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## Photochemistry of 2,5-dimethyl-1,3,5-hexatrienes in argon matrices. Formation of isomers and rotamers

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**Abstract.** Irradiation of argon matrix-isolated *E*-2,5-dimethyl-1,3,5-hexatriene results in the formation of thermodynamically less stable rotamers. In contrast, the corresponding *Z*-triene readily undergoes light-induced double bond isomerization to produce the *E* isomer. The *cZc* rotamer of *Z*-2,5-dimethylhexatriene is obtained by irradiation of 1,4-dimethyl-1,3-cyclohexadiene. Characteristic features in the UV and IR absorption spectra of the various rotational and geometric isomers are discussed. Recent theoretical work has indicated that single and double bond isomerizations are both possible starting from the *A* excited state surface of *E* and *Z*-hexatriene. Experimentally, we have found clear preferences for either of the two, depending on the initial geometry.

### 1. Introduction

The photophysical and photochemical properties of short polyenes have received ample attention over the past three decades<sup>1</sup>. 1,3,5,7-Octatetraene and longer polyenes show fluorescence, which greatly facilitated the study of their photophysical properties. On the other hand, butadiene and hexatriene and simple derivatives do not fluoresce with an appreciable quantum yield, with the exception of the recently described locked *Z*-triene 1,2-divinylcyclopentene ( $\phi_F$  0.01 at room temperature in solution)<sup>2</sup>. In spite of considerable efforts and recent progress, in particular due to molecular beam studies<sup>3,4</sup>, the photophysical properties of simple trienes and dienes are not thoroughly understood. It seems certain now that the symmetric covalent excited state ( $A_1$  in  $C_{2v}$ ,  $A_g$  in  $C_{2h}$ ) is the lowest excited state in the case of isolated *Z*-1,3,5-hexatriene (*Z*-HT). It is not known what the state ordering is in solution<sup>a</sup> or for *E* isomers or rotamers. It is also not clear how the excited molecule reaches this state following the allowed transition from the ground state to the  $B_1$  ( $B_u$ ) Franck-Condon-excited state. Resonance Raman spectroscopy<sup>5,6</sup> indicates that there are in-plane displacements in the Franck-Condon state, but these experiments cannot give information about the dynamics on longer timescales than tens of femtoseconds.

In contrast to the longer polyenes, hexatrienes reveal a wealth of photochemical isomerization processes, which have been studied systematically mainly by two groups in

Leiden and Berkeley<sup>7</sup>. Historically, an important reason for these studies has been that the triene chromophore plays a crucial role in the chemistry of vitamin D. Thus, considerable efforts have been devoted to the study of rather heavily substituted derivatives, in which the coexistence of rotamers (conformational isomers) is a central aspect. This theme appears to be almost irrelevant in the field of the longer polyenes. Conformationally perturbed longer polyenes have been studied only in the protein environment of rhodopsins, in which the isomerization of formally double bonds is significantly enhanced relative to the solution conditions<sup>8</sup>.

An important paradigm in triene photochemistry has been the Non-Equilibration of Excited Rotamers (NEER) principle<sup>1b</sup>, which notes that equilibration of excited rotamers during the singlet-excited state lifetime does not occur, implying unique photochemistry and photophysics for each rotamer.

There appears to be an empirical and qualitative relationship between the efficiency of photoisomerization and the structure of the chromophore in the sense that planar trienes generally show inefficient isomerization, while compounds in which non-planarity has been induced by alkyl substituents produce geometric (and other) isomers much more efficiently. We speculated<sup>9</sup> that this has to do with the fate of the Franck-Condon excited state, because planar species cannot have a gradient on the potential energy surface for out-of-plane modes of deformation, and thus undergo out-of-plane motion only after the in-plane modes have mostly relaxed, whereas initially non-planar excited molecules can directly move in out-of-plane directions, thus in a sense utilizing the excess energy of the in-plane coordinates to reach different areas on the potential energy surface. The activity of vibrational modes in resonance Raman spectra has been taken as a measure

<sup>a</sup> For 1,2-divinylcyclopentene, the available evidence obtained from solution experiments points to the  $2A_1$  state as the lowest excited singlet state<sup>2b,c</sup>.

Table I Relative energies (kcal/mol) of 2,5-dimethyl-1,3,5-hexatriene isomers and conformers calculated with different computational methods.

Rotamer	HF/3-21G	HF/6-31G <sup>a</sup>	MP2/6-31G <sup>a</sup> // HF/6-31G <sup>a</sup>	MM3 E <sub>s</sub> <sup>b</sup>	MM3 H <sub>f</sub> <sup>c</sup>
<i>tEt</i>	0	0	0	0	0
<i>cEt</i> <sup>d</sup>	1.91	2.29	2.24	1.35	1.67
<i>cEc</i> <sup>d</sup>	3.68	4.49	4.46	2.47	3.38
<i>cZt</i>	0	0	0	0	0
<i>cZc</i> <sup>e</sup>	0.23	0.31	0.93	0.34	-0.05
<i>tZt</i> <sup>e</sup>	1.38	1.88	1.72	0.47	0.42

<sup>a</sup> Single-point-energy calculation. <sup>b</sup> Steric energy. <sup>c</sup> Heat of formation. <sup>d</sup> Relative to *tEt*. <sup>e</sup> Relative to *cZt*.

of the dynamics starting from the Franck-Condon region<sup>10</sup>. This can be applied in straightforward manner only to totally symmetric modes. Information on non-totally symmetric modes can be derived from overtone bands in the resonance Raman spectra<sup>11</sup>, and is much less precise.

In addition to the geometric isomerizations about ground state double bonds and to processes in which new  $\sigma$  bonds are formed, dienes<sup>12,13</sup>, trienes<sup>14,15</sup> and tetraenes<sup>16</sup> can also undergo photo-isomerization about their formal single bonds, giving rise to rotational isomers, which could be observed in low-temperature matrices. This process was not well understood until recent theoretical work from the groups of Robb, Bernardi and Olivucci showed that the simultaneous twisting of a number of bonds on

the A-excited-state surface can lead to a conical intersection with the ground state, which gives access to all known isomerization products, including single-bond rotamers<sup>17</sup>. Interestingly, although this mechanism permits photo-induced single-bond isomerization, it does not preclude the validity of the NEER principle, since different ground state rotamers still give rise to different pathways of isomerization. Decay to the initial structure or to a rotamer about one bond are among the "recoupling" pathways from the conical intersection. The conical intersections reached after excitation of different rotamers are in general different. We note that in the original paper in which the NEER principle as such was formulated<sup>1h</sup> it was explicitly considered that "one of the pathways of

Table II Computed vibrational frequencies (scaled by 0.893) and intensities in the region below 1700 cm<sup>-1</sup> for conformers of E-2,5-dimethyl-1,3,5-hexatriene (HF/6-31G<sup>a</sup>).

