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TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF 1,3,5-HEXATRIENES IN THE LOWEST EXCITED TRIPLET STATE. THE POTENTIAL ENERGY SURFACE IN T_1 .

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SUMMARY

Time-resolved resonance Raman spectroscopy is applied to the study of the T_1 state of 1,3,5-hexatriene and deuteriated and methylated derivatives in solution. The technique is described briefly. The experimentally obtained resonance Raman spectra are discussed in the light of theoretical Quantum Chemical Force Field calculations. Implications for the potential energy surface of the T_1 state are discussed.

INTRODUCTION

The isomerization process around a C=C double bond is one of the most basic and important reactions in chemistry. One of the simplest model molecules for a characterization of isomerization processes is 1,3,5-hexatriene, the isomerization process being the interconversion between the two stable isomers E and Z.

In order to understand isomerization processes in detail, a characterization of the potential energy surfaces on which they occur is necessary. The excitation of 1,3,5-hexatriene from the ground state S_0 to the lowest excited triplet state T_1 corresponds to a promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (see Fig. 1). Upon such a transition C=C double bonds are expected to be weakened and C-C single bonds strengthened. Hence while the potential energy surface (PES) in S_0 shows a high barrier with respect to torsion around the central C=C bond, in the T_1 state a relatively flat PES is expected along this twisting coordinate. In contrast, while the PES along twisting of C-C single bonds in S_0 is relatively flat, a higher barrier is expected in T_1 along this coordinate. In the ground state two distinct isomers

Figure 1. π -orbitals of hexatriene

(E- and Z-hexatriene) exist, while different rotamers are known to equilibrate rapidly, the trans,trans-rotamer being the predominant one for both E and Z isomers. One may ask the question whether the opposite is the case in T_1 , such that equilibration of ground state isomers and non-equilibration of ground state rotamers take place. Furthermore, one may be interested in the shape of the T_1 PES, in particular with respect to the geometries and energies of the minima and maxima on the PES along torsional coordinates.

The present paper deals with information obtained on the PES of the lowest triplet state T_1 by time-resolved resonance Raman (RR) spectroscopy. Molecules studied are the two isomers of 1,3,5-hexatriene and deuteriated and methylated derivatives. More detailed reports on the presented work have been published previously (refs. 1-3).

METHODS

The experimental setup is shown schematically in Figure 2. Time-resolved RR spectra are recorded in a pump-probe arrangement using two pulsed lasers with pulse durations of 10-15 ns. An excimer laser emitting at a wavelength of 308 nm is used as pump and a YAG-pumped, frequency-doubled dye laser as probe source. The two laser pulses can be delayed in time with respect to each other. The sample is contained in a spinning cylindrical quartz cell. The scattered light is dispersed in a single monochromator and detected by an intensified gated optical multi-channel analyzer (OMA). The collected data are stored and handled in a PDP11/23 computer.

All solutions were purged with Ar for at least 30 min and transferred to the optical cells under an Ar atmosphere in a glove box.

Figure 2. Experimental setup

RESULTS AND DISCUSSION

Figure 3. Excitation scheme

Direct excitation populates the 1^1B_u state, the lifetime of which is believed to be very short. No fluorescence has been detected and the intersystem crossing efficiency is zero. In order to populate the T_1 state, sensitization is required. The $T_1 \rightarrow T_n$ absorption spectrum with a maximum at 300 nm and a lifetime of 214 ns in benzene has been observed (ref. 4). The excitation scheme used in our experiments is shown in Fig. 3. We use acetone as sensitizer which is known to have a high intersystem crossing efficiency and a triplet state energy E_T of about 3.5 eV. Triplet energy transfer to E-hexatriene ($E_T = 2.03$ eV) is thus exothermic and expected to be essentially diffusion controlled. Probing of the T_1 state of hexatriene is performed with an excitation wavelength of 315 nm in resonance with the $T_1 \rightarrow T_n$ transition. In a time-resolved RR spectrum obtained under such conditions frequencies are characteristic for the normal modes of vibration in the T_1 state, while intensities reflect the changes in equilibrium geometries on going from T_1 to T_n .

