogonal Ligation. *Chemistry-An European Journal*, **20**(4): 946-951.

Popłoński, J., Tronina, T., and Huszcza, E. 2013. Photochemical transformations of xanthohumol. *Tetrahedron Letters*, **54**: 6035-6036.

Prasad, S. K., Nair, G. G., and Hegde, G. 2005. Dynamic Self-Assembly of the Liquid-Crystalline Smectic A Phase. *Advanced Materials*, **17**(17): 2086-2091.

Prasad, S. K., Nair, G. G., and Hegde, G. 2007. Nonequilibrium liquid crystalline layered phase stabilized by light. *Journal of Physical Chemistry B*, **111**(2): 345-350.

Prasad, V., Kang, S. W., Qi, X., and Kumar, S. 2004. Photo-responsive and electrically switchable mesophases in a novel class of achiral bent-core azo compounds. *Journal of Materials Chemistry*, **14**(9): 1495-1502.

Praveen, P. L., and Ojha, D. P. 2012. Calculation of spectral shifts in UV-visible region and photo stability of thermotropic liquid crystals: Solvent and alkyl chain length effects. *Journal of Molecular Liquids*, **169**: 110-116.

Puntoriero, F., Ceroni, P., Balzani, V., Bergamini, G., and Vögtle, F. 2007. Photoswitchable dendritic hosts: A dendrimer with peripheral azobenzene groups. *Journal of the American Chemical Society*, **129**(35): 10714-10719.

Quick, M., Dobryakov, a. L., Gerecke, M., Richter, C., Berndt, F., Ioffe, I. N., and Kovalenko, S. A. 2014. Photoisomerization dynamics and pathways of trans-And cis -azobenzene in solution from broadband femtosecond spectroscopies and calculations. *Journal of Physical Chemistry B*, **118**(29): 8756-8771.

Rabek, J. F., and Rau, H. 1991. Photochemistry and photophysics. *CRC Press: E-Publishing Inc*, **4**(2): 119-201.

Radziszewski, J. G., Downing, J. W., Jawdosiuk, M., and Kovacic, P. 1985. 4-Azahomoadamant-3-ene : Spectroscopic Characterization and Photoresolution of a Highly Reactive Strained Bridgehead Imine. *Journal of the American Chemical Society*, 107(3), 594-603.

Rahman, L., Hegde, G., Sarkar, S. M., and Yusoff, M. M. 2014. Synthesis and photoswitching properties of azobenzene liquid crystals with a pentafluorobenzene terminal. *Chinese Chemical Letters*, **25**(12): 1611-1614.

Rahman, L., Kumar, S., Tschierske, C., Israel, G., Ster, D., and Hegde, G. 2009. Synthesis and photoswitching properties of bent-shaped liquid crystals containing azobenzene monomers. *Liquid Crystals*, **36**(4): 397-407.

Rahman, M. L., Hegde, G., Azazpour, M., Yusoff, M. M., and Kumar, S. 2013. Synthesis and characterization of liquid crystalline azobenzene chromophores with fluorobenzene terminal. *Journal of Fluorine Chemistry*, **156**: 230-235.

Rahman, M. L., Hegde, G., Yusoff, M. M., Malek, M. N. F. A., Srinivasa, H. T., and Kumar, S. 2013. New pyrimidine-based photo-switchable bent-core liquid crystals. *New Journal of Chemistry*, **37**(8): 2460-2467.

Rahman, M. L., Yusoff, M. M., and Kumar, S. 2014. Synthesis and photoswitching properties of liquid crystals derived from myo-inositol. *RSC Advances*, **4**(66): 35089-35098.

Rajakumar, P., Thirunarayanan, A., Raja, S., Ganesan, S., and Maruthamuthu, P. 2012. Photophysical properties and dye-sensitized solar cell studies on thiadiazole-triazole-chalcone dendrimers. *Tetrahedron Letters*, **53**: 1139-1143.

Rau, H. 1984. Further evidence for rotation in the π, π* and inversion in the n, π* photoisomerization of azobenzenes. *Journal of Photochemistry*, **26**(2): 221-225.

Rau, H. 2002. Photoisomerization of azobenzene. *Photoreactive Organic Thin Films, Germany: Elsevier*, 3-47.

Rau, H., and Luddecke, E. 1982. On the Rotation-Inversion Controry on Photoisomerization of Azobenzene. Experimental Proof of Inversion. *Journal of the American Chemical Society*, **104**(6): 1616-1620.

