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Molecular and Vibrational Structure of 1,6,6aλ^4-Trithiapentalene. Infrared Linear Dichroism Spectroscopy and *ab Initio* Normal-Mode Analyses†

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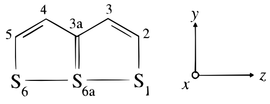
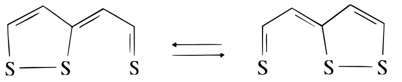
The vibrational structure of the title compound (TTP) was studied by experimental and theoretical methods. IR absorption spectra were recorded in argon matrix and in stretched polyethylene at 12 K. The linear dichroism (LD) observed in the latter solvent provided experimental symmetry assignments of the observed vibrational states. Molecular geometries and harmonic force fields were calculated *ab initio* with the 6-311G** basis set using three different procedures: restricted Hartree−Fock theory (HF), second-order Møller−Plesset perturbation theory (MP2), and density functional theory (DFT). In the latter, Becke's gradient-corrected exchange functional was combined with Perdew and Wang's correlation functional (BPW91), leading to excellent agreement with observed IR transitions. The combined experimental and theoretical evidence enabled an essentially complete assignment of the fundamental vibrations. Of particular importance is the assignment for the first time of the long-sought "bell-clapper" mode associated with the unique S−S−S structural element of TTP, giving rise to an intense, long-axis polarized transition in the far-IR (153 cm^{-1}).

1. Introduction



TTP

The unusual molecular and electronic structure of 1,6,6aλ^4-trithiapentalene (TTP) has been a subject of investigation for decades.[1−12] The main question has been whether TTP is adequately described by a rigid C_{2v} symmetrical molecular structure or whether there is rapid equilibration between two equivalent C_s structures, *e.g.*, the valence tautomers I and I′.



I I'

The available evidence indicates that TTP can be considered as a naphthalene-like 10π-electron ring system with C_{2v} symmetrical equilibrium structure, incorporating a unique linear arrangement of three sulfur atoms with weak and unusually long S−S bonds; the bond distance is close to 2.35 Å.[3,4] The central S atom is assumed to be situated in a broad U-shaped potential, giving rise to a low-frequency antisymmetrical S−S stretching vibration, the so-called "bell-clapper" vibration where the central S atom moves in a clapperlike manner toward one or the other of the two neighboring S atoms. The normal coordinate for this vibrational mode would correspond to the reaction coordinate for interconversion of the hypothetical C_s tautomers I and I′.

As emphasized 20 years ago by Gleiter,[5] analysis of the infrared (IR) absorption spectrum of TTP together with a theoretical normal-coordinate analysis would contribute greatly to the understanding of the peculiar properties of TTP. Part of the mid-IR spectrum of 2,5-dimethyl-TTP was published recently,[8] but no experimental investigation of the vibrational structure of the parent compound have been published; in particular, the postulated bell-clapper vibration has never been observed. Theoretical studies of TTP are complicated by the circumstance that *ab initio* Hartree−Fock (HF) calculations fail to reproduce the observed symmetrical structure but predict an equilibrium structure of C_s symmetry.[9,10] Post-HF single-point calculations indicate that inclusion of electron correlation leads to predictions in agreement with the observed symmetrical structure,[9] but complete geometry optimizations and vibrational frequency calculations with correlated wave functions have not been reported.

In this paper we report the results of an extensive experimental and theoretical study of the vibrational transitions of TTP in the mid- and far-IR regions, including linear dichroism (LD) spectroscopy in stretched polyethylene and high-quality *ab initio* calculations of the harmonic vibrational frequencies.

2. Experimental Section

TTP was prepared and purified as previously described.[13] Additional substance was kindly provided by Rolf Gleiter and Carl Th. Pedersen. Ordinary ($-h_4$) and perdeuterated ($-d_4$) stretched polyethylene (PE) samples were prepared using standard procedures.[13,14] The uniaxially stretched samples were pretreated at 60 °C for 28 h to avoid further orientational relaxation. Undesirable fringing effects were minimized by sanding the samples with fine sand paper.

Initial IR absorption spectra were recorded at room temperature on a Perkin Elmer FT-IR SPECTRUM 2000 spectrophotometer. Final spectra were measured at low temperature on Nicolet Magna-550 or evacuated Bomem DA-3 FT spectrophotometers using an APD-Cryogenics 202-E closed-cycle helium cryostat. Mid-IR measurements were carried out with

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† Dedicated to Professor Rolf Gleiter on the occasion of his 60th birthday.