Typical observed spectra are shown in Figure 4. Spectrum A in Fig. 4 is obtained without pumping and consists of bands from ground state hexatriene and solvent (denoted by S). Spectrum B is obtained at 60 ns delay between pump and probe pulses. New bands are observed attributable to the T_1 state of hexatriene and a total decrease in intensity is seen due to the transient $T_1 \rightarrow T_n$ absorption. Spectra C and D are the S_0 and T_1 spectra derived from spectra A and B by subtraction procedures. The RR spectrum of hexatriene in T_1 (spectrum D) is obtained by subtraction of the probe-only spectrum from the pump-and-probe spectrum after appropriate rescaling. It is seen from Fig. 4 that the observed preresonance Raman spectrum in S_0 (spectrum C) and the RR spectrum in T_1 (spectrum D) are considerably different showing large shifts in wavenumbers and changes in intensity.

We now turn to the question whether different ground state isomers equilibrate in T_1 . To investigate this point, T_1 RR spectra were recorded from solutions containing either E- or Z-hexatriene. The obtained spectra (with solvent and ground state hexatriene bands subtracted) are shown in Fig. 5. It is seen that identical RR spectra within limits of error are seen from the T_1 states of the two isomers. We conclude from this that either a common minimum on the T_1 PES is populated or an eq-

Figure 4. Typical resonance Raman spectra, obtained from an Ar-saturated solution of E-hexatriene in acetonitrile containing acetone as sensitizer.

equilibrium between populations in different minima is established within 60 ns (the pump-probe delay in our experiments). This allows us to estimate an upper limit for a barrier along the pathway of equilibration in T_1 , a point which shall be discussed below.

The question concerning the equilibration of ground state rotamers in T_1 shall now be addressed. As unsubstituted hexatriene at room temperature in solution is present only in rotameric forms which are trans around C-C single bonds, it is necessary to consider substituted hexatrienes. The E isomer

Figure 5. RR spectra of E- and Z-hexatriene in T_1 (from ref.1)

Figure 6. RR spectra of E- and Z-2,5-dimethyl-1,3,5-hexatriene in T_1 (from ref.2)

of 2,5-dimethyl-1,3,5-hexatriene is known (ref. 5) to be in a trans form around C-C single bonds, whereas for the Z-isomer in S_0 an equilibrium is found between cZt and cZc forms (lower case letters indicating rotameric, capital letters isomeric forms).

As identical T_1 RR spectra were observed for the two isomers of hexatriene, it is reasonable to expect equilibration in T_1 with respect to torsion around the central C=C bond of 2,5-dimethyl-hexatriene as well. Hence, a comparison between the T_1 RR spectra of the two isomers of 2,5-dimethyl-hexatriene, which differ in C-C single bond conformation, may throw light on the question raised. The observed RR spectra of the two isomers of 2,5-dimethyl-hexatriene are shown in Fig. 6. Clearly different RR spectra are seen from the different isomers. The simplest interpretation of these differences is that different rotamers do **not** equilibrate in T_1 . As these differences persist for at least 100 ns (our pump-probe delay in the present experiments), a lower limit for a barrier along the path of equilibration on the T_1 PES along the C-C torsional coordinate can be estimated (see below).

We shall now discuss the observed T_1 RR spectra of hexatriene in the light of theoretical calculations. Most of the calculations in the literature (refs. 6-8) on the T_1 state of hexatriene predict a perpendicular form which is twisted around the central C=C bond to be the most stable one. Calculated stabilization energies with respect to the planar E form range from -1.9 to -6 kcal/mol. We have performed Quantum Chemical Force Field (QCFF/ π) calculations using a modified version of the QCFF/ π program originally developed by Warshel (refs. 9,10). As a result of these calculations relative minima are computed on the T_1 PES for planar E and Z geometries, whereas the perpendicular form is computed at a local maximum. The energy of the perpendicular form may be somewhat overestimated by QCFF/ π because of the neglect of σ/π interaction. The energies of the Z and

Figure 7. Calculated energy diagram for the triplet states of 1,3,5-hexatriene. (from ref. 3)

perpendicular forms are calculated at 1.1 and 7.1 kcal/mol above the energy of the planar E form. As these results are in disagreement with previous calculations it is interesting to ask whether the observed T₁ RR spectra can contribute to solve the theoretical discrepancies.

