Effect of Pressure on Molecular Conformations. 4. The Flattening of Trithiane As Measured by Its Infrared Spectrum†

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Abstract: The effect of pressure at room temperature on the infrared spectrum of 1,3,5-trithiane in the frequency range 500–4000 cm^{-1} has been measured in order to follow the flattening of the molecule induced by pressure. The integrated intensities of the A_1 CH_2 bend, A_1 ν_2 ring stretch, E CH_2 twist, and E CH_2 rock, measured relative to the intensity of the A_1 CH_2 rock, all declined rapidly in the first 20 to 40 kbar, and then changed little up to 100 kbar. The intensities of the three bands that were not seriously overlapped by other bands, i.e., the A_1 ring stretch and the E CH_2 rock and twist, were analyzed on the basis of simple models, and they clearly show that trithiane becomes flat at ~60 kbar, which confirms the conclusion from earlier Raman spectra up to 18 kbar. The ratio of the integrated intensities of the CH_2 asymmetric and symmetric stretches decreases from ~13 at zero pressure to ~2 at 50 kbar, which implies that the angle between the dipole-moment derivatives of the two bonds decreases from 150° at zero pressure to approximately the tetrahedral angle at ~50 kbar. Both the infrared spectrum and the change of volume with pressure show that a phase transition occurs at 20 ± ~1 kbar in the range 22–92 °C with a volume change of ca. −0.4 cm^3 mol^{-1}.

I. Introduction

In earlier papers in this series, the internal rotation angles of 1,3,5-trithiane, $(CH_2S)_3$,[1] and of *g*-1,2-dichloroethane and *g*-1,2-dibromoethane[2] were shown to change steadily toward the cis conformation at the rate of ~1.3 and ~2° $kbar^{-1}$, respectively, when squeezed. In trithiane[1] the Raman intensity of the A_1 ν_3 internal rotation or ring-flattening vibration at 309 cm^{-1} should be zero in the flat conformation if the symmetry is D_{3h}. Its integrated intensity in crystalline trithiane, relative to that of the neighboring bands, decreases with increasing pressure up to 17.8 kbar by an amount corresponding to the molecule being about halfway to being flat. By extrapolating the results, it was suggested[1] that the molecule would become flat at about 40 kbar. Some earlier infrared spectra[3] showed that four bands of trithiane lose significant intensity at pressures up to several tens of kilobars, and the authors speculated that it might be due to a flattening of the molecule but did not analyze the spectra on this basis. Later, it was shown[1] that, after three of the four bands were reassigned, the loss of intensity is qualitatively consistent with flattening.

Of the seven A_1 bands of trithiane under C_{3v} symmetry, four should lose infrared activity and the remaining three should lose Raman activity on flattening to a D_{3h} molecule. Of the ten E bands, three should lose infrared and seven should retain both infrared and Raman activity. Therefore, of the seventeen infrared and Raman bands, only seven E bands do not lose either infrared or Raman activity on flattening. The only Raman bands that should lose activity are weak, but the infrared bands that should lose activity include some of the strongest in the spectrum, and the change of spectrum should be very spectacular, as has already been observed qualitatively.[3]

Quantitative measurements of the loss of infrared intensity should therefore confirm the flattening and provide several independent estimates of the rate. The purpose of this paper is to report such measurements.

The molecules in crystalline trithiane do not, in fact, have C_{3v} symmetry but rather C_s symmetry,[4,5] and they probably do not flatten to D_{3h} symmetry but perhaps to C_{2v}. Few of the bands should, therefore, lose all their activity. This complication could not be allowed for in the analysis of the Raman spectra because the molecule appeared to be only about halfway to being flat at the highest pressure. The infrared spectra, on the other hand, were taken well past the flattening pressure, and so the residual activity can be allowed for.