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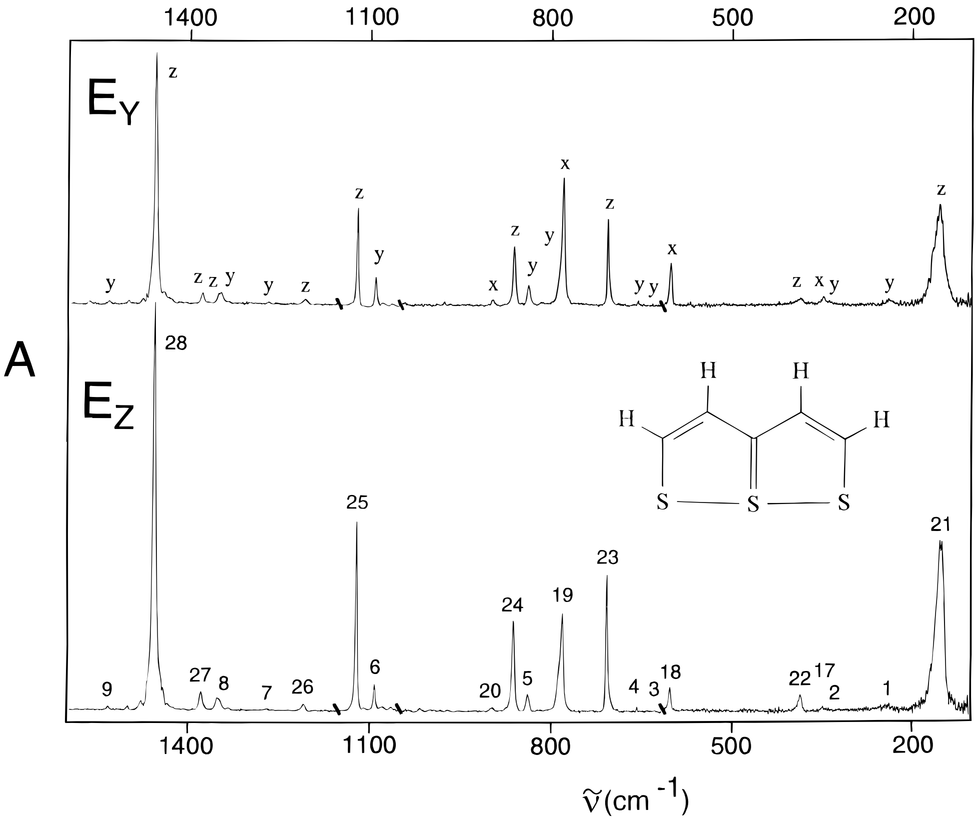

Figure 1. IR linear dichroism spectra of 1,6,6aλ^4-trithiapentalene (TTP) aligned in stretched polyethylene (PE) at 12 K. The figure shows the baseline corrected absorbance curves recorded with the IR electric vector parallel (E_Z, bottom) and perpendicular (E_Y, top) to the stretching direction. The 614−1050 and 1150−1600 cm^{-1} regions were recorded from a perdeuterated PE sample, the remainder from an ordinary PE sample.

a liquid nitrogen cooled MCT-B detector and an IGP-225 polarizer (Cambridge Physical Sciences, Ltd.). In the far-IR region a helium-cooled Si bolometer (Infrared Laboratories), IGP-223 and IGP-224 polarizers, and solid substrate Si beam-splitter were applied. Each spectrum consisted of 1000 scans with a resolution of 0.5 cm^{-1}.

Low-temperature LD spectra were recorded as follows: First, a pure stretched PE sample was mounted in a copper holder, attached to the cold tip of the cryostat, and cooled to 12 K (initially kept under reduced Ar pressure), and two baseline LD spectra were recorded corresponding to $E_Z(\tilde{\nu})$ and $E_Y(\tilde{\nu})$ (see below). The sample was then warmed to room temperature and TTP was introduced from the vapor phase by sublimation in a small evacuated container at 52 °C for 40−60 h. Excess TTP was washed from the surface of the sample with methanol, and after cooling to 12 K two LD absorbance curves were measured: $E_Z(\tilde{\nu})$ with the electric vector of the linearly polarized IR radiation parallel to the stretching direction Z, and $E_Y(\tilde{\nu})$ with the vector perpendicular to it; in both cases the direction of the beam was perpendicular to the surface of the sample sheet.[13,14] The resulting baseline-corrected LD absorbance curves are shown in Figure 1. The 1600−1150 and 1050−614 cm^{-1} regions of the spectra were obtained from a perdeuterated PE sample, the remainder from an ordinary PE sample.

