

processes in thiophosgene and other thiocarbonyl compounds will be discussed.

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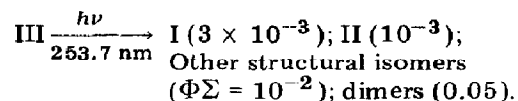
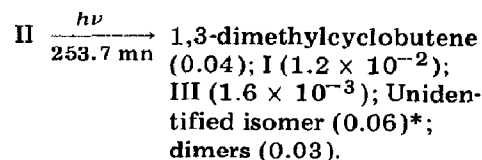
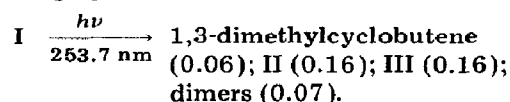
Photochemical Behavior of Acyclic 1,3 Dienes: Mechanistic Implications of 1,5-Hydrogen Shifts in the S_1 State[†]

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The present knowledge of the photochemical behavior of acyclic conjugated dienes and the properties of the S_1 state which were subsequently deduced are largely based on quantitative studies carried out on the 1,3-pentadienes and to a smaller extent on the 2,4-hexadienes [1]. Thus it has been proposed that the S_1 dienes first relax by a twist of one p_π orbital, yielding an allylmethylene entity which then internally converts into the corresponding geometry of S_0 [1], unless the possibility exists (for the *s-cis* conformers) that a concerted 1,4 overlap leads to a cyclobutene, this last process being then preferred [2]. The alternative hypothesis has been put forward that prior to internal conversion the S_1 state relaxes by acquiring a "bicyclobutane-like" conformation via a double twist of p_π orbitals [3]. Thus far the 1,5 shift of hydrogen has not been envisioned as a possibly efficient way for deactivating the S_1 state of dienes, presumably because it was considered as arising exclusively from a *cis-s-cis* configuration whose population is generally negligible at room temperature. However, since most quantitative anal-

[†] A full paper on this work has been submitted for publication in the *J.C.S. Perkin II*.

yses have dealt with the pentadienes, should a 1,5 shift have taken place it would not have been observed for it corresponds to an identity reaction. Therefore we looked at the three photochemically interconvertible dienes *cis*-2-methylpenta-1,3-diene(I), *trans*-2-methylpenta-1,3-diene(II) and 4-methylpenta-1,3-diene(III) which constitute a well suited system for studying photochemical competitive processes and in particular the efficiency of 1,5 hydrogen migrations relative to the 1,4 cyclomerization and to the geometrical isomerization [4]. The data are summarized hereunder, the initial Φ being given in parentheses for a starting concentration ranging around $10^{-1} \text{ mol l}^{-1}$.



The kinetic study shows that in opposition to former conclusions [4], 1,3-dimethylcyclobutene directly arises from the singlet excited state of I, indicating that this diene largely assumes a *s-cis* ground state conformation as was suggested by its UV spectrum. The results emphasize that both the isomerization to cyclobutenes and the 1,5 shift of a hydrogen may play an important role in the $S_1 \rightarrow S_0$ decay of a *s-cis* diene while *s-trans* conformers mainly return to their ground state by internal conversion. It was shown however unambiguously that *trans* configurations do undergo, though with a low quantum yield, the 1,5 sigmatropic shift (II \rightarrow III and III \rightarrow II); this definitely rules out the allylmethylene structure for at

*This compound proved photochemically labile and it was not possible, in a preparative run, to accumulate enough of it for spectroscopic analyses.

least one of the possible vibrationally relaxed S_1 states of acyclic 1,3 dienes and lends further support to the doubly twisted (bicyclobutane-like) conformation on the basis of which one predicts that a 1,5 antarafacial shift is possible for either a *cis-s-trans* or a *trans-s-cis* configuration, independently of the faster shift taking place prior to relaxation in *cis-s-cis* conformers. This prediction was tested in irradiating the methyl d_3 *cis*-penta-1,3-diene in which the migration of deuterium could be significantly reduced to the benefit of other processes: we found indeed that Φ (3-methylcyclobutene) increases by a factor of 2.8 rela-

tive to the non-deuteriated molecule.

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Photophysics of Organic Crystal Surfaces

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Surface, subsurface and bulk exciton transitions have been observed in aromatic hydrocarbon crystals by means of low temperature (2 K) reflection spectroscopy. Because of their sensitivity to surface conditions, deposited films etc., the surface exciton transitions act as probes of physical and chemical processes occurring near the surface. This has been demonstrated by observing the effects of photo-oxidation and condensed gas films on the b-polarized reflection spectrum of the 4000 Å transition of anthracene. Figure 1 shows the shift in the main surface transition caused by a thin film of gas condensed on the (001) face at temperatures below 20 K. Condensed films of N_2 , O_2 , Ar, Kr and Xe shift the surface of 100 cm^{-1} to lower energies. Methane films gave a shift of 100 cm^{-1} . Figure 2 demonstrates that disruption of the crystal surface by photo-oxidation obliterates the fine structure in the low temperature spectrum due to surface and surface transitions. Spectrum 1 was

recorded before and spectrum 2 after photo-oxidation of the (001) face of an anthracene crystal.

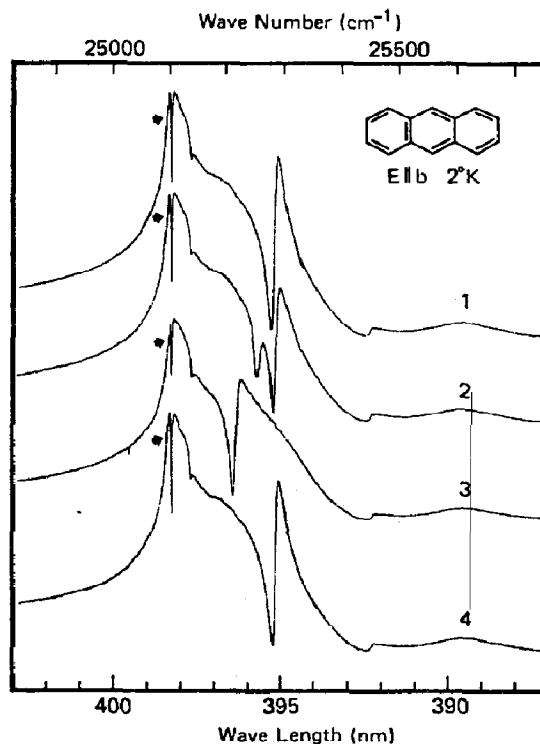


Figure 1. Reflection spectra of crystals with a solid air coating.