<i>tEt</i>			<i>cEt</i>		<i>cEc</i>		
Frequency	Symmetry	Intensity	Frequency	Intensity	Frequency	Symmetry	Intensity
55	a <sub>u</sub>	0	50	0	47	a	0
130	b <sub>u</sub>	1	112	1	107	a	1
131	a <sub>u</sub>	1	134	1	128	b	0
183	b <sub>g</sub>	0	166	0	149	b	0
211	b <sub>g</sub>	0	178	1	176	b	0
211	a <sub>u</sub>	1	209	0	177	a	0
249	a <sub>g</sub>	0	256	1	259	a	1
352	a <sub>g</sub>	0	330	2	337	a	1
419	b <sub>u</sub>	3	418	7	381	b	7
431	b <sub>g</sub>	0	423	2	414	b	10
499	b <sub>u</sub>	8	497	0	509	a	0
520	a <sub>g</sub>	0	520	2	515	b	7
533	a <sub>u</sub>	6	538	4	542	a	2
681	b <sub>g</sub>	0	685	2	698	b	2
729	a <sub>u</sub>	0	723	2	715	a	0
806	b <sub>u</sub>	1	800	1	806	b	0
813	a <sub>g</sub>	0	853	1	878	a	1
886	b <sub>g</sub>	0	887	4	889	b	6
938	a <sub>u</sub>	86	940	72	942	b	40
940	b <sub>g</sub>	0	941	15	942	a	46
958	a <sub>g</sub>	0	954	2	951	a	1
971	b <sub>u</sub>	2	966	2	962	b	2
997	a <sub>u</sub>	53	996	22	996	a	27
1005	b <sub>u</sub>	3	1005	24	1003	b	2
1030	a <sub>g</sub>	0	1022	2	1011	a	12
1049	b <sub>g</sub>	0	1050	0	1050	b	1
1051	a <sub>u</sub>	0	1053	1	1056	a	1
1256	b <sub>u</sub>	3	1214	4	1206	b	9
1291	b <sub>u</sub>	11	1285	3	1228	a	1
1294	a <sub>g</sub>	0	1293	14	1300	a	0
1312	a <sub>g</sub>	0	1310	2	1321	b	18
1392	a <sub>g</sub>	0	1393	2	1394	a	0
1395	b <sub>u</sub>	8	1395	7	1395	b	8
1417	a <sub>g</sub>	0	1416	1	1414	b	1
1426	b <sub>u</sub>	1	1422	0	1417	a	0
1454	a <sub>u</sub>	12	1452	5	1452	b	5
1454	b <sub>g</sub>	0	1454	7	1452	a	7
1470	a <sub>g</sub>	0	1465	8	1465	a	1
1473	b <sub>u</sub>	16	1471	7	1465	b	14
1624	a <sub>g</sub>	0	1640	20	1663	b	14
1663	b <sub>u</sub>	29	1663	12	1664	a	2
1689	a <sub>g</sub>	0	1688	1	1677	a	9

relaxation could lead to another rotamer", a proposition that has now been put into a more thorough theoretical framework.

The recent breakthrough on the theoretical side has prompted us to publish some of our own results on the effect of alkyl substituents on the photoisomerization pathways of trienes in argon matrices, with the hope of stimulating further discussion, computation and experiments in this field.

## 2. Experimental

*E*- and *Z*-2,5-Dimethyl-1,3,5-hexatriene (*E*-DMH and *Z*-DMH) and 1,4-dimethyl-1,3-cyclohexadiene (DMCHD) were prepared as described<sup>9,18</sup>.

The experimental set-up for argon-matrix-isolation spectroscopy is basically that described by Hagen et al.<sup>19</sup>. Briefly, samples (at room temperature) containing a mixture of the substrate and argon, in the specified molar ratio, were deposited onto an aluminum block mounted in an Air Products Displex cryostat. The sample temperature was about 15 K. The cryostat was equipped with a KBr window and up to three quartz windows. IR spectra were obtained using a Digilab FTS-15 BD FTIR spectrometer. We will only report IR data from the region 1800–700 cm<sup>-1</sup>. To measure UV spectra, light from an Oriel deuterium lamp was focussed onto the entrance slit of a home-built monochromator, placed in front of one of the quartz windows. The sample was placed at an angle of 45° and the reflected light was detected using a photomultiplier, fitted to a quartz window at right angles to the first one. A reference spectrum (*I*<sub>0</sub>) was taken

prior to depositing the sample. The intensity spectra were digitized manually and converted to absorbance spectra. The effective band width of the monochromator was about 1.5 nm, measured from the full width at half maximum of the 254-nm line of a low-pressure Hg lamp used for wavelength calibration. The use of narrower slits, or of a double monochromator did not reveal a more pronounced fine-structure in the UV absorption spectra. For irradiation at 254 nm an Osram 10-W low-pressure Hg lamp was used. Irradiation at wavelengths greater than about 280 nm was performed using an Oriel 200-W high-pressure Hg source, filtered through water and Pyrex glass.

*Ab-initio* calculations of structures and vibrational spectra were performed using Gaussian92<sup>20</sup>.

## 3. Results and interpretation of spectra

### 3.1. Preliminary considerations: conformations of dimethyl-hexatrienes

The initial distribution of conformers of *E*- and *Z*-2,5-dimethyl-1,3,5-hexatriene in the argon matrix is likely to be the same as it is at room temperature in the gas phase. Experimentally, the conformational analysis was performed in solution, using UV and NMR spectroscopy<sup>18</sup>, but there is no reason to assume that the situation in the gas phase would be very different. In solution the *E* isomer (*E*-DMH) exists almost exclusively in the *tEt* conformation. For the *Z* isomer (*Z*-DMH), the *cZt* confor-

Table III Computed vibrational frequencies (scaled by 0.893) and intensities in the region below 1700 cm<sup>-1</sup> for conformers of *Z*-2,5-dimethyl-1,3,5-hexatriene (HF/6-31G\*).

<i>tZt</i>			<i>cZt</i>		<i>cZc</i>		
Frequency	Symmetry	Intensity	Frequency	Intensity	Frequency	Symmetry	Intensity
12	b	0	34	0	44	a	0
67	a	0	59	0	46	b	0
137	a	0	137	0	129	a	0
162	b	0	178	0	176	b	0
176	a	0	211	0	176	a	0
212	a	1	224	0	194	a	0
274	b	2	261	2	283	b	0
381	a	0	359	2	365	a	0
383	b	6	409	9	368	b	6
415	b	6	425	5	408	b	14
452	a	1	456	3	474	a	3
571	a	4	569	3	572	a	1
628	b	3	646	1	621	b	1
701	a	1	703	7	708	b	9
730	b	12	713	1	708	a	0
741	a	1	743	3	752	a	0
756	b	14	802	16	801	b	23
842	b	2	853	1	879	b	1
924	a	0	928	1	924	a	0
942	b	54	943	48	944	b	78
945	a	25	952	53	948	a	19
959	b	17	964	4	954	b	6
999	a	0	1001	7	994	a	2
1015	a	0	1018	1	1010	b	6
1017	b	13	1019	2	1019	a	0
1053	a	0	1050	1	1048	a	0
1059	b	3	1055	3	1058	b	2
1192	a	0	1216	3	1219	a	0
1258	b	15	1234	14	1224	b	20
1290	a	1	1306	1	1236	a	0
1369	b	9	1380	3	1392	b	3
1394	a	2	1392	2	1392	a	1
1399	b	3	1404	2	1406	b	3
1416	a	1	1415	1	1418	a	1
1426	b	4	1435	2	1423	b	1
1450	b	6	1450	5	1451	a	3
1454	a	5	1455	8	1452	b	8
1465	b	12	1463	8	1464	a	10
1469	a	2	1469	17	1466	b	7
1624	a	0	1632	12	1671	a	3
1665	b	33	1670	13	1672	b	19
1698	a	0	1688	1	1682	a	1