The Ar-matrix sample was prepared on a CsI spectroscopic window attached to the cryostat by subliming TTP at 60 °C into a stream of Ar (0.5 mmol/min for 37 min). The mid-IR absorbance spectrum measured at 12 K is shown in Figure 2. The bands listed in Table 1 were established as belonging to TTP on the basis of identical rate of disappearance during irradiation at 454.5, 514.5 (Ar ion laser), or 248 nm (KrF excimer laser). The photochemistry of TTP in Ar matrix at 12 K is under investigation and the results will be published elsewhere.

Observed wavenumbers $\tilde{\nu}_i$ and relative integrated intensities I_i are given in Table 1. In the stretched PE experiment (Figure 1) I values were determined from the isotropic absorbance curve $E_Z(\tilde{\nu}) + 2E_Y(\tilde{\nu})$[13,14] and normalized relative to the strongest observed transition at 153 cm^{-1}. This transition is not observable in the Ar matrix; the intensities measured in Ar were normalized such that the transition corresponding to the second strongest band in PE (1449 cm^{-1}) appears with equal intensity in both solvents. The wavenumbers observed in Ar and in stretched PE are generally similar, but the relative intensities differ significantly in several instances.

3. Calculations

Molecular geometries and harmonic force fields for TTP were calculated *ab initio* at the restricted Hartree-Fock (HF) level,[15] and by using second-order Møller−Plesset perturbation theory (MP2)[15] and density functional theory (DFT).[15−17] The calculations were performed with GAUSSIAN 94[18] using standard basis set 6-311G**, including 192 basis functions (322 primitive Gaussians). The MP2 expansion considered the complete space of all molecular orbitals (keyword MP2=full).[18] In the DFT calculation Becke's gradient-corrected exchange functional[19] was combined with Perdew and Wang's correlation functional[20] (keyword BPW91).[18]

Within the constraints of C_{2v} symmetry, previous HF calculations on TTP using 4-21G, 3-21G(*), 6-31G(*), and 6-31G* basis sets lead to total energies −1371.413 964,[10] −1377.536 783,[9] −1384.055 281,[12] and −1384.131 800[9] au, respectively, indicating slow basis set convergence. The present HF/6-311G** (C_{2v}) calculation yields −1384.239 116 au; the optimized geometrical parameters are listed in Table 2. However, the C_{2v} structure corresponds to a first-order saddle point on the HF potential energy surface, characterized by one imaginary vibrational