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II. Experimental Methods and Results

1. The Infrared Spectra. 1,3,5-Trithiane obtained from Eastman Kodak Co. was used as supplied.

The spectra were recorded at 2-cm^{-1} nominal resolution on a Nicolet 7199 Michelson interferometer having a mercury cadmium telluride photodetector operating at 77 K and a scan time of 1.7 s for 8192 data points. For each spectrum, 512 scans were recorded and averaged. The peak frequencies were determined to ±~1 cm^{-1} by fitting Lorentzians to the bands. The high-pressure spectra were taken with use of a diamond-anvil cell. A spectrum at atmospheric pressure of an ~25-μm film pressed onto a sodium bromide disk is shown in the top frame of Figure 1. It agrees with earlier spectra,[6-9] so there were no significant impurities unless all samples were similarly contaminated.

Three separate variable-pressure experiments were done. In the first, an ~25-μm film of trithiane was pressed onto a 25-μm film of sodium bromide containing 0.26% sodium nitrite as a pressure gauge,[10] and the pressure was determined to ±~1 kbar from the frequency shift, $\Delta\nu$, of the ν_3 band of the uncoupled nitrite ion by the equation[10]

$$p/\text{kbar} = 2.356(\Delta\nu/\text{cm}^{-1}) - 1.334(\Delta\nu/\text{cm}^{-1})\exp(-\Delta\nu/92\ \text{cm}^{-1})$$

A piece of the wafer, 300 μm in diameter, was placed in a gasket of type 302 stainless steel, 50-μm thick, between the anvils of a hydraulically operated diamond-anvil cell. Spectra were recorded in sequence at 16, 25, 36, 42, 53, and 12 kbar. In the second experiment, the spectra of a similar specimen were taken at pressures in sequence of 18, 19, 25, 26, 30, 31, 35, 39, 40, and 41 kbar. The spectra at 18 and 41 kbar are typical and are shown in the center and bottom frames of Figure 1.

In many of these spectra, the very intense band at 729 cm^{-1} (at 1 bar) was off scale, and so a third experiment was done to determine the effect of pressure on it. An approximately 15% w/w dispersion of trithiane in the sodium bromide containing 0.26% sodium nitrite was made by intimately grinding the two substances together at liquid-nitrogen temperature in a Spex Freezer Mill, the trithiane being too soft to grind at room temperature. A small portion of the resultant mixture was pressed into a 50-μm-thick film and placed in the diamond cell as for the earlier

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Table I. Vibrational Frequencies of Polycrystalline Trithiane at Zero Pressure, the Properties of the Bands under Various Symmetries, and the Effect of Pressure on Band Frequencies and Intensities