mation is thought to be the predominant form, with a smaller fraction of molecules in the *cZc* conformation<sup>21</sup>. The *cZc* species can be generated by photo-induced ring opening of 1,4-dimethyl-1,3-cyclohexadiene<sup>22</sup>. At room temperature rapid conformational equilibration occurs, but in the low-temperature matrix it may be possible to trap the *cZc* form.

The optical absorption spectra of *s-cis* conformers of the *E* isomer are characterized by a reduced absorbance and a small blue-shift of the maximum, and a longer tail on the long-wavelength side of the band<sup>9a,14,18</sup>. In the case of the *Z* isomer the optical absorption spectra in liquid solution are devoid of fine structure. Model compounds<sup>21</sup> indicate that the *cZt* and *cZc* forms are characterized by absorption maxima at *ca.* 235–240 nm, with molar absorption coefficients of *ca.* 13000 and 4000 M<sup>-1</sup>·cm<sup>-1</sup>, respectively.

The IR spectra of several conformers of *E* and *Z* hexatriene have been reported<sup>14,22,23</sup>. Some of the characteristic features will be reviewed below and a comparison made with the data obtained in the present work.

In order to facilitate the interpretation of the IR spectra, we performed quantum-chemical calculations of structures, energies and vibrational spectra of the relevant conformations of 2,5-dimethylhexatriene. We have previously found<sup>24</sup> that Hartree-Fock calculations give satisfactory accounts of the relative energies of substituted hexatriene rotamers, but that molecular mechanics calculations [MM2(87)] gave incorrect results. In particular, MM2(87) seriously underestimated the energy difference between the conformers. In the present work we have used MM3(94)<sup>25</sup> and, as can be seen in Table I, the results are much more consistent with the *ab-initio* results. It is well known that uniform scaling of Hartree-Fock calculated harmonic frequencies by a factor of 0.893 usually gives reasonable agreement with experimental frequencies. For the present purpose we consider a more sophisticated approach unnecessary. The results are presented in Tables I, II, and III.

For the *E* isomer all calculations are in agreement with the known predominance of the *tEt* form. Introduction of each *s-cis* linkage increases the energy by roughly 2 kcal/mol. For the *Z* isomer the energy difference between *cZt* and *cZc* is small, but essentially in agreement with the predominance of *cZt*. The MP2 calculations are the most reliable, and agree best with the experimental ratio of *ca.* 9:1 of *cZt* and *cZc* estimated from room temperature UV absorption and NMR data<sup>18,21</sup>. The calculations indicate that the *tZt* form (actually non-planar, *trans-gauche*) is rather insignificant.

### 3.2. Experiments starting from *E*-2,5-dimethylhexatriene (*E*-DMH)

A matrix of *E*-DMH in argon (1:300, deposition time 10 min) was irradiated for 10 min at 254 nm. The UV-absorption spectra before and after irradiation are shown in Figure 1. Subsequently, the sample was irradiated at  $\lambda > 280$  nm, whereupon the initial spectrum almost completely reappeared (Figure 1c).

The large reduction of the UV absorption (Figure 1b) indicates that most of the *tEt* rotamer is removed by irradiation. The absorption coefficients at the maxima are typically 43 000, 17 000 and 10 000 M<sup>-1</sup>·cm<sup>-1</sup> at *ca.* 260 nm for *tEt*, *cEt* and *cEc* species<sup>9a,18</sup>. The result of the second irradiation at  $\lambda > 280$  nm indicates that the photo-products are almost exclusively the *s-cis* rotamers which can be converted back into the *tEt* form by selective excitation.

To obtain IR spectra an approximately four-fold thicker sample was prepared. Because of the strong absorption at

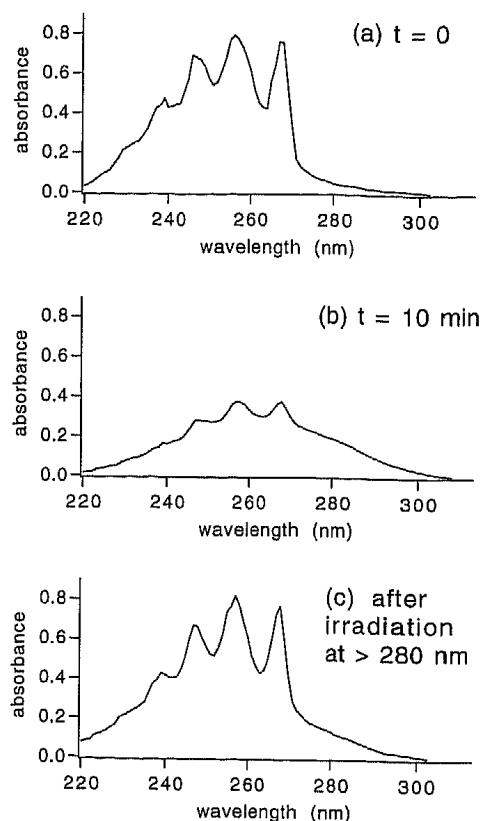


Figure 1. UV absorption spectra of *E*-DMH before (a) and after (b) irradiation at 254 nm, and after subsequent irradiation at  $\lambda > 280$  nm (c).

254 nm, which hampers light penetration, irradiation of the sample was not effective. A greater conversion was achieved by irradiating during deposition. Parts of the IR spectra of *E*-DMH and the irradiated sample are shown in Figure 2. Frequencies are listed in Table IV.

The spectra prior to irradiation are attributed to the *tEt* form. The IR and Raman spectra of *E*-DMH have been assigned by Langkilde *et al.*<sup>26</sup>. The matrix-isolated samples show a few more bands than expected. For example, there should be one IR active C=C mode, but the band appears to be split into two bands at 1621 and 1624 cm<sup>-1</sup>. It is likely that these splittings are due to the presence of different matrix sites.