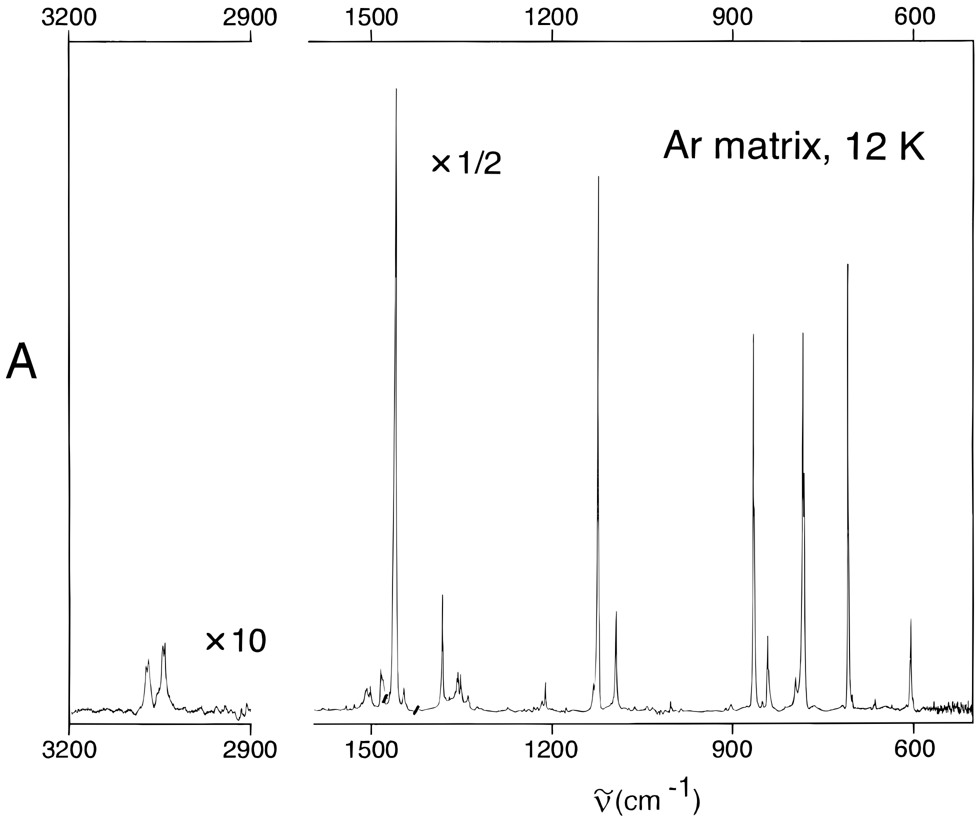

Figure 2. Mid-IR absorption spectrum of 1,6,6aλ^4-trithiapentalene (TTP) isolated in argon matrix at 12 K.

TABLE 1: 1,6,6aλ^4-Trithiapentalene (TTP). Observed Vibrational Absorption Bands and Their Assignment to Calculated Fundamental Transitions[a]

		Ar matrix		stretched PE[c]			BPW91/6-311G**[d]		
	sym[b]	$\tilde{\nu}$	I[e]	$\tilde{\nu}$	I[f]	K[g]	$\tilde{\nu}$	I[h]	approximate description[i]
ν_1	a_1			237	0.1	0.320	220	0.1	$S_{1(6)}-S_{6a}$ st; skel d
ν_2				337	0.02	0.306	320	0.1	$S_1-S_{6a}-S_6$ b; skel d
ν_3		633	0.7	629	0.03	0.303	603	0.1	$C_{3(4)}-C_{3a}$ st + iph $C_{3a}-S_{6a}$ st; skel d
ν_4		661	2.7	654*	1.3	0.310	644	1.0	$C_{3a}-S_{6a}$ st; skel d
ν_5		835	2.9	839	4.9	0.300	825	7.7	$C_{2(5)}-S_{1(6)}$ st + $C_{3(4)}-H$ b; skel d
ν_6		1091	5.1	1090	5.8	0.303	1083	10.4	$C_{2(5)}-H$ b + oph $C_{3(4)}-H$ b
ν_7		1268	0.5	1266	0.3	0.301	1231	0.2	$C_{3(4)}-H$ b
ν_8		1347	0.4	1346	2.23	0.305	1331	6.6	$C_{2(5)}-H$ b + iph $C_{3(4)}-H$ b
ν_9		1534	0.3	1532	0.3	0.31	1507	7.6	$C_{2(5)}-C_{3(4)}$ st + oph $C_{3(4)}-C_{3a}$ st; $C-H$ b
ν_{10}		3044	0.4				3102	0.9	$C_{2(5)}-H$ st
ν_{11}		3073	0.2				3123	8.0	$C_{3(4)}-H$ st
ν_{16}	b_1						127	1.0	S_{6a} op d + iph C_{3a} op d + oph $C_{2(5)}$ op d; op skel d
ν_{17}				347	1.7	0.22	336	1.9	S_{6a} op d + oph C_{3a} op d + iph $C_{2(5)}$ op d; op skel d
ν_{18}		602	6.8	602	11.7	0.240	585	11.5	C_{3a} op d + oph $C_{3(4)}-H$ op b
ν_{19}		781	17.3	778	20.2	0.259	761	55.7	$C_{2(5)}-H$ op b + iph $C_{3(4)}-H$ op b
ν_{20}		904	0.4	896	0.6	0.24	884	0.1	$C_{2(5)}-H$ op b + oph $C_{3(4)}-H$ op b
ν_{21}	b_2			153	100	0.462	228	100	$S_{1(6)}-S_{6a}$ st; skel d (bell-clapper)
ν_{22}				384	3.9	0.520	378	7.4	$S_{1(6)}-S_{6a}$ st + $C_{2(5)}-S_{1(2)}-S_{6a}$ b; skel d
ν_{23}		707	19.3	706*	16.8	0.445	699	17.8	$C_{2(5)}-C_{3(4)}-C_{3a}$ b + $C_{2(5)}-S_{1(2)}-S_{6a}$ b; skel d
ν_{24}		863	23.4	857	14.4	0.457	849	30.3	$S_{1(2)}-C_{2(5)}-C_{3(4)}$ b + $C-H$ b; skel d
ν_{25}		1121	22.4	1121	17.9	0.483	1123	23.3	$C_{2(5)}-H$ b + oph $C_{3(4)}-H$ b
ν_{26}		1207	2.3	1205	2.1	0.435	1207	0.0	$C_{2(5)}-H$ b + iph $C_{3(4)}-H$ b
ν_{27}		1378	5.1	1373	2.8	0.446	1370	4.5	$C_{2(5)}-H$ b + iph $C_{3(4)}-H$ b + $C_{2(5)}-C_{3(4)}-C_{3a}$ b
ν_{28}		1456	75.6	1449*	75.6	0.450	1479	130.2	$C_{2(5)}-C_{3(4)}$ st + oph $C_{3(4)}-C_{3a}$ st + $C_{3(4)}-H$ b
ν_{29}		3040	0.1				3101	0.7	$C_{2(5)}-H$ st
ν_{30}		3068	0.3				3121	1.2	$C_{3(4)}-H$ st

