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Publication date

1992

Document Version

Final published version

Published in

Time Resolved Vibrational Spectroscopy

[Link to publication](#)

Citation for published version (APA):

Wilbrandt, R., Møller, S., Langkilde, F. W., Brouwer, A. M., Negri, F., & Orlandi, G. (1992). The potential energy surfaces of the T₁ state of 1,3,5-hexatrienes and methylated derivatives: a survey of present knowledge. In H. Takahashi (Ed.), *Time Resolved Vibrational Spectroscopy: proceedings of the 5th International Conference on Time-Resolved Vibrational Spectroscopy, Tokyo, Japan, June 3-7, 1991* (pp. 155-158). (Springer proceedings in physics; Vol. 68). Springer.

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The Potential Energy Surface of the T_1 State of 1,3,5-Hexatrienes and Methylated Derivatives: A Survey of Present Knowledge

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1. Introduction

In previous studies[1,2] we considered the time-resolved resonance Raman (TRRR) spectra of 1,3,5-hexatriene (HT) in its lowest excited triplet state in order to obtain information about the geometry of the T_1 intermediate and the mechanism of the cis-trans photoisomerization in T_1 .

In the present paper some results of the most recent experimental and theoretical studies are presented, and the present picture of the potential energy surface in the lowest excited T_1 state of 1,3,5-hexatrienes evolving from these and our previous investigations is summarized. A more detailed account of this work is to be published[3-5].

In order to obtain information on the T_1 state of HT, several experimental and theoretical methods are used:

Time-resolved resonance Raman spectroscopy: The experimental method giving the most detailed structural information on equilibrium geometries in the excited T_1 state is TRRR spectroscopy. Vibrational *frequencies* in the T_1 state provide characteristic fingerprints of the equilibrium geometry or geometries in the T_1 state. Thereby, detailed structural information on the relative minima of the potential energy surface is obtained. *Intensities* of resonance Raman bands are dependent on the relative populations of scattering molecules and characteristic of the changes in molecular geometry occurring upon excitation from the T_1 to the T_n state of the resonance transition. Hence, information not only on the T_1 , but also the T_n state is available from the spectra.

By variation of the *temperature* in TRRR experiments information on the relative populations among different minima and hence on the *relative energy of different minima* is obtained.

The *kinetics of equilibration* among different minima on the T_1 potential energy surface at various temperatures, as revealed by TRRR spectra, allows to draw conclusions about the *height of barriers* separating different minima from each other.

If barriers are sufficiently small, equilibration occurs rapidly, i.e. within the lifetime of the T_1 state; if they are large, on the other hand, no equilibration will be observed. Equilibration along torsional coordinates around formal C=C double and C-C single bonds can be studied by *varying the ground state configurations and conformations* of the HT derivatives by studying different isomers and rotamers.

The study of *deuteriated molecules* provides a means to further support the assignment of vibrational spectra.

Time-resolved absorption spectroscopy: Time-resolved absorption spectroscopy allows to determine triplet-triplet absorption spectra and kinetics of triplet state formation and decay. In particular, $T_1 \rightarrow T_n$ *absorption spectra* are important for an assignment of the T_n state active in the resonance transition, which is necessary to calculate TRRR intensities. *Kinetics* of triplet decay as a function of temperature yield activation energies and frequency factors of Arrhenius plots and are interpreted in terms of *torsional barriers* on the T_1 potential energy surface. The measurement of *rate constants of triplet energy transfer* using HT as either donor or acceptor yields information on energies of vertical and relaxed triplet states of HT.

Photostationary triplet state photochemistry: The measurement of *photostationary states* and *quantum yields of photoisomerization* by sensitized stationary photochemistry for a variety of donors and acceptors with different triplet energies is an additional, more indirect, method to determine triplet state energies and minima on the T_1 potential energy surface.

Theoretical quantum chemical calculations: The understanding of the results of the above mentioned experimental investigations are crucially dependent on a comparison with results from theoretical calculations. The experimental TRRR spectra were interpreted by quantum mechanical calculations (QCFF/PI and CNDO/S) of equilibrium geometries and vibrational frequencies at the trans (E), cis (Z) and centrally twisted (P) geometries in T_1 and in the T_n state responsible for the TRRR activity. On the basis of these calculations the T_1 normal modes showing the strongest Franck-Condon activity in the TRRR spectra can be identified for each geometric isomer of HT.

2. Results and Discussion

The observed TRRR spectra for unsubstituted HT are shown[1-3] to result from a superposition of the spectra of the Z and E forms with possible weak contributions from the P form. It was concluded that the transient T_1 intermediate in the photoisomerization of HT, monitored by TRRR spectra, exists as an equilibrium between several geometric structures, in which planar molecules represent a substantial fraction, and that a possible minimum of the potential energy curve at the centrally twisted geometry must be rather shallow. An example of experimental and calculated spectra is shown in Figure 1 for 3-d-HT.