Irradiation produces some clear new IR bands, in particular at 1632, 1608, 1379, 1340, and 1336 cm<sup>-1</sup>, while the band at 966 cm<sup>-1</sup> increases in intensity indicating the presence of a more intense band of the photoproduct(s) at that wavenumber. As in the experiment with UV detection, the extent of conversion of the *tEt* form by irradiation must have been considerable, because some bands almost completely disappear (*e.g.* 1256 and 1313 cm<sup>-1</sup>). The bands in the region 1600–1650 cm<sup>-1</sup> obviously correspond to C=C stretching modes. The calculations predict that the *s-cis* rotamers of *E*-DMH have a higher frequency IR active C=C mode, while *cEt* also has one at lower frequency. Thus, the band at 1632 cm<sup>-1</sup> may be from *cEt* or *cEc*, while that at 1608 is probably due to *cEt*. Similar results have been reported for the parent *E*-1,3,5-hexatriene<sup>14</sup>. Although the computed IR intensities are not very reliable, they suggest that the high-frequency C=C band should be attributed to *cEc* rather than *cEt*.

The bands in the 1350–1500 cm<sup>-1</sup> region are essentially deformation modes of the methyl groups, and CH<sub>2</sub> scissoring. Several new bands are found here but they cannot be unequivocally assigned. The *tEt* rotamer has bands at 1313 and 1256 cm<sup>-1</sup> which can be assigned to C–C stretching and CH bending, respectively<sup>26</sup>. According to

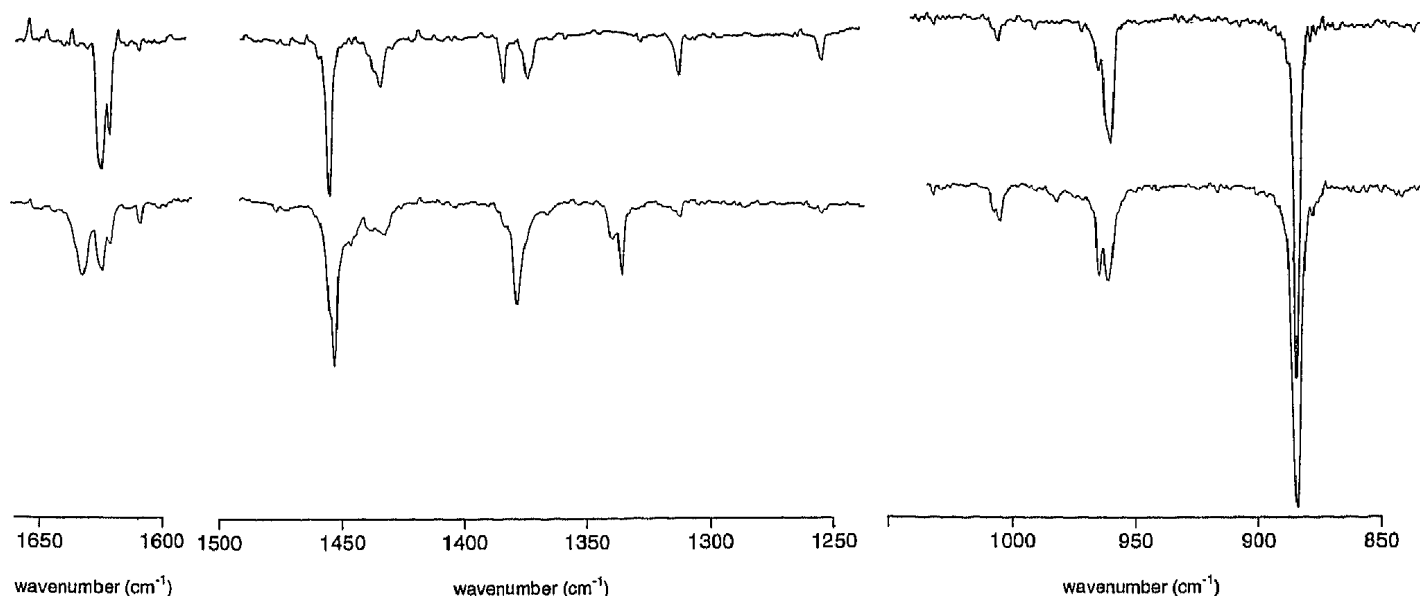


Figure 2. Partial IR spectra of *E*-DMH in argon (top) and of *E*-DMH irradiated during deposition (bottom).

calculation, the CH bending mode ( $1256\text{ cm}^{-1}$ ) has its counterparts in *cEt* at  $1310$  and in *cEc* at  $1206\text{ cm}^{-1}$ . The C-C stretching mode is predicted to occur at  $1291$  in *tEt*, at  $1293$  in *cEt* and at  $1321$  in *cEc*. Two new bands are found, at  $1336$  and  $1340\text{ cm}^{-1}$ , and they can be best assigned to a CH bending mode of *cEt* and the C-C stretching of *cEc*.

The strong band at  $962\text{ cm}^{-1}$  in *tEt* must be the CH wag of the central double bond, the weaker one at  $966\text{ cm}^{-1}$  the  $\text{CH}_2$  rocking mode. In the irradiated sample the  $966$  band is stronger. According to the calculations, all rotamers have their CH wag mode at nearly the same frequency. The strongest band in the spectrum, the  $\text{CH}_2$  wag at  $885\text{ cm}^{-1}$ , is also at nearly the same frequency for all rotamers. The absence of the strong  $\omega(\text{CH}_2)$  bands of

the *Z* isomer ( $900$  and  $890\text{ cm}^{-1}$ , see below) implies that irradiation has not led to *E-Z* isomerization.

In conclusion, the UV and IR data show that irradiation of *E*-DMH in argon at  $15\text{ K}$  produces the *cEt* and *cEc* rotamers, which can be reconverted to the *tEt* form by selective irradiation. The IR data can possibly be accounted for by *cEt* being the only photorotamer because all its vibrations can have some IR intensity, but the large reduction of the UV absorption can only be explained if a considerable fraction of *cEc* is also formed.

### 3.3. Experiments starting with *Z*-2,5-dimethylhexatriene (*Z*-DMH)

In the case of *Z*-DMH, UV and IR spectra were measured of the same series of samples (1:280 in Ar). The

Table IV Infrared bands of *E*-DMH in the region  $600\text{--}1700\text{ cm}^{-1}$ . Assignments for *tEt* are based on Ref. 26 and ab-initio calculations. Assignments for the photoproduct bands to *cEt* or *cEc* are tentative, and based on ab-initio calculations (Table II). Abbreviations used: *vs* = (very) strong, *m* = medium, *v(w)* = (very) weak, *sh* = shoulder; in the assignments: *d* = deformation,  $\nu$  = stretching, *r* = rocking, *s* = scissoring, *w* = wagging.