[a] Wavenumbers $\tilde{\nu}$ in cm^{-1}. Additional weak transitions observed, *e.g.*, at 785 (a_1) and 1349 cm^{-1} (b_2) were not assigned as fundamentals, see text. [b] Irreducible representations in the C_{2v} point group. In the designation of symmetry labels, the molecular axes are redefined: z and yz are taken as the C_2 axis and the molecular plane. [c] Stretched polyethylene (12 K); wavenumbers marked with an asterisk (*) indicate transitions observed in perdeuterated polyethylene. [d] Table 3. [e] Integrated intensity relative to $I_{28} \equiv 75.6$. [f] Integrated isotropic intensity $E_z + 2E_Y$ relative to $I_{21} \equiv 100$. [g] Orientation factor.[13,14] [h] Theoretical intensities relative to $I_{21} \equiv 100$. [i] st = stretching, b = bending, d = deformation, skel = skeleton, op = out-of-plane, iph = in-phase, oph = out-of-phase.

frequency, ν_{21} (Table 3). This is the transition structure on the reaction coordinate between two equivalent C_s minima on the HF potential energy hypersurface, as mentioned in the Introduction. The HF/6-311G** C_s energy minimum is $-1384.255\,660$ au which is 0.016 544 au (10.38 kcal/mol) lower than the corresponding C_{2v} transition state. But consideration of electron

TABLE 2: 1,6,6aλ^4-Trithiapentalene (TTP). Calculated C_{2v} Geometries in Comparison with Structural Data from X-ray, Electron Diffraction, and Nematic Phase ^{1}H NMR Investigations

	HF/6-311G**^{c}	MP2/6-311G**	BPW91/6-311G**	X-ray^d	ED^e	NMR^f
S1−C2^a	1.6834	1.6813	1.7019	1.684	1.698	
C2−C3	1.3585	1.3750	1.3774	1.354	1.364	1.387
C3−C3a	1.4110	1.4141	1.4177	1.409	1.422	1.404
C3a−S6a	1.7363	1.7325	1.7633	1.748	1.708	
S1−S6a	2.3797	2.3723	2.4272	2.363	2.328	
C2−H	1.0764	1.0876	1.0920		1.114	1.084
C3−H	1.0736	1.0862	1.0909		1.114	1.109
S1−C2−C3^b	120.11	119.48	120.41	120.1	118.7	
C2−C3−C3a	119.82	119.97	120.78	120.3	119.4	120.7
C3−C3a−S6a	119.48	119.08	118.70	118.5	119.2	119.0
H−C2−C3	120.69	121.61	121.48			122.3
H−C3−C3a	118.60	118.80	118.48			119.4
C3a−S6a−S1	88.70	89.23	88.99	89.1	90.1	
S6a−S1−C2	91.89	92.24	91.12	92.0	92.6	

[a] Bond lengths in angstrøms. [b] Bond angles in degrees. [c] C_{2v} symmetry imposed. [d] Reference 3. [e] Reference 4. [f] Reference 6.

TABLE 3: 1,6,6aλ^4-Trithiapentalene (TTP). Comparison of Fundamental Vibrations Calculated at Three Different Levels of Theory (See Text)^a