Rijeesh, K., Hashim, P. K., Noro, S., and Tamaoki, N. 2015. Dynamic induction of enantiomeric excess from a prochiral azobenzene dimer under circularly polarized light. *Chemical Science*, **6**(2): 973-980.

Roberts, J. D., and Caserio, M. C. 1977. Basic principles of organic chemistry-Edition II. *WA Benjamin Inclusion, New York*, ISBN 0-8053-8329-8:1504-1507.

Rodier, J. M., and Myers, A. B. 1993. cis-Stilbene photochemistry: solvent dependence of the initial dynamics and quantum yields. *Journal of the American Chemical Society*, **115**(23): 10791-10795.

Ronayette, J., Arnaud, R., Lebourgeois, P., and Lemaire, J. 1974. Isomérisation photochimique de l'azobenziine en solution. *Canadian Journal of Chemistry*, **52**(6): 1848-1852.

S. Zacharias, P., Ameerunisha, S., and R. Korupoju, S. 1998. Photoinduced fluorescence changes on E-Z isomerisation in azobenzene derivatives. *Journal of Chemical Society. Perkin Transitions*, **2**(9): 2055-2060.

Saint-Jalm, S., Miniewicz, a., Karpinski, P., Jarek-Mikulska, YU., and Galewski, Z. 2012. Photo-induced birefringence in a nematic liquid crystal mixture doped with light-switchable mesogenic azobenzene derivatives. *Journal of Molecular Liquids*, **168**: 21-27.

Satzger, H., Root, C., and Braun, M. 2004. Excited-state dynamics of trans- and cis-azobenzene after UV excitation. *Journal of Physical Chemistry A*, **108**(30): 6265-6271.

Satzger, H., Spörlein, S., Root, C., Wachtveitl, J., Zinth, W., and Gilch, P. 2003. Fluorescence spectra of trans- and cis-azobenzene-Emission from the Franck-Condon state. *Chemical Physics Letters*, **372**(1-2): 216-223.

Sauer, P., and Allen, R. E. 2008. Influence of laser pulse parameters on dynamical processes during azobenzene photoisomerization. *Journal of Physical Chemistry A*, **112**(44): 11142-11152.

Schultz, T., Quenneville, J., Levine, B., Toniolo, A., Martínez, T. J., Lochbrunner, S., and Stolow, A. 2003. Mechanism and dynamics of azobenzene photoisomerization. *Journal of the American Chemical Society*, **125**(27): 8098-8099.

Schweighauser, L., Häussinger, D., Neuburger, M., and Wegner, H. A. 2014. Symmetry as a new element to control molecular switches. *Organic and Biomolecular Chemistry*, **12**(21): 3371-9.

Seki, T., Tanaka, K., and Ichimura, K. 1998. Photopolymerization of Diacetylene Langmuir-Blodgett Films on an Azobenzene-Containing Monolayer. *Polym Journal*, **30**(8): 646-652.

Sepelj, M., Lesac, A., Baumeister, YU., Diele, S., Nguyen, H. L., and Bruce, D. W. 2007. Intercalated liquid-crystalline phases formed by symmetric dimers with an [small alpha],[small omega]-diiminoalkylene spacer. *Journal of Materials Chemistry*, **17**(12): 1154-1165.

Serra, F., and Terentjev, E. M. 2008. Effects of solvent viscosity and polarity on the isomerization of azobenzene. *Macromolecules*, **41**(3): 981-986.

Sévigny, S., Bouchard, L., Motallebi, S., and Zhao, . 2005. Azobenzene polymer stabilized ferroelectric liquid crystals: simultaneous photopolymerization and photoalignment. *Liquid Crystals*, **32**(5): 599-607.

Shannon, P. J., Gibbons, W. M., and Sun, S. T. 1994. Patterned optical properties in photopolymerized surface-aligned liquid-crystal films. *Nature*, **368**(6471): 532-533.

Shen, .-Q., and Rau, H. 1991. The environmentally controlled photoisomerization of probe molecules containing azobenzene moieties in solid poly(methyl methacrylate). *Die Makromolekulare Chemie*, **192**(4): 945-957.

Shettigar, S., Chandrasekharan, K., Umesh, G., Sarojini, B. K., and Narayana, B. 2006. Studies on nonlinear optical parameters of bis-chalcone derivatives doped polymer. *Polymer*, **47**(10): 3565-3567.