<i>tEt</i> <sup>a</sup>	Assignment (calculated)	Product bands	Assignment
		1632	C=C <i>cEt</i> (1688) or <i>cEc</i> (1677)
1624 <i>s</i> 1621 <i>s</i>	C=C (1663)	1608	C=C <i>cEt</i> (1640)
1456 <i>s</i>	<i>d</i> ( $\text{CH}_3$ ) (1473)	1454 1448	<i>d</i> ( $\text{CH}_3$ ) <sup>b</sup> <i>s</i> ( $\text{CH}_2$ ) or <i>d</i> ( $\text{CH}_3$ ) <sup>b</sup>
1437 <i>m</i> 1384 <i>m</i>	<i>s</i> ( $\text{CH}_2$ ) (1426) or <i>d</i> ( $\text{CH}_3$ ) (1454) <i>d</i> ( $\text{CH}_3$ ) (1395)	1379	<i>d</i> ( $\text{CH}_3$ ) <sup>b</sup>
1374 <i>m</i>	<i>d</i> ( $\text{CH}_3$ ) (1395)	1340 1336	$\nu$ (C-C) <i>cEc</i> (1321) <i>r</i> (CH) <i>cEt</i> (1310)
1313 <i>m</i> 1256 <i>m</i> 1007 <i>m</i>	$\nu$ (C-C) (1291) <i>r</i> (CH) (1256) <i>w</i> ( $\text{CH}_3$ ) (1005)	983 <sup>w</sup> 966	<i>r</i> ( $\text{CH}_2$ ) <i>cEc</i> (1011) <i>w</i> (CH)
966 <i>m</i> 962 <i>s</i> 885 <i>vs</i>	<i>r</i> ( $\text{CH}_2$ ) (971) <i>w</i> (CH) (997) <i>w</i> ( $\text{CH}_2$ ) (938)	885	<i>w</i> ( $\text{CH}_2$ )

<sup>a</sup> Prior to irradiation. <sup>b</sup> There are several possible assignments to *d*( $\text{CH}_3$ ) or *s*( $\text{CH}_2$ ) modes of *cEt* or *cEc*.

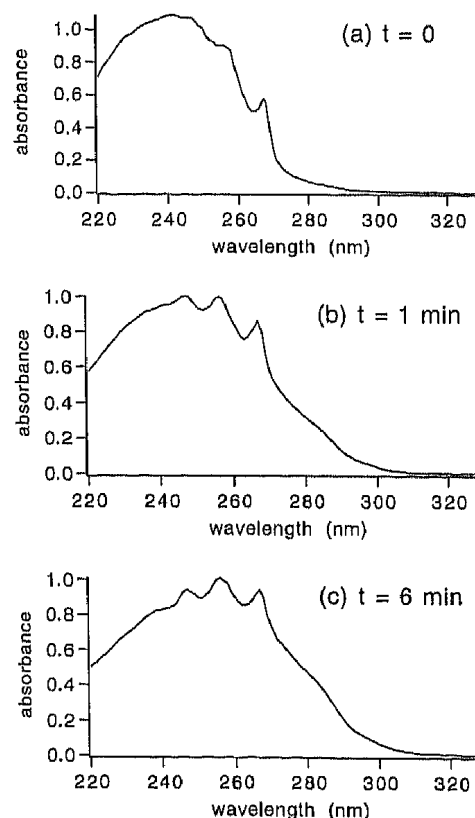


Figure 3. UV absorption spectra of *Z*-DMH in argon (a), irradiated at  $254\text{ nm}$  for  $1\text{ min}$  (b) and  $6\text{ min}$  (c).

UV-absorption spectra showing the effect of irradiation at 254 nm are displayed in Figure 3. According to the relative energies, the sample must initially contain predominantly the *cZt* conformer, with a minor contribution from *cZc* (at most *ca.* 10%). Note that the spectrum of *Z*-DMH shows some vibrational fine-structure (origin at 267 nm, other peaks at 255 and 247 nm), which is completely absent in liquid phase spectra. We cannot completely exclude the possibility that these peaks are due to contamination of the matrix sample with some *E*-DMH (see below).

Irradiation of the fresh *Z*-DMH sample at wavelengths greater than 280 nm had no effect. This should convert the *cZc* rotamer to 1,4-dimethyl-1,3-cyclohexadiene (DMCHD) (see below), but apparently the proportion of the *cZc* form is so small that its conversion to DMCHD does not visibly change the spectrum. Upon irradiation at 254 nm, a band appears at the long-wavelength tail, while the characteristic peaks of the *E* isomer (267, 256, 246, 239 nm) are seen to emerge.

IR data of *Z*-DMH and its photoproducts are given in Table V. In Figure 4, the changes upon irradiation in the 800–1000  $\text{cm}^{-1}$  region of the IR spectrum of *Z*-DMH are shown.

The C=C stretching region shows six distinct peaks, at 1638, 1634, 1624, 1608, 1605, and 1600  $\text{cm}^{-1}$ . Three bands may be IR active for *cZt* and three for *cZc*, but the calculation indicates that the latter rotamer should give only one intense IR band, coincident with a *cZt* band. As

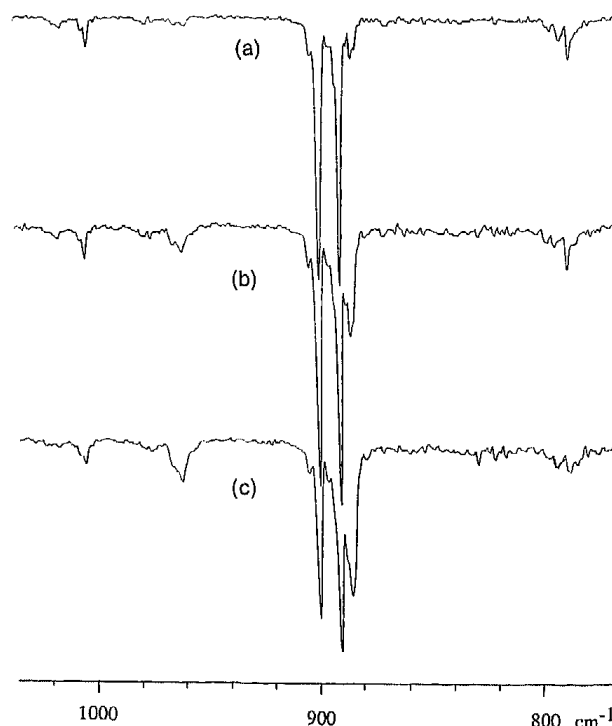


Figure 4. Parts of the IR spectra of *Z*-DMH in argon (a), after 1 minute of irradiation at 254 nm (b) and after 6 minutes of irradiation (c).

Table V IR bands of *Z*-DMH (*cZt*) and its photoproducts.