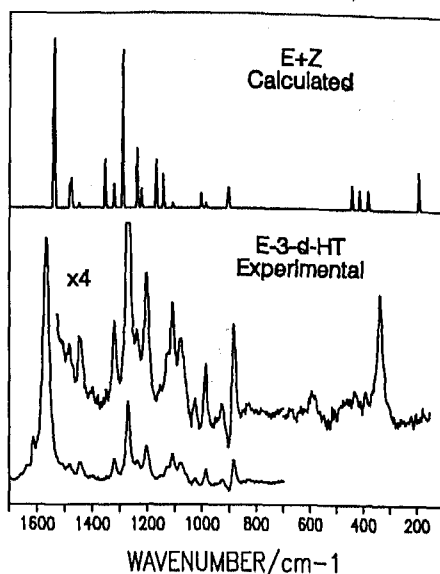


Figure 1: Calculated and experimental T_1 resonance Raman spectrum of 3-d-HT.

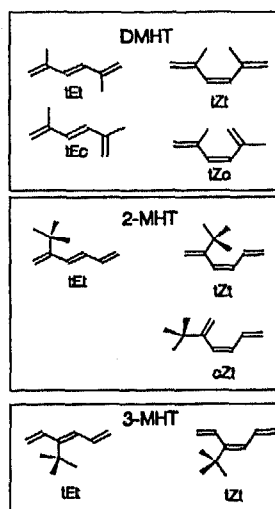


Figure 2: Planar geometries of DMHT, 2-MHT and 3-MHT.

In this paper we consider the combined results of TRRR spectra and decay kinetics of the T_1 intermediate of HT, some of its deuteriated derivatives, and of its 2,5-dimethyl- (DMHT), 2-methyl- (2-MHT), and 3-methyl- (3-MHT) derivatives. The T_1 TRRR spectra of the two isomers of non-deuteriated DMHT have been reported previously[6]. We now report the spectra of E- and Z-3,4-d₂-DMHT and of E-3-d-DMHT together with remeasured spectra of DMHT-d₆. Furthermore, resonance Raman spectra of E-2-MHT, E-4-d-2-methyl-1,3,5-hexatriene (E-4-d-2-MHT), Z-2-methyl-1,3,5-hexatriene (Z-2-MHT), E-3-methyl-1,3,5-hexatriene (E-3-MHT), and Z-3-methyl-1,3,5-hexatriene (Z-3-MHT) in the lowest triplet state T_1 are reported and discussed. QCFF/PI calculations are performed to determine energies and optimized geometries in the S_0 , T_1 , and T_n electronic states. For each T_1 species, $T_1 \rightarrow T_n$ transitions, vibrational frequencies, and RR intensities are calculated and compared with the observed frequencies and intensities (as exemplified in Fig.1). An example of determination of the activation energy of the decay of the T_1 state is shown in Fig. 3 for 2-MHT and 3-MHT.

Finally, in Fig. 4 the qualitative potential energy surfaces in the T_1 state of the methyl substituted HT's are shown, resulting from different pieces of information as discussed above. It can be seen that characteristic differences are found for the different molecules. The T_1 potential energy surface of 3-MHT is very similar to that of unsubstituted HT[1]. Steric interaction is responsible for the high energy of the Z isomers of DMHT. The barrier along the torsional coordinate of the central CC bond at the P geometry is seen to vary, being 0.7-0.8 Kcal/mol for HT, cPt-DMHT and 3-MHT, while 2-MHT shows a lower barrier of 0.4 kcal/mol and no barrier is found for the tPt form of DMHT.

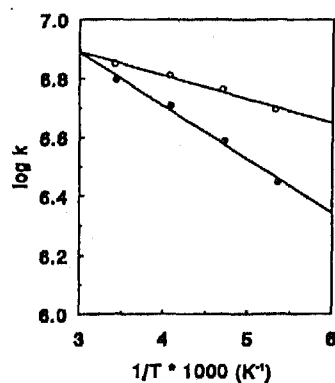


Figure 3: First order rate constant for T_1 decay for 2-MHT (open circles) and 3-MHT (filled circles).

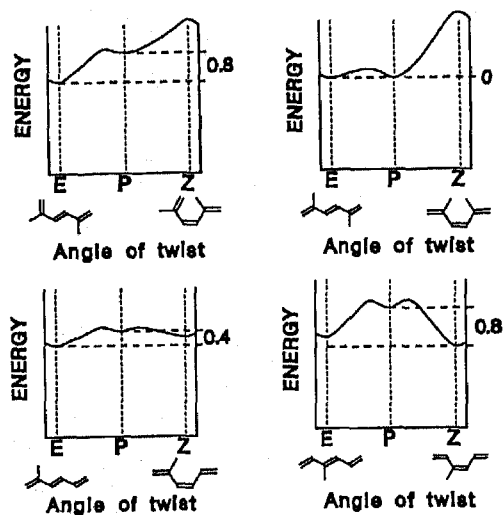


Figure 4: Potential energy curves in T_1 for DMHT, 2-MHT and 3-MHT.

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