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Title: Tuning, Controlling and Applications of Cis-isomer Stability in Azoheteroarenes and Multiple Azoarenes Connected Systems

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Abstract: Photoswitchable molecules can exhibit light induced reversible bistability between two different states or isomers. So often it accompanies changes in the molecular properties such as structure, dipole moment, colour etc. Due to this, photoswitchable molecules are attractive candidates in many applications such as optical data storage, sensors, molecular switches, molecular wires, biomedicines etc. Azobenzenes are one of the robust photoswitchable molecules with great efficiency in photoisomerization between E- and Z-isomers, and also can easily be synthesised and functionalized. For many practical applications, tuning and controlling the photoswitching behaviour, and Z-isomer stability of azoarenes are crucial. Due to the increasing popularity of phenylazopyrazoles as photoswitches in recent times, and their improved Z-isomer stability, we attempted at understanding the effects of substituents on their photoswitching ability and Z-isomer stability. In this regard, 38 aryl substituted arylazo 1H-3,5-dimethylpyrazoles have been synthesized. For understanding the steric and electronic effects on their Z-isomer stability, Taft and Hammett's relationships have been utilized. Additionally, the N-methyl derivatives with meta substitutions have been synthesized and their substituent effects have also been studied. Furthermore, the role of hydrogen bonding has been investigated through concentration and solvent effects in the Z-isomer stability. Based on these studies, we demonstrated a complex interplay of steric, and electronic effects and also the hydrogen bonding in dictating the stability of Z-isomers in phenylazo-1H-3,5- dimethylpyrazoles. In the next part of the work, functionalization of the arylazopyrazoles has been carried out. In this regard, we have connected arylazopyrazole units to a trimesic acid, and using this strategy 18 derivatives have been synthesized. Through UV-Vis and NMR spectroscopic studies, we envisaged the multi-state photochromic properties of these tripodal derivatives. These new class of molecules exhibited many interesting properties such as better solubility, higher photoisomerization conversions towards ZZZ-isomers, enhanced stability of ZZZ- isomers, and long-term switching stability etc. Above all, these molecules showed solid-state reversible photoisomerization as well as colour changes that make them excellent candidates for rewritable imaging applications. In the last part of the work, we have synthesized long alkoxy chain (viz, C 6 , C 8 and C 10) containing multiple arylazo-3,5-dimethylpyrazole and azobenzene connected systems for making photoswitchable liquid crystals. This work has been done in collaboration with Dr. Santanu Kumar Pal's group. Despite exhibiting good photoswitching properties, the arylazo- 3,5-dimethylpyrazole based systems did not show any liquid crystalline properties. On the other hand, polarized optical microscopic (POM) imaging and small angle X-ray scattering (SAXS) studies revealed the discotic liquid crystal properties of the azobenzene-based tricarboxamide derivatives. All of the three molecules exhibited solution phase as well as solids (thin films) DLC mesophase photoswitching. Interestingly, the compounds with peripheral C 6 alkyl chain exhibits two different mesophases, namely a columnar rectangular (Col r) phase at low temperature, and a columnar hexagonal (Col h) phase at a higher temperature. In contrast, the other two higher homologues revealed only Col h phases at all temperature ranges. Despite the molecules undergoing switching in the LC phase, no changes have been observed with respect to the LC phase. Thus, we were able to develop a new DLC based system that can undergo photoswitching without losing its LC properties .

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