Before	Assignment (calculated) <sup>a,b</sup>	After 6 min 254-nm irradiation <sup>c</sup>	Comments/assignment
1638 m	C=C (1688)		
1633 m	C=C (1682)	1633	C=C <i>cEt</i> / <i>cEc</i>
1624 m	C=C (1670)	1624 (+)	C=C <i>cEt</i> / <i>cEc</i> / <i>tEt</i>
1608 w	C=C (1632)	1608	C=C <i>cEt</i> / <i>cEc</i>
1605 w	C=C (1632)		
1600 m	C=C (1632)	1600 (-)	
1452 s	<i>d</i> (CH <sub>3</sub> ) (1469)	1456	<i>d</i> (CH <sub>3</sub> ) any triene
1444 m	<i>d</i> (CH <sub>3</sub> ) (1450)		
1388 w	<i>d</i> (CH <sub>3</sub> ) (1392)	1440	<i>d</i> (CH <sub>3</sub> ) <i>cEc</i> or <i>cEt</i>
1376 m	<i>s</i> (CH <sub>2</sub> ) (1380)	1379	<i>d</i> (CH <sub>3</sub> ) <i>cEt</i> or <i>cEc</i>
1373 m	<i>s</i> (CH <sub>3</sub> ) (1380)		
1312 vw	<i>d</i> (CH <sub>3</sub> ) (1306)	1340	$\nu$ (C-C) <i>cEc</i>
1249 m	<i>r</i> (CH)/ <i>r</i> (CH <sub>2</sub> )/ <i>r</i> (CH <sub>3</sub> ) (1234)	1336	<i>r</i> (CH) <i>cEt</i>
1046 w	<i>r</i> (CH <sub>3</sub> ) (1055)		
1039 w	<i>r</i> (CH <sub>3</sub> ) (1050)		
1010 w	<i>w</i> (CH <sub>3</sub> ) (1019)		
1005 m	<i>w</i> (CH <sub>3</sub> ) (1001)		
961 w	<i>s</i> (CH <sub>2</sub> ) (964)	967	<i>w</i> (CH) <i>cEt</i> / <i>cEc</i>
905 sh		964	<i>w</i> (CH) <i>tEt</i> / <i>cEt</i> / <i>cEc</i>
900 vs	<i>w</i> (CH <sub>2</sub> ) (952)	900 (-)	
890 vs	<i>w</i> (CH <sub>2</sub> ) (943)	890 (-)	
886 m	<i>r</i> (CH <sub>2</sub> ) (928)	886 (+)	<i>w</i> (CH) <i>tEt</i> / <i>cEt</i> / <i>cEc</i>
793 w			
789 m	<i>w</i> (CH) (801)		
735 m	<i>d</i> (CCC)/ $\tau$ (C=C) (741)		
701 m	<i>d</i> (CCC)/ $\tau$ (C=C) (703)		

<sup>a</sup> Characterization of the normal modes is only very approximate because separation between in-plane and out-of-plane modes is not possible. <sup>b</sup> For the meaning of symbols and abbreviations see Table IV. <sup>c</sup> (+) = increase, (-) = decrease of intensity; only the bands that clearly change in intensity are given.

in the case of *E*-DMH, matrix effects are a likely cause for the splitting of bands. In liquid solution, bands are observed<sup>27</sup> at 1635  $\text{cm}^{-1}$  and at 1595  $\text{cm}^{-1}$ . The presence of the IR bands at 1624 and 886  $\text{cm}^{-1}$  and the peaks in the UV absorption spectrum could be due to a small amount of *E*-DMH present in the sample. The band at 886  $\text{cm}^{-1}$  has about the same intensity as the one at 1624  $\text{cm}^{-1}$ , while in *E*-DMH the ratio is about 3:1. Gas chromatographic analysis indicated that the *Z*-DMH sample was at least 98% pure, but it is hard to exclude the possibility that some isomerization occurs during the preparation of the matrix sample. Thus, the peaks in the UV spectrum may be due to a small contamination with *E*-DMH.

Irradiation at 254 nm for only one minute immediately enhances the band at 1624  $\text{cm}^{-1}$  at the expense of the band at 1600  $\text{cm}^{-1}$ . The product bands can be attributed to the rotameric forms of the *E* isomer. *Z*-DMH shows two strong bands due to wagging of the CH<sub>2</sub> groups at 900 and 890  $\text{cm}^{-1}$ , and weaker bands at 905 (shoulder) and 885  $\text{cm}^{-1}$ . The CH wag is at 789/793  $\text{cm}^{-1}$ . Upon irradiation the bands of the *E* isomer appear at 962/968  $\text{cm}^{-1}$  and at 885  $\text{cm}^{-1}$ . The changes in this spectral region are shown in Figure 4.

The changes in the spectra are consistent with the isomerization *cZt* → *cEt*. The other rotamers may be formed in small amounts. Even after prolonged irradiation (6 minutes) the characteristic band of the *tEt* rotamer at 1256  $\text{cm}^{-1}$  is not seen, and the UV absorbance remains low. As expected, the *tEt* form could be produced in another experiment, in which irradiation at 254 nm during deposition was followed by irradiation at  $\lambda > 280$  nm (not shown).

### 3.4. Experiments with 1,4-dimethyl-1,3-cyclohexadiene (DMCHD)

The samples of DMCHD (1:330) allowed sufficient light penetration for UV and IR measurements to be made of the same samples. Upon irradiation at 254 nm (Figure 5) a new absorption rapidly appears at long wavelength,

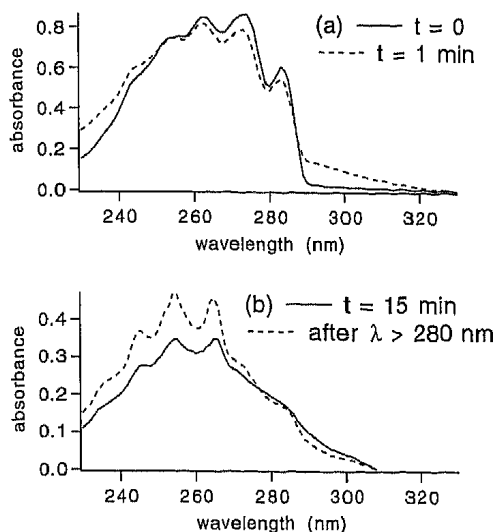


Figure 5. UV absorption spectrum of DMCHD in argon and the spectrum resulting after irradiation at 254 nm for 1 min (a); another sample of DMCHD irradiated for 15 min at 254 nm, followed by irradiation at  $\lambda > 280$  nm (b).

Table VI IR bands of photoproducts of DMCHD in the range 700–1400  $\text{cm}^{-1}$ <sup>a</sup>.

After 1 min irradiation at 254 nm	After 4 min irradiation at 254 nm	After subsequent irradiation at $\lambda > 280$ nm	Comments
1376 s	1376 s		<i>cZc</i> , <i>cEc</i> , <i>cEt</i>
	1340 w		<i>cEc</i> ?
1244 m	1244 m	disappears	<i>cZc</i>
1007 w	1007		any triene
	965 w		<i>cEt</i> / <i>cEc</i>
907 s	905	almost disappears	<i>cZc</i>
899 m/s	899 (-)	900 sh	<i>cZc</i> or <i>cZt</i>
892 m/s	893 (-)	893 sh	<i>cZc</i> or <i>cZt</i>
885 s	886 (+)	886	<i>cZc</i> , any <i>E</i> -triene
	830 w	830 w	
	795 <sup>b</sup>	794	
790 (broad)	790 (+)	absent	<i>cZc</i>
785 (broad)	785	785	
	724		
	712		

<sup>a</sup> The ranges 1600–1650  $\text{cm}^{-1}$  (C=C stretches) and 1430–1460  $\text{cm}^{-1}$  (methyl deformation) show a complex pattern of weak bands. <sup>b</sup> Decreases in intensity upon prolonged irradiation at 254 nm.

extending to about 330 nm. This long red tail is highly characteristic of the *cZc* conformer<sup>21,28</sup>. Continued irradiation causes a blurring of the initial fine structure (peaks at 284, 273, 264 and 256 nm), followed by the appearance of peaks at 266, 256 and 246 nm, which are further amplified by irradiating at wavelengths greater than 280 nm. Apparently, the *tEt* form is ultimately formed via photoinduced *Z* → *E* and *s-cis* → *s-trans* isomerizations.