mode	species and activity under C_{3v}	C_s	D_{3h}	C_{2v}	ν, cm^{-1} IR[a]	R[b]	Raman polarization[c]	$(\partial\nu/\partial p)$, cm^{-1} kbar^{-1} IR[d]	R[b]	intensity change with pressure IR[e]	R[e]
C–H asym stretch	A_1; IR, R	A′; IR, R	A_2''; IR, –	A_1; IR, R	2954	2954	–[f]	0.340	0.325	–	dec
	E; IR, R	A′ + A″; IR R	E″; –, R	A_2 + B; IR, R	2968	2961	D	0.550	0.675	–	nc
					–	2954					
C–H sym stretch	A_1; IR, R	A′; IR, R	A_1'; –, R	A_1; IR, R	2906	2904	P	0.425	0.683	–	nc
	E; IR, R	A′ + A″; IR, R	E′; IR, R	A_2 + B_2; IR, R	2893	2891	–	0.390	0.490	–	nc
CH_2 bend	A_1; IR, R	A′; IR, R	A_1'; –, R	A_1; IR, R	1375	1372	P	0.110	–	dec	nc
	E; IR, R	A′ + A″; IR, R	E′; IR, R	A_1 + B_2; IR, R	1392	1394	–	~0	–	nc	nc
					1382	1385	–	~0	–	–	–
CH_2 twist	A_2; –, –	A″; IR, R	A_1''; –, –	A_2; IR, R	1048	–	–	~0	–	nc	nc
	E; IR, R	A′ + A″; IR, R	E″; –, R	B_1 + A_2; IR, R	1225	1225	–	0.220	0.288	dec	nc
					1217	–	–	0.310	–	–	–
CH_2 wag	A_2; –, –	A″; IR, R	A_2'; –, –	B_2; IR, R	1182	–	–	0.340	0.435	nc	nc
	E; IR, R	A′ + A″; IR, R	E′; IR, R	A_1 + B_2; IR, R	1172	1179	–	0.235	0.280	nc	nc
					1164	1172	–	0.115	–	–	–
CH_2 rock	A_1; IR, R	A′; IR, R	A_2''; IR, –	B_2; IR, R	908	910	–	0.240	–	nc	nc
	E; IR, R	A′ + A″; IR, R	E″; –, R	B_1 + A_2; IR, R	729	729	D	0.580	0.485	dec	nc
ring stretch[g]	A_1; IR, R	A′; IR, R	A_1'; –, R	A_1; IR, R	654	652	P	0.515	0.670	dec	nc
	E; IR, R	A′ + A″; IR, R	E′; IR, R	A_1 + B_2; IR, R	796	794	?	0.580	0.485	inc	nc
	E; IR, R	A′ + A″; IR, R	E′; IR, R	A_1 + B_2; IR, R		744	D	–	–	–	–
						738	–	–	–	–	–
ring bend[g]	A_1; IR, R	A′; IR, R	A_2''; IR, –	B_2; IR, R	–[h]	398	–	–[h]	0.223	–	nc
	E; IR, R	A′ + A″; IR, R	E′; IR, R	A_1 + B_2; IR, R	662	660	–	0.490	–	nc	nc
internal rotation[g]	A_1; IR, R	A′; IR, R	A_2''; IR, –	B_2; IR, R	–[h]	309	P	–[h]	0.15	–	dec
	E; IR, R	A′ + A″; IR, R	E″; –, R	B_1 + A_2; IR, R	–[h]	–	–	–[h]	–	–	–

[a] This work. [b] Reference 1. [c] In solution according to ref 9. [d] $\partial\nu/\partial p$ for the region $0 \leqslant p \leqslant 20$ kbar. [e] dec = decreased; nc = no change; inc = increased. [f] The symbol – means not known. [g] The forms of the ring vibrations are sketched in ref 7. [h] Band beyond observable range of experiment.

specimens. The effective thickness of the trithiane was ~10 μm. Spectra were recorded in sequence at 1, 4, 8, 9, 13, 20, 21.5, 22.5, 33.5, 39, 101, 79, 68, 41, and 28 kbar. The spectra at 1, 9, 20, 39, 68, and 101 kbar are shown in Figure 2.

Many of the bands in Figures 1 and 2 broaden at the highest pressures, and some neighboring bands overlap nearly completely so that only a mean frequency can be obtained. This is probably caused by nonhydrostatic pressures due to the increased hardness of the sodium bromide[10] and the trithiane.

2. Effect of Pressures on the Frequencies. Both the frequencies and the relative intensities changed with pressure. The frequencies of the principal bands are plotted against the pressure in Figure 3. The band at 654 cm^{-1} became so weak at high pressures that its frequency could not be accurately determined above ~40 kbar.

Most of the bands have a sudden change in either the frequency or its pressure dependence or in both at ~20 kbar. The biggest changes of frequency were decreases of 7 and 8 cm^{-1} respectively for the symmetric C–H stretching bands at 2893 and 2906 cm^{-1}. Other bands changed by 0–4 cm^{-1}, usually decreasing, but the 1225-cm^{-1} band increased by 3 cm^{-1}. The changes are, no doubt, due to a first-order phase change, and the phases at low and high pressure are designated I and II, respectively.