A calculation of the energies of higher triplet states up to T₈ of the three forms (E, perpendicular and Z) and of the oscillator strengths of the T₁ → T_n (n = 2–8) transitions revealed that for the planar E and Z geometries only one transition, namely the T₁ → T₅ transition with a transition energy of 4.32 (E) and 4.24 eV (Z), corresponding to 287 and 292 nm was of considerable intensity. Correspondingly, for the perpendicular form representing two allylic moieties, only the T₁ → T₆ transition at 5.49 eV (226 nm) showed appreciable oscillator strength (see Fig. 7). From a comparison of the experimentally observed T₁ → T_n transition energy (300 nm corresponding to 4.13 eV) with the calculated ones it seems most likely that only the two planar forms contribute to the T₁ → T_n absorption at 315 nm. Consequently, also T₁ RR spectra are expected to arise predominantly from the planar forms as the RR enhancement of the perpendicular form at the used excitation wavelength of 315 nm is estimated to be ten times smaller compared to the planar forms.

TABLE 1

Calculated geometries of the hexatriene carbon skeleton in S_0 , T_1 and T_n ($n = 5$ or 6), (bond lengths in Å).

State	Geometry	C_1C_2	C_2C_3	C_3C_4	$C_1C_2C_3$	$C_2C_3C_4$
S_0	E	1.343	1.470	1.354	122.2°	121.8°
	Z	1.343	1.471	1.355	121.8°	125.3°
T_1	E	1.397	1.386	1.470	122.5°	121.5°
	Z	1.397	1.387	1.472	122.0°	124.8°
	Perpendicular	1.384	1.388	1.480	122.6°	121.5°
T_n	E ($n = 5$)	1.410	1.428	1.415	121.2°	121.4°
	Z ($n = 5$)	1.411	1.432	1.412	121.2°	123.9°
	Perpendicular ($n=6$)	1.411	1.415	1.470	121.2°	121.0°

We also calculated optimized geometries for the planar and perpendicular forms. The calculated geometries after geometry optimization in the S_0 , T_1 and T_n ($n = 5, 6$) states of hexatriene are given in Table 1. It is seen that in T_1 the central CC bond has become a single bond while the remaining bonds are of nearly equal length, intermediate between that of a double and single bond. On going from T_1 to T_n all bonds are weakened and become similar in length.

We shall now see whether the observed T_1 resonance Raman spectra support the conclusions derived from absorption spectra only. As the RR scattering efficiency is dominated by the strongly allowed $T_1 \rightarrow T_n$ transition, the most active modes of vibration are the totally symmetric a_g modes gaining their intensity from the Franck-Condon scattering mechanism. The RR intensity is mainly governed by the displacements between the equilibrium geometries of T_1 and T_n ($n = 5$ or 6). We have calculated the frequencies and dimensionless displacement parameters γ_i for the i -th totally symmetric normal mode (for details see ref. 3). Under the given conditions the γ_i are expected to be approximately proportional to the RR intensity, when excited in the 0-0 vibrational band of the respective $T_1 \rightarrow T_n$ transition. The results for hexatriene are schematically shown in Fig. 8 together with the experimentally observed spectrum. Corresponding results for 3,4- d_2 -hexatriene are shown in Fig. 9. It should be noticed that the overall RR intensity of the perpendicular form, according to the higher $T_1 \rightarrow T_n$ transition energy, is expected to be approximately ten times weaker relative to the planar forms than shown in Figs. 8 and 9.