Shi, . W., Liu, X. Q., Shi, P., and Zhang, X. . 2010. Characterization of zinc-binding properties of a novel imidase from Pseudomonas putida Z-26. *Archives of Biochemistry and Biophysics*, **494**(1): 1-6.

Shinkai, S., Nakaji, T., Nishida, ., Ogawa, T., and Manabe, O. 1980. Photoresponsive crown ethers. 1. Cis-trans isomerism of azobenzene as a tool to enforce conformational changes of crown ethers and polymers. *Journal of the American Chemical Society*, **102**(14): 5860-5865.

Siampiringue, N., Guyot, G., Monti, S., and Bortolus, P. 1987. The cis→trans photoisomerization of azobenzene: an experimental re-examination. *Journal of Photochemistry*, **37**(1): 185-188.

Siewertsen, R., Neumann, H., Buchheim-Stehn, B., Herges, R., Näther, C., Renth, F., and Temps, F. 2009. Highly efficient reversible Z-E photoisomerization of a bridged azobenzene with visible light through resolved $S_1(n\rightarrow\pi^*)$ absorption bands. *Journal of the American Chemical Society*, **131**(43): 15594-15595.

Singlet, E. 1983. Geomdrical Relaxation in the Ground and Excited Singlet and Triplet States of Unprotonated Schiff Bases: Allylidenimine and Formaldimine. *Society*, **247**(10): 3388-3395.

Ster, D., Baumeister, YU., Chao, J. L., Tschierske, C., and Israel, G. 2007. Synthesis and mesophase behaviour of ionic liquid crystals. *Journal of Materials Chemistry*, **17**(32): 3393-3400.

Stewart, D., and Imrie, C. T. 1996. Synthesis and characterization of spin-labelled and spin-probed side-chain liquid crystal polymers. *Polymer*, **37**(15): 3419-3425.

Stoll, R. S., Peters, M. V., Kuhn, A., Heiles, S., Goddard, R., Bühl, M., and Hecht, S. 2009. Photoswitchable catalysts: Correlating structure and conformational dynamics with reactivity by a combined Experimental and computational approach. *Journal of the American Chemical Society*, **131**(5): 357-367.

Struve, W. S. 1977. Emission from the (n, π^*) state of azobenzene: Spectrum and ultrashort decay time. *Chemical Physics Letters*, **46**(1): 15-19.

Stuart, C. M., Frontiera, R. R., and Mathies, R. A. 2007. Excited-state structure and dynamics of cis- and trans-Azobenzene from resonance Raman intensity analysis. *Journal of Physical Chemistry A*, **111**(48): 12072-12080.

Szymański, W., Beierle, J. M., Kistemaker, H. A. V, Velema, W. A., and Feringa, B. L. 2013. Reversible Photocontrol of Biological Systems by the Incorporation of Molecular Photoswitches. *Chemical Reviews*, **113**(8): 6114-617.

Tahara, R., Morozumi, T., Nakamura, H., and Shimomura, M. 1997. Photoisomerization of Azobenzocrown Ethers . Effect of Complexation of Alkaline Earth Metal Ions. *The Journal of Physical Chemistry B*, **101**(97): 7736-7743.

Takei, M., ui, H., Hirose, ., and Sawada, T. 2001. Femtosecond time-resolved spectroscopy of photoisomerization of methyl orange in cyclodextrins. *Journal of Physical Chemistry A*, **105**(51): 11395-11399.

Tamai, N., and Miyasaka, H. 2000. Ultrafast Dynamics of Photochromic Systems. *Chemical Reviews*, **100**(5), 1875-1890.

Tegeder, P. 2012. Optically and thermally induced molecular switching processes at metal surfaces. *Journal of Physics: Condensed Matter*, **24**(39): 394001-394006.

Tehfe, M. A., Dumur, F., Xiao, P., Delgove, M., Graff, B., Fouassier, J.-P., and Lalevee, J. 2014. Chalcone derivatives as highly versatile photoinitiators for radical cationic thiol-ene and IPN polymerization reactions upon exposure to visible light. *Polymer Chemistry*, **5**(2): 382-390.

Tiberio, G., Muccioli, L., Berardi, R., and Zannoni, C. 2010. How Does the Trans-Cis Photoisomerization of Azobenzene Take Place in Organic Solvents. *Chemical Physics Physical Chemistry*, **11**(5): 1018-1028.