The existence of the phase change was confirmed by pressure–volume measurements on a sample confined in a cylinder. A 20-mm-long Teflon cup containing trithiane was placed in a 12.5-mm-i.d. cylinder and compressed by means of a piston driven by a hydraulic press. The existence of phase changes and the pressures at which they occur were determined from a plot of piston displacement against nominal pressure. The experiment was done with both increasing and decreasing pressure at 22, 47, and 92 °C, and a typical pressure–displacement plot, at 22 °C, is plotted in Figure 4. During compression, the transition appeared to be completed within the interval of ~0.4 kbar between two points and was assigned to the mean pressure of these two points. During decompression it was more sluggish. The transition pressures for rising and falling pressures respectively were 21.1 and 19.2 kbar at 22 °C, 21.7 and 18.8 kbar at 47 °C, and 21.7 and 18.5 kbar at 92 °C. The hysteresis is mostly accounted for by the ~12% friction in the press and between the piston and cylinder. The transition pressure was taken as the mean of the rising and falling transition pressures and is 20 ± ~1 kbar, independent of temperature. The volume change at the transition I to II, as estimated

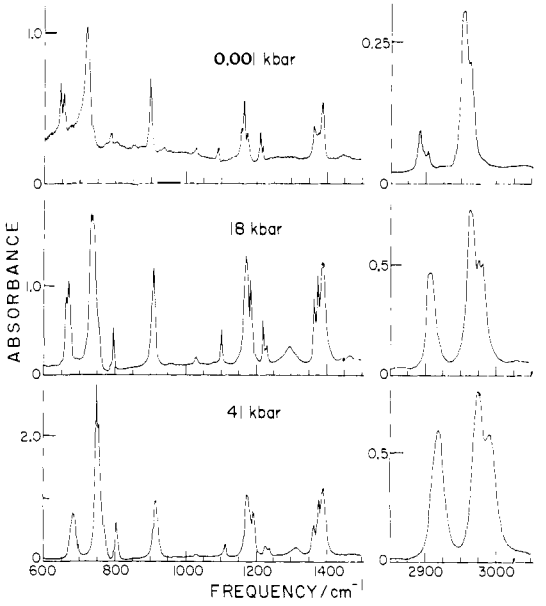

Figure 1. Infrared spectra of an approximately 25-μm film of trithiane at 22 °C. The upper frame is of a 12-mm-diameter sample in a standard sample holder at 1 bar. The lower two frames are of a 300-μm-diameter sample in a diamond-anvil cell at 18 and 41 kbar, respectively. The band at ~1300 cm^{-1} in the high-pressure spectra is the nitrite ion band that was used as a pressure gauge.

from the pressure-displacement plots, is ca. –0.5% or ca –0.4 cm^3 mol^{-1}, and the entropy change as estimated from the effect of temperature on the transition pressure and the volume change is 0 ± ~1 J K^{-1} mol^{-1}.

In phase I, the frequencies are linear in the pressure to the experimental precision, perhaps because of the short pressure range. In phase II they are not. The largest nonlinearity occurs for the 2968-cm^{-1} band, whose frequency reaches a maximum at ~60 kbar and then declines at