In the region 700–1700  $\text{cm}^{-1}$  IR bands of DMCHD are observed at 1668 (s), 1624 (w), 1608 (w), 1453 (vs), 1440 (m), 1436 (w), 1431 (w), 1380 (m), 1370 (w), 1302 (w), 1240 (w), 1170 (w), 1086 (m), 1058 (w), 1033 (w), 1023 (m), 974 (w), 822 (vs), 758 (w), and 708 (w)  $\text{cm}^{-1}$ . The bands of the photoproducts are reported in Table VI. In Figure 6, difference spectra of the region around 900  $\text{cm}^{-1}$  are shown at different stages of irradiation.

The difference spectrum after one minute of irradiation (Figure 6a) reveals strong bands that must be attributed to the  $\text{CH}_2$  wagging vibrations of *Z*-DMH: upon irradiation DMCHD undergoes ring opening to produce *cZc*-DMH. It is known<sup>1h,9</sup> that irradiation of a *cZc* triene can lead to ring closure and *Z-E* isomerization. The question is whether there is also formation of *cZt*, either thermally or photochemically. At most, two of the four peaks seen in the region 885–905  $\text{cm}^{-1}$  may be due to the *cZt* form. The high-frequency band (905) must certainly be due to *cZc*, the rotamer initially formed in the ring-opening process. Also the lowest-frequency band in this area, at 885  $\text{cm}^{-1}$ , is not due to *cZt*. Other bands (not shown) in the difference spectra occur at 1376 and 1244  $\text{cm}^{-1}$ . The former could be due to several species, but the 1244 band cannot be attributed to either an *E* triene or to *cZt*.

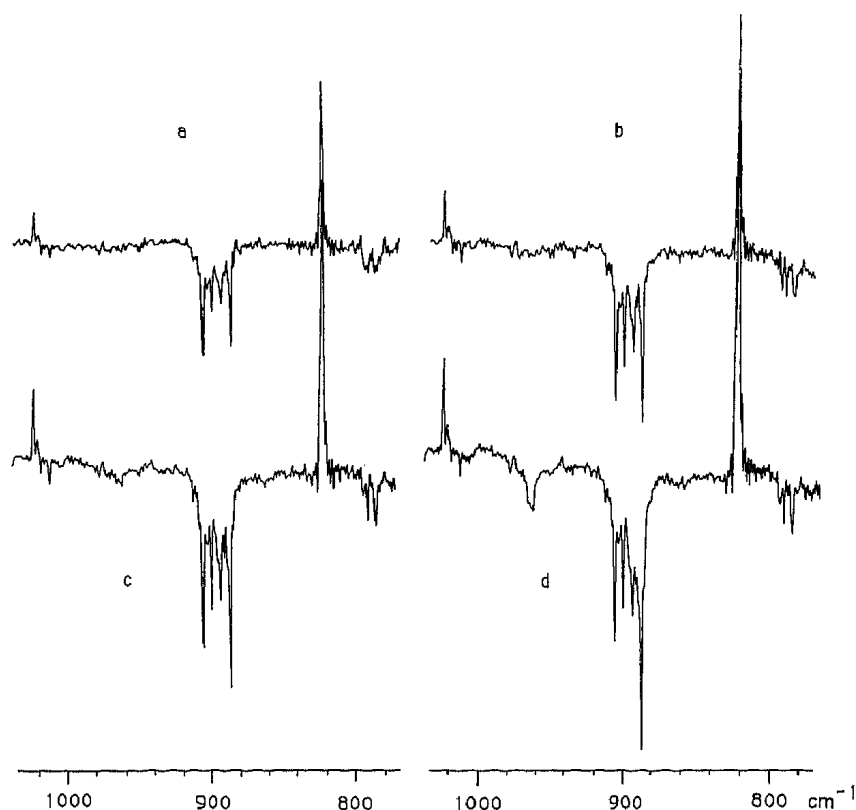
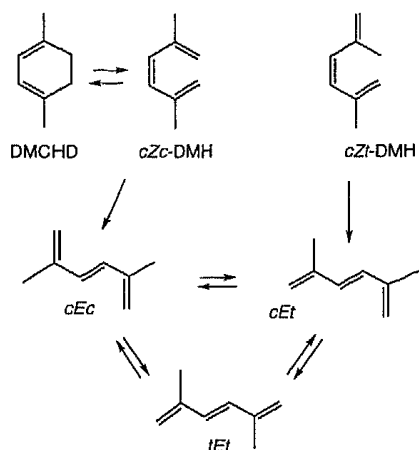


Figure 6. Partial difference IR spectra from a sample of DMCHD irradiated at 254 nm for 1 min (a), 2 min (b), 4 min (c) and 16 min (d). The peaks due to disappearance of the starting material are shown as positive.





Scheme 1. Major photo-isomerization pathways in DMH and DMCHD

According to the calculations this band probably corresponds to a mode (calculated at  $1224\text{ cm}^{-1}$ ) consisting mostly of in-plane deformation of the C=CH angles of the central double bond [ $r(\text{CH})$ ]. The corresponding band of cZt occurs at  $1249\text{ cm}^{-1}$ , and this difference of  $5\text{ cm}^{-1}$  is easily resolved with the present experiments. In conclusion, it is likely that the species observed are cZc- and E-trienes. Upon prolonged irradiation the latter accumulate, even more so when irradiation at  $\lambda > 280\text{ nm}$  is applied which converts *s-cis* E-trienes to tEt and irreversibly isomerizes cZc-DMH to DMCHD (not shown).

Similar sets of experiments have been carried out with E- and Z-DMH deuterated at the central double bond: E-2,5-dimethyl-3,4-dideuteriohexatriene and Z-2,5-dimethyl-3,4-dideuteriohexatriene. The spectra obtained yield essentially the same information as reported above for the nondeuterated compounds.

#### 4. Discussion

In the previous section we have interpreted the spectra resulting from irradiation experiments starting from different isomers and rotamers of 2,5-dimethyl-1,3,5-hexatriene. Our observations can be summarized by the reactions in Scheme 1.

The experiments described here have limited quantitative significance. The method used is not sensitive enough to detect low yields of side products that can be expected to result from cyclization reactions. We only observed the processes that occur with significant efficiency in the argon matrix environment. It was not possible to excite species completely selectively. Once the starting material is converted to a product, the product absorbs light and will undergo secondary reactions. Some selectivity could however be achieved by exciting either at  $\lambda 254\text{ nm}$  or at  $\lambda > 280\text{ nm}$ . Measurement of quantum yields of the processes observed was obviously not possible. We can only make an estimate of the order of magnitude of the efficiency of rotamerization if we assume that the quantum yields of formation of geometric isomerization products are similar to those in solution.