Tong, X., Pelletier, M., Lasia, A., and Zhao, . 2008. Fast Cis-Trans Isomerization of an Azobenzene Derivative in Liquids and Liquid Crystals under a Low Electric Field. *Angewandte Chemie International Edition*, **47**(19): 3596-3599.

Traetteberg, M., Hilmo, I., and Hagen, K. 1977. a Gas Electron Diffraction Study of the Molecular Structure of Trans-Azobenzene. *Journal of Molecular Structure*, **39**: 231-239.

Turansky, R., Konopka, M., Doltsinis, N. L., Stich, I., and Marx, D. 2010. Switching of functionalized azobenzene suspended between gold tips by mechanochemical, photochemical, and opto-mechanical means. *Physical Chemistry Chemical Physics*, **12**(42): 13922-13932.

Vapaavuori, J., Goulet-Hanssens, A., Heikkinen, I. T. S., Barrett, C. J., and Priimagi, A. 2014. Are Two Azo Groups Better than One Investigating the Photoresponse of Polymer-Bisazobenzene Complexes. *Chemistry of Materials*, **26** (17): 5089-5096.

Várhegyi, P., Kerekes, a., Sajti, S., Ujhelyi, F., Koppa, P., Szarvas, G., and Lorincz, E. 2003. Saturation effect in azobenzene polymers used for polarization holography. *Applied Physics B: Lasers and Optics*, **76**: 397-402.

Velate, S., Danilov, E. O., and Rodgers, M. a J. 2005. Ultrafast dynamics of the azobenzene-coumarin complex: Investigation of cooling dynamics measured by an integrated molecular thermometer. *Journal of Physical Chemistry A*, **109**(40): 8969-8975.

Velema, W. A., Szymanski, W., and Feringa, B. L. 2014. Photopharmacology : beyond proof of principle. *Journal of the American Chemical Society*, **136** (6): 2178-2191.

Volgraf, M., Gorostiza, P., Szobota, S., Helix, M. R., Isacoff, E. ., and Trauner, D. 2007. Reversibly caged glutamate: A photochromic agonist of ionotropic glutamate receptors. *Journal of the American Chemical Society*, **129**(2): 260-261.

Vorländer, D. 1929. Die Richtung der Kohlenstoff-Valenzen in Benzol-Abkömmlingen. *Berichte Der Deutschen Chemischen Gesellschaft*, **62**(10): 2831-2835.

Wang, D., Wang, J., Zhang, D., and Li, Z. 2012. N-H---X (X = F, Cl, Br, and I) hydrogen bonding in aromatic amide derivatives in crystal structures. *Science China Chemistry*, **55**(10): 1-9.

Wang, J., Liu, H. B., and Ha, C. S. 2009. Zinc-supported azobenzene derivative-based colorimetric fluorescent “turn-on” sensing of bovine serum albumin. *Tetrahedron*, **65**(47): 9686-9689.

Wang, L., and Wang, X. 2007. Ab initio study of photoisomerization mechanisms of push-pull p,p???-disubstituted azobenzene derivatives on S1 excited state. *Journal of Molecular Structure: Theorical Chemistry*, **847**: 1-9.

Wang, L., Xu, W., i, C., and Wang, X. 2009. Isomerization and electronic relaxation of azobenzene after being excited to higher electronic states. *Journal of Molecular Graphics and Modelling*, **27**: 792-796.

Wang, Q., Zhang, Z., Zhang, X., Zhang, J., Kang, ., and Peng, J. 2015. Synthesis of 7a-phenyl-1a{,}7a-dihydro-benzopyrano[2, 3-b]azirin-7-ones via photoisomerization reaction. *RSC Advances*, **5**(7): 4788-4794.

Wen, W., Meng, L., Feng, M., Jiang, G., Yuan, W., and Song, . 2005. Photochemical-controlled switching based on azobenzene monolayer modified silicon (III) surface. *Journal of Physical Chemistry B*, **109**(111): 14465-14468.

Wenker, H. 1934. Nitrazine ellow a New Indicator. *Industrial and Engineering Chemistry*, **26**(3): 350.

Westphal, E., Bechtold, I. H., and Gallardo, H. 2010. Synthesis and optical/thermal behavior of new Azo photoisomerizable discotic liquid crystals. *Macromolecules*, **43**(3): 1319-1328.