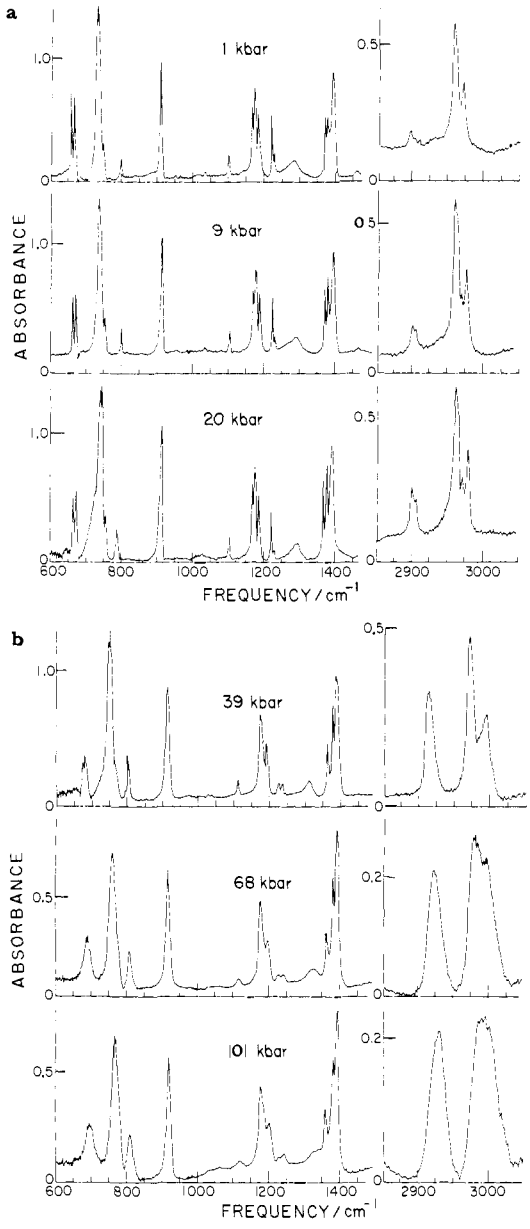

Figure 2. Infrared spectra in a diamond anvil of an approximately 50-μm film, 300 μm in diameter, of a dispersion of trithiane in sodium bromide with 0.26% w/w sodium nitrite as a pressure gauge. The sample was equivalent to a film about 10-μm thick. The pressure in kilobars is shown in each frame. The 68-kbar spectrum was run after the pressure had been reduced from 101 kbar. The band at ~1300 cm^{-1} is the nitrite ion band that was used as a pressure gauge.

higher pressures. The 1172-cm^{-1} band also decreases in frequency above ~35 kbar and merges with the 1164-cm^{-1} band.

The frequencies of the principal bands at 1 bar, their assignments,[1,7-9,11-13] and the pressure coefficient of the frequencies in phase I are listed in Table I. The frequencies agree well with earlier values.[1,6-9,11-13] According to Figure 3, the reproducibility of the frequencies is ±~1 cm^{-1}, so that the uncertainty of the pressure coefficients is ±~0.07 cm^{-1} $kbar^{-1}$. The pressure coefficients of the frequencies in the Raman spectrum[1] are also listed in Table I. They also have an uncertainty of ±~0.07 cm^{-1} kbar. The pressure coefficients of the infrared and Raman bands are usually consistent within this uncertainty, although the coefficients of the Raman bands are usually higher.

3. Effect of Pressure on the Intensities. If the area of the sample does not change and if the sample keeps a uniform thickness, the intensities of bands at different pressures should be comparable. However, at the highest pressures, the gasket sometimes extruded slightly and the area of the sample increased. Then, only relative areas within a spectrum can be compared at different pressures. Perhaps the ideal measurement is the intensity of a band relative to the whole spectrum, but there are too many uncertainties for this to be practicable. Consequently, the A_1 CH_2 rock at 908 cm^{-1}, which is predicted to retain its intensity in the flat conformation and has a convenient intensity, has been chosen as the reference band.

The integrated areas of the bands at each pressure were measured by either a planimeter or computer integration or both. The two methods agreed to 2–3%. The areas of the bands that decreased significantly, divided by the area of the A_1 CH_2 rock, are plotted in Figure 5.