Starting from E-DMH, which exists almost exclusively in the tEt form, cEt and cEc rotamers are obtained. Characteristic IR bands could be seen, but the product rotamers could not be identified individually. The large decrease in UV absorption in the 260 nm region indicates that the product must have a much lower absorption coefficient and, moreover, it must have a long tail to the red side of the band. Spectra of model compounds<sup>9a</sup> (and theoretical considerations<sup>18,29,30</sup>) indicate that this is especially true for the cEc form. The cisoid rotamers could be

almost completely reverted to the tEt form by selective excitation at the long wavelength edge of the UV band. E-DMH in solution isomerizes to the Z isomer with a quantum yield of 0.4%, to the cyclobutene derivative with a yield of 0.1%<sup>9a</sup>. The formation of the latter compound is attributed to the presence of a small fraction of *s-cis* rotamers. Under the present conditions there is no indication for formation of the Z isomer or the vinylcyclobutene, and we only see an enrichment in the cisoid rotamers. For the cEc rotamer model compound 2,5-di-tert-butyl-1,3,5-hexatriene we found in solution quantum yields of isomerization of 2.9% to the cyclobutene derivative and of 4.6% to the Z isomer<sup>9a</sup>. Long-wavelength irradiation of the matrix containing *s-cis* rotamers of E-DMH leads to essentially complete re-formation of the tEt form. There is no evidence for the occurrence of E → Z isomerization. In particular, the strong bands of the CH<sub>2</sub> wag vibration of the Z isomer would have been easily detected. Thus, it is likely that the rotamerization has an efficiency which is significantly greater than a few percent.

The Z isomer contains only a small fraction of the helical cZc conformation, but probably exists in solution at room temperature predominantly in the cZt form, which cannot undergo  $6\pi$  electrocyclozation to cyclohexadiene. The matrix experiments are in agreement with this. The cZc form, on the other hand, can be produced by ring opening of 1,4-dimethyl-1,3-cyclohexadiene. Irradiation of cZt, similar to the liquid solution ( $\Phi_{Z-E} = 0.37$ )<sup>9a</sup> leads to the E isomer. Different rotameric forms of the E isomer are observed, but this may well be due to secondary isomerization reactions. The cZc species can be photo-isomerized reversibly to the CHD isomer, irreversibly to E-triene. We have no direct evidence for photo-induced interconversions between cZc and cZt.

Clearly, there are two different types of reaction appearing in the two geometric isomers. The Z-trienes undergo relatively efficient isomerization reactions at the central double bond, whereas the E-trienes isomerize at the single bonds. For the parent hexatrienes similar experiments have indicated only single-bond isomerization, for E- as well as for Z-hexatriene<sup>14</sup>. It is most likely that the reactions discussed here proceed in the singlet manifold, as in solution. After excitation to the B singlet state intersystem crossing probably cannot compete with other processes. Moreover, the photochemical isomerization processes in the triplet manifold are restricted to E-Z interconversion<sup>32,33</sup>.

Thanks to the theoretical work of the groups of Robb, Olivucci and Bernardi<sup>17</sup>, all singlet isomerization processes can be discussed within a single theoretical framework. The theory rationalizes the known photochemistry of hexatrienes and many other reactions, so it is likely to be essentially correct. Unfortunately, the computational models are not sufficiently developed at present to predict accurately the pathways followed on the excited state surface, *i.e.* the choice between accessible intersection regions, or to calculate the ground state dynamics that initiate from the intersection region. For Z-hexatriene, the calculations of Olivucci et al.<sup>31</sup> reveal barriers on the excited state potential energy surface of 1.0 kcal/mol on the pathway leading to single-bond isomerization, and 1.5 kcal/mol for double-bond isomerization. The lower barrier on the former pathway is in agreement with the finding of mostly single bond isomerization of Z-HT<sup>14</sup> and a low quantum yield for Z-E isomerization<sup>32</sup>. The computed barriers are so low that the excited state lifetime cannot be expected to be long enough to permit strong fluorescence. Experimentally, fluorescence from Z-hexatriene has been observed in a supersonic beam<sup>4</sup>, but only when a very low excess energy above the 0–0

transition is applied. Apparently, the barrier to escape from the fluorescent state is at most a few hundred  $\text{cm}^{-1}$ . At 15 K in the argon matrix the thermal energy is very small, and even the smallest barriers should be insurmountable. On the other hand, a considerable amount of excess energy is deposited into the sample by excitation at 254 nm (corresponding to ca. 5000  $\text{cm}^{-1}$  relative to the relaxed  $A$  state of isolated  $Z$ -hexatriene<sup>3,4</sup>), and due to the rather inefficient energy dissipation by the argon matrix, some of this energy may be used to cross small barriers.

For  $E$ -hexatriene calculations have revealed two types of single bond isomerization modes, an adiabatic one, and a non-adiabatic one. The former, which would lead to excited rotamers, has a higher barrier<sup>31a</sup>, and apparently does not occur, in contrast to the case of octatetraene<sup>1c</sup>. The diabatic process, in which the system evolves on the  $A_g$  surface towards a conical intersection appears to be barrierless. The selectivity of single-bond *vs.* double-bond isomerization appears to be determined by the properties of the ground state surface, since the nature of the conical intersection structure is consistent with both<sup>31a,b</sup>.

From the experimental point of view the question is still open as to whether the photorotamerization processes detected in matrices also occur in other media, such as the gas phase or liquid solution. This question should nowadays be easy to address using time-resolved transient absorption and vibrational spectroscopy, on time scales of micro- to picoseconds depending on the temperature and viscosity. In this connection we note that, to the best of our knowledge, no attempts have been published to directly observe the excited state of hexatrienes. Either investigators have been discouraged by the lack of fluorescence which suggests (but does not prove) a short-lived excited state, or negative results were obtained, which were not considered worth publishing.

In spite of the large body of results that has been achieved in the mechanistic photochemistry of the isomerization processes there is a lot of experimental work left to be done. The roles of temperature and solvent viscosity have rarely been addressed. Together with isotope effects these are tools that can be very fruitful to explore regions of the potential energy surface to which spectroscopy is not applicable because it is not possible to prepare a large population of species in non-equilibrium conditions.

Of theoretical and spectroscopic interest is how exactly the molecule goes from the initially prepared vibronic state of  $B$  electronic character to the  $A$  surface on which subsequent processes take place. A great challenge is also to predict quantitatively the outcome of the process of photon absorption. The progress made in recent years has generated expectations in this respect.

#### Note added in proof

From recent femtosecond timedelayed photoionization studies Hayden and Chandler (J. Phys. Chem. **99**, 7897 (1995)) conclude that the internal conversion of  $^1B_u$  excited 1,3,5-hexatriene proceeds through an intermediate, likely to be the  $2^1A_g$  excited state, which is observed to rise within less than 100 fs delay from the excitation, and has a decay time constant of about 250 fs.

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