		HF/6-311G**^{c}				MP2/6-311G**				BPW91/6-311G**			
	sym^b	$\tilde{\nu}$	I	k	μ	$\tilde{\nu}$	I	k	μ	$\tilde{\nu}$	I	k	μ
ν_1	a$_1$	260	0.1	0.79	19.7	239	0.1	0.64	19.0	220	0.1	0.55	19.2
ν_2		363	0.1	0.87	11.2	336	0.2	0.75	11.3	320	0.2	0.70	11.7
ν_3		667	0.1	1.66	6.3	626	0.3	1.45	6.3	603	0.2	1.31	6.1
ν_4		703	3.1	2.37	8.1	697	0.5	2.26	7.9	644	1.5	2.10	8.6
ν_5		902	45.1	2.49	5.2	892	10.6	2.27	4.8	825	11.9	2.04	5.1
ν_6		1211	30.2	1.23	1.4	1130	13.5	1.01	1.3	1083	16.0	1.00	1.5
ν_7		1355	0.8	2.43	2.2	1280	0.7	1.88	1.9	1231	0.3	1.69	1.9
ν_8		1510	17.5	2.24	1.7	1383	5.1	2.13	1.9	1331	10.1	1.81	1.7
ν_9		1664	42.3	7.80	4.8	1567	4.1	9.42	6.5	1507	11.7	8.13	6.1
ν_{10}		3329	5.0	7.11	1.1	3201	4.3	6.56	1.1	3102	1.4	6.21	1.1
ν_{11}		3360	9.4	7.29	1.1	3229	7.5	6.73	1.1	3123	12.4	6.29	1.1
ν_{12}	a$_2$	148	0	0.07	5.3	147	0	0.07	5.4	142	0	0.06	5.4
ν_{13}		468	0	0.44	3.4	425	0	0.43	4.0	436	0	0.39	3.5
ν_{14}		818	0	0.46	1.2	729	0	0.37	1.2	718	0	0.36	1.2
ν_{15}		1054	0	0.86	1.3	879	0	0.56	1.2	875	0	0.58	1.3
ν_{16}	b$_1$	150	1.5	0.09	6.8	98	1.9	0.03	6.1	127	1.5	0.08	8.0
ν_{17}		353	7.9	0.37	5.0	334	1.5	0.41	6.2	336	2.9	0.35	5.2
ν_{18}		670	11.0	0.81	3.1	561	17.5	0.91	4.9	585	17.7	0.70	3.5
ν_{19}		887	101.1	0.70	1.5	748	91.7	0.44	1.3	761	86.0	0.48	1.4
ν_{20}		1049	1.0	0.89	1.4	877	0.2	0.57	1.3	884	0.1	0.62	1.3
ν_{21}	b$_2$	392i^d	342.0	−2.36	26.1	271	159.7	0.86	19.9	228	154.4	0.67	21.8
ν_{22}		416	1.5	1.19	11.7	399	23.1	1.27	13.6	378	11.5	1.08	12.9
ν_{23}		750	233.1	2.94	8.9	730	39.4	2.46	7.9	699	27.6	2.33	8.1
ν_{24}		907	205.7	2.20	4.5	913	77.3	2.07	4.2	849	46.8	1.85	4.4
ν_{25}		1204	407.3	1.27	1.5	1157	54.4	0.85	1.1	1123	36.1	0.83	1.1
ν_{26}		1297	56.8	1.77	1.8	1250	0.5	1.44	1.6	1207	0.0	1.37	1.6
ν_{27}		1469	393.5	3.45	2.7	1428	3.4	4.39	3.7	1370	6.9	4.10	3.7
ν_{28}		1559	175.6	3.47	2.4	1600	288.2	10.34	6.9	1479	201.0	6.84	5.3
ν_{29}		3328	3.2	7.10	1.1	3200	1.3	6.56	1.1	3101	1.1	6.15	1.1
ν_{30}		3353	3.1	7.27	1.1	3226	1.2	6.73	1.1	3121	1.8	6.29	1.1

[a] $\tilde{\nu}$ = wavenumber in cm^{-1} (unscaled), I = IR intensity in km/mol, k = force constant in mdyn/Å, μ = reduced mass in amu. [b] Irreducible representations in the C_{2v} point group. In the designation of symmetry labels, the molecular axes are redefined: z and yz are taken as the C_2 axis and the molecular plane. [c] C_{2v} symmetry imposed. [d] Imaginary wavenumber, see text.

correlation is expected to change the situation in favor of the bridged, symmetrical structure, as indicated by recent single-point MP4/3-21G(*) and MP2/6-31G* results by Cimiraglia and Hofmann.[9] This expectation is confirmed by the present MP2/6-311G** and BPW91/6-311G** calculations with full geometry optimization that predict a stable C_{2v} symmetrical equilibrium structure; no minima coresponding to the valence tautomeric C_s structures I and I′ were found. The calculated total energies are −1385.803 292 6 (MP2) and −1387.600 610 1 (BPW91) au. Calculated bond lengths and angles are in good agreement with experimental data, particularly in the case of MP2. The C−S and S−S bond lengths tend to be slightly overestimated by BPW91; the S−S bond is thus predicted to be 2.43 Å, compared with experimental values in the range 2.33−2.36 (Table 2).