Wildes, P. D., Pacifici, J. G., Irick, G., and Whitten, D. G. 1971. Solvent and Substituent Effects on the Thermal Isomerization of Substituted Azobenzenes. A Flash Spectroscopic Study. *Journal of the American Chemical Society*, **93**(11): 2004-2008.

Winter, N. W., and Pitzer, R. M. 1975. Theoretical description of the diimide molecule. *The Journal of Chemical Physics*, **62**(4): 1269-1272.

Yamashita, S., Ono, H., and Toyama, O. 1962. The cis-trans Photoisomerization of Azobenzene. *Bulletin of the Chemical Society of Japan*, **35**(1): 1849-1853.

Yeap, G. ., am, W. S., Dominiak, P., and Ito, M. M. 2010. Synthesis and structural study on heterocyclic compounds 7-decanoyloxy-3-(4-substitutedphenyl)-4H-1-benzopyran-4-ones: Crystal structure of 7-decanoyloxy-3-(4^1-methylphenyl)-4H-1-benzopyran-4-one. *Journal of Molecular Structure*, **967**(1): 25-33.

Yeap, G., am, W., Ito, M. M., Takahashi, ., Nakamura, ., Kamil Mahmood, W. A., and Gorecka, E. 2007. Synthesis and mesomorphic properties of 7-acyloxy-3-(4-acyloxyphenyl)-4H-1-benzopyran-4-one. *Liquid Crystals*, **34**: 649-654.

Yeap, G.-., Chan, T.-N., am, W.-S., Madrak, K., Pociecha, D., and Gorecka, E. 2012. Non-symmetric chiral isoflavone dimers: synthesis, characterisation and mesomorphic behaviour. *Liquid Crystals*, **39**: 1041-1047.

Yeap, G.-., am, W.-S., Dobrzyscky, L., Gorecka, E., Takeuchi, D., Boey, P.-L., and Ito, M. M. 2009. Synthesis, mesomorphic properties and X-ray diffraction studies on 7-alkyloxy-3-(4-alkyloxyphenyl-4H-1-benzopyran-4-one: Crystal structure of 7-hexyloxy-3-(4-hexyloxyphenyl)-4H-1-benzopyran-4-one. *Journal of Molecular Structure*, **937**(1): 16-24.

Yeh, P. . P. 2007. Optics of Liquid Crystal Displays. *John Wiley & Sons*, **67**: 1-8.

York, N. 1993. cis-Stilbene Photochemistry: *Solvent Dependence*, **37**: 10791-10795.

Yoshizawa, T., and Wald, G. 1963. Pre-lumirhodopsin and the bleaching of visual pigments. *Nature*, **197**(4874): 1279-1286.

Yu, and Ikeda, T. 2004. Alignment modulation of azobenzene-containing liquid crystal systems by photochemical reactions. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, **5**(3): 247-265.

Yu, Z., and Hecht, S. 2013. Control over unfolding pathways by localizing photoisomerization events within heterosequence oligoazobenzene foldamers. *Angewandte Chemie-International Edition*, **52**: 13740-13744.

Yuan, S., Dou, ., Wu, W., Hu, and Zhao, J. 2008. Why does trans-azobenzene have a smaller isomerization yield for ππ* excitation than for nπ* excitation. *Journal of Physical Chemistry A*, **112**(51): 13326-13334.

Yuan, S., Wu, W. F., Dou, and Zhao, J. S. 2008. Trans-cis photoisomerization of azobenzene by n → π* excitation: A semiclassical dynamics study. *Chinese Chemical Letters*, **19**(11): 1379-1382.

Zhang, Q., and Bazuin, C. G. 2009. Liquid crystallinity and other properties in complexes of cationic azo-containing surfactomesogens with poly (styrenesulfonate). *Macromolecules*, **42**(13): 4775-4786.

Zhang, Q., Wang, K., Ren, Q., Niu, L., and Chen, B. 2011. Synthesis and properties of new ionic liquid crystals based on para-nitroazobenzene with substitution vinylimidazolium ion group. *Liquid Crystals*, **38**(10): 1349-1355.

Zimmerman, G., Paik, YU., and Chow, L. . 1958. The Photochemical Isomerization of Azobenzene. *Journal of the American Chemical Society*, **80**(14), 3528-3531.