

PHOTOISOMERIZATION OF CIS-1,2-DI(1-METHYL-2-NAPHTHYL)ETHENE (c-D-1-MNE) IN GLASSY MEDIA AT 77 K. Christopher E. Redwood,[†] Ratheesh Kumar V.K.,[†] Stuart Hutchinson,[†] Frank B. Mallory,[‡] Clelia W. Mallory,[#] Olga Dmitrenko* and Jack Saltiel.[†] Departments of Chemistry and Biochemistry, Florida State University,[†] Tallahassee, FL 32306-4390 Bryn Mawr College,[‡] Bryn Mawr, PA, 19010, University of Pennsylvania,[#] Philadelphia, PA 19104, University of Delaware,^{*} Newark, DE 19716

c-D-1-MNE undergoes λ_{exc} -dependent cis-trans photoisomerization in glassy media at 77 K. As the reaction progresses, the structureless fluorescence of c-D-1-MNE is replaced by t-D-1-MNE fluorescence. Unexpectedly, the structured fluorescence of t-D-1-MNE in solution becomes a broad, λ_{exc} -dependent fluorescence at 77 K. Principal component analysis of the t-D-1-MNE spectral matrix yields major and minor pairs of structured spectra, which, with the aid of calculations [DFT using B3LYP/6-311+G(d,p)], are assigned to two structural modifications of two t-D-1-MNE conformers. The two structures in each pair differ in the relative direction of deviation of the naphthyl groups from the plane of the olefinic bond (+/- vs. +/+ for the signs of the naphthyl/vinyl dihedral angles). The conformer specific λ_{exc} -dependent c-D-1-MNE photoisomerization will be discussed.