Vibrational transitions computed at the three levels of theory are compared in Table 3, and an approximate description of the IR-active modes is included in Table 1. As anticipated, the ν_{21} mode obtained with MP2 and BPW91 is a low-frequency bell-clapper type vibration (see below).

4. Results and Discussion

The orientational properties that can be determined from the LD curves in Figure 1 are the so-called orientation factors[13,14] for the observed vibrational transitions. The orientation factor K_i for an optical transition i is the average over all solute molecules of cosine square of the angle between the molecular transition moment vector $\mathbf{M}_i$ and the uniaxial stretching direction Z of the sample:[13,14]

$$K_i = \langle \cos^2(\mathbf{M}_i,Z) \rangle$$

The K_i value for a nonoverlapped transition i is related to the dichroic ratio $d_i = E_Z(\tilde{\nu}_i)/E_Y(\tilde{\nu}_i)$ through the equation $K_i = d_i/(2 + d_i)$.[13,14] In the present investigation the d values were determined from the ratios of the integrated absorbances and overlapping transitions were analyzed by the TEM method.[14] The resulting K values are given in Table 1.

The observed K_i fall in three distinct groups with values equal to 0.240 ± 0.01, 0.306 ± 0.02, and 0.462 ± 0.02; the three characteristic values add up to unity within experimental error (1.008 ± 0.02). As in the case of 2,5-dimethyl-TTP,[8] this observation is only consistent with the assumption of high molecular symmetry and provides an independent confirmation of the presence of a C_{2v} symmetrical equilibrium molecular geometry on the time scale of IR spectroscopy. Under the assumption that the alignment of TTP in stretched PE reflects its molecular dimensions,[13,14] we assign the three characteristic Ks as $(K_x, K_y, K_z) = (0.240, 0.306, 0.462)$. The labeling of the axes is chosen according to the convention $K_x \leq K_y \leq K_z$. A recently published UV−vis LD investigation of TTP in stretched PE obtained Ks corresponding to $(K_y, K_z) = (0.3, 0.53)$;[12] the larger K_z observed in this experiment can be explained by the circumstance that a freshly stretched (and not annealed) PE sample was applied, resulting in more efficient molecular alignment. The identification of the labels x, y, and z with the individual symmetry axes of the molecule represents an absolute polarization assignment and allows experimental identification of the symmetries of the observed vibrational states. With the present definition of molecular axes, x forms a basis for the b_1, y for the a_1, and z for the b_2 irreducible representation of the C_{2v} point group. The resulting symmetry assignments of the observed transitions are given in Table 1 and indicated graphically in the top panel of Figure 3.

The suggested assignment of observed peaks to fundamental transitions is indicated in Table 1. This assignment is strongly supported by the theoretical results. Calculated wavenumbers and intensities of the 30 fundamental transitions of TTP ($\Gamma = 11a_1 + 4a_2 + 5b_1 + 10b_2$) are listed in Table 3, and illustrated graphically in Figure 3, lower panel. The observed wavenumbers are well reproduced by simple scaling of the theoretical values: $\tilde{\nu}_{\text{obs}} = 0.9555\tilde{\nu}_{\text{MP2}}$ (SD = 39 cm^{-1}) and $\tilde{\nu}_{\text{obs}} = 0.9904\tilde{\nu}_{\text{BPW91}}$ (SD = 28 cm^{-1}), indicating an effective scaling factor close to unity in the case of BPW91. The performance of BPW91 is highly satisfactory and slightly superior to that of MP2 (the relative success of BPW91 is remarkable in view of the much shorter computation time). Detailed comparison of observed and calculated IR intensities is complicated by the significant solvent sensitivity of the experimental values, but the observed trends seem well reproduced by the calculations.

One fundamental is apparently not observed, ν_{16}, which is predicted by the theoretical procedures to give rise to a weak transition around 100 cm^{-1}. Experimental features due to this transition are probably obscured by the strong broad band with maximum at 153 cm^{-1} (assigned to ν_{21} as discussed below). A number of additional transitions are observed that are not assigned to fundamentals. Two are indicated in Figure 1, a y-polarized shoulder at 785 cm^{-1} and a z-polarized one at 1349 cm^{-1}; both are observed as distinct peaks in the Ar matrix spectrum (Figure 2). The latter is an alternative candidate for assignment of the ν_{27} fundamental.