It is immediately clear from Figs. 8 and 9 that the strongest observed bands around 1570 cm^{-1} can only be assigned to planar forms. This is in good agreement with the conclusions derived from absorption measurements. Furthermore, it is obvious to assign the observed band at 1106 cm^{-1} in Fig. 8 to the calculated one at 1154 cm^{-1} and correspondingly the two experimental bands at 937 and 890 cm^{-1} in Fig. 9 to the calculated ones at 964 and 896 cm^{-1} . This seems to indicate that the planar E form is the predominant one. However, as the total number of bands in our spectra cannot be

Figure 8. Calculated wavenumbers and approximate intensities for the a_g modes of the E, Z and perpendicular forms of hexatriene in T_1 together with the experimental T_1 RR spectrum (from ref. 3).

Figure 9. Calculated wavenumbers and approximate intensities of the a_g modes of the E, Z and perpendicular forms of 3,4-d₂-hexatriene in the T_1 state together with the experimental T_1 RR spectrum (from ref.3).

explained by the E form only, it seems likely that the planar Z form contributes to the T_1 RR spectra as well. While we do not need to invoke the perpendicular form to explain the spectra, it may well be present, absorbing at shorter wavelength and therefore showing less resonance enhancement.

Hence from a comparison of the theoretically calculated spectra with experimentally observed ones we conclude that an equilibrium is established in the T_1 state between planar E and Z forms, the E form probably being the predominant one. It is not possible to exclude the presence of the perpendicular form, but its contribution to the T_1 RR spectra under the present experimental conditions is expected to be small or negligible.

We now discuss the implications for the energy barriers along the CC double and single bond torsional coordinates on the PES of T_1 and for the energy difference between the E and Z forms. When two minima 1 (E) and 2 (Z) at energies E_1 and E_2 on the PES are separated by a barrier of energy E_3 , the rate constant for the process leading from minimum 1 to minimum 2 can be expressed as

$$k_{1 \rightarrow 2} = \frac{k_b T}{h} e^{-\frac{E_3 - E_1}{k_b T}}$$

and correspondingly

$$k_{2 \rightarrow 1} = \frac{k_b T}{h} e^{-\frac{E_3 - E_2}{k_b T}}$$

which, in equilibrium leads to the well known Boltzmann factor

$$\frac{N_1}{N_2} = e^{-\frac{E_1 - E_2}{k_b T}}$$

where k_b is the Boltzmann constant and N_1 and N_2 the equilibrium populations at the minima 1 (E) and 2 (Z). As equilibration experimentally occurs in a time shorter than 60 ns, this yields an upper limit of ca. 7.6 kcal/mol for the barrier $E_3 - E_1$ and $E_3 - E_2$, i.e. for the barrier along the C=C torsional coordinate from one planar form to the other. Furthermore, the observation of vibrational bands from both the planar E and Z forms in T_1 indicates that $N_2/N_1 \geq 0.1$. This leads to an upper limit of 1.4 kcal/mol for $E_2 - E_1$. Finally, the fact that different rotamers in 2,5-dimethyl-hexatriene do not equilibrate within 100 ns, indicates a lower limit of ca 7.9 kcal/mol for the barrier of torsion around the C-C single bond on the PES of the T_1 state.

In conclusion, a qualitative picture of the PES of the T_1 state of hexatriene emerges from the present work: The PES is rather flat along the C=C central double bond torsional coordinate. Two relative, nearly isoenergetic minima, at the planar E and Z geometries are separated by a barrier of less than 7.6 kcal/mol with a possible dip at the perpendicular geometry. The PES in T_1 along the C-C single bond torsional coordinate shows two relative minima at planar geometries as well, separated, however, by a barrier larger than 7.9 kcal/mol. While the last statement strictly has been shown to be true only for 2,5-dimethyl-hexatriene, it is reasonable to assume its qualitative validity for unsubstituted hexatriene as well.

Further investigations on hexatriene and methylated derivatives are in progress. These include the study of the temperature dependence of the RR spectra in T_1 as well as the study of other isotopomers. Preliminary results support the conclusions of the present paper.

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