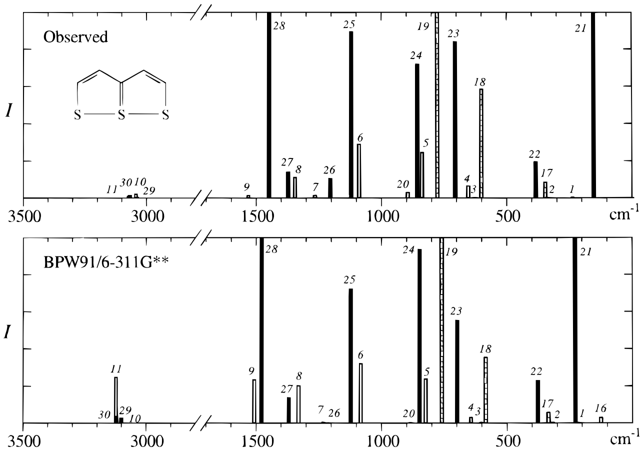

Figure 3. Graphical illustration of observed (top) and calculated (bottom) vibrational transitions for 1,6,6aλ^4-trithiapentalene (TTP). Solid, white, and hatched bars indicate transitions of b_2, a_1, and b_1 symmetry, respectively. The length of the bars indicates the relative intensity; the transitions labeled 19, 21, and 28 are too intense to be displayed in full on the present scale. The experimental diagram refers to measurements in stretched PE (100−1700 cm^{-1}) and Ar matrix (>1700 cm^{-1}) and indicates the suggested assignment of fundamental transitions. The theoretical diagram shows results obtained with BPW91 density functional theory, see text.

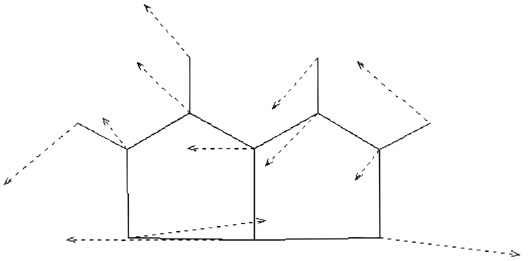

Figure 4. Normal coordinate of the bell-clapper mode ν_{21} for 1,6,6aλ^4-trithiapentalene (TTP) as predicted with BPW91 density functional theory, see text. The normal coordinate predicted with MP2 theory is very similar.

Of particular interest is assignment of the first b_2 fundamental (ν_{21}), corresponding to the bell-clapper mode of TTP that has been a topic of discussion for so many years.[1−12] The normal coordinate of this mode calculated with BPW91 is indicated in Figure 4; the molecular vibration can be described as primarily antisymmetric S−S stretching, with admixture of some skeleton deformation. As indicated in Table 3, HF theory yields a negative force constant and an imaginary wavenumber, but MP2 and BPW91 predict this mode to give rise to a strong transition with wavenumber equal to 271 cm^{-1} (MP2) or 228 cm^{-1} (BPW91); the values obtained using the scaling factors defined above are 259 and 226 cm^{-1}. The prominent long-axis polarized absorption band observed in stretched PE with a maximum at 153 cm^{-1} must be assigned to the bell-clapper fundamental. This band is relatively broad and seems to be characteristic for the S−S−S structural element in trithiapentalenes.[21] The theoretical procedures overestimate the wavenumber of the transition; the point for this transition deviates from the regression line by an amount significantly larger than the standard deviation. A preliminary theoretical investigation[22] of the shape of the bell-clapper potential indicates that this can be explained by the expected inadequacy of the harmonic approximation for this vibrational mode, an assumption that is supported by the breadth of the observed band.

5. Concluding Remarks

The experimental and theoretical characterization of the normal vibrational modes of TTP obtained in this study settles a number of questions concerning the unusual molecular structure of this compound that has been investigated for decades. Most importantly, the so-called bell-clapper mode is observed for the first time in this investigation; it gives rise to a very strong, long-axis polarized, and relatively broad band with maximum at 153 cm^{-1} (stretched polyethylene at 12 K). Harmonic frequencies predicted by *ab initio* MP2 and DFT calculations at the 6-311G** level are in general agreement with the observed data. The DFT procedure, using Becke's gradient-corrected exchange functional and Perdew and Wang's correlation functional, is particularly successful. The results for the bell-clapper mode indicate a possible shortcoming of the harmonic approximation; a detailed theoretical investigation of the anharmonicity of this mode is in progress.

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