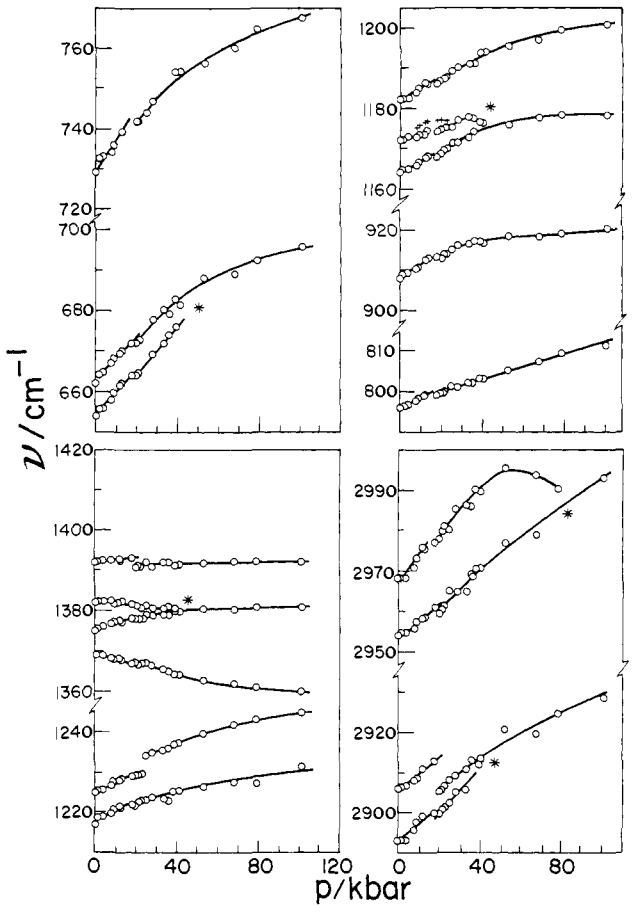

Figure 3. Effect of pressure on the principal infrared frequencies of trithiane at ~22 °C. One-half to one-third of the 26 measurements below 40 kbar are not plotted to avoid congestion; the unplotted points do not deviate significantly from the drawn curves. The plus signs denote the higher frequency of a close pair, and the asterisks show where two bands merge.

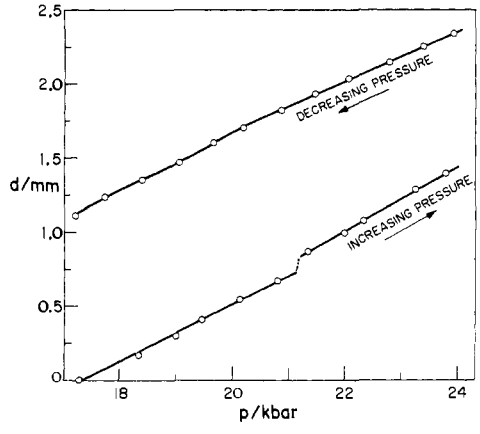

Figure 4. Graph of piston displacement against pressure for a sample of trithiane in a 20-mm-long Telfon cup compressed in a 12.5-mm-diameter metal cylinder at 22 °C.

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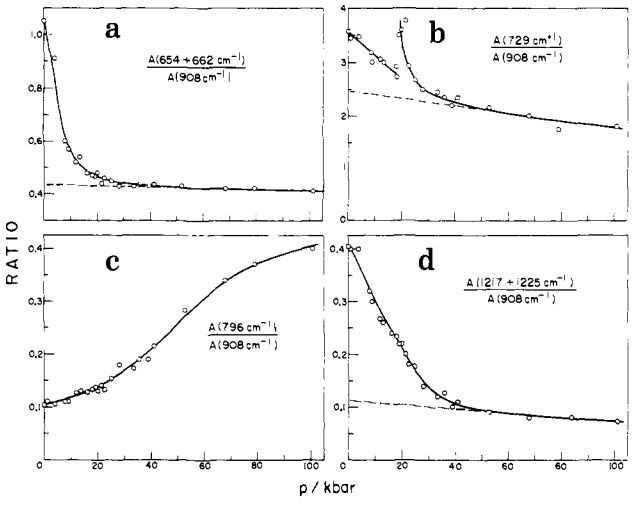


Figure 5. Graph of the integrated areas of the 654 (A_1 CH_2 rock) + 662 (E ring bend), 729 (E CH_2 rock), 796 (E ring stretch), and 1217 + 1225 (E CH_2 twist) cm^{-1} bands relative to that of the 908 cm^{-1} (A_1 CH_2 rock) band as a function of pressure.

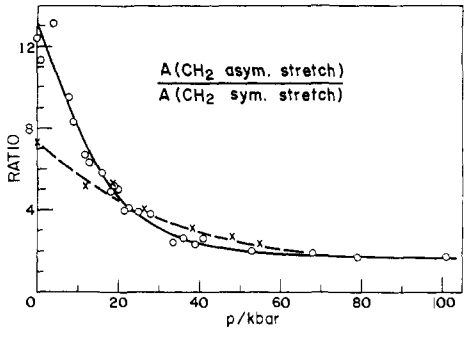


Figure 6. Graph of the ratio of the integrated intensities of the asymmetric and symmetric CH_2 stretching bands of trithiane against pressure at ~22 °C. The solid line is for a dispersion in sodium bromide, and the dashed line is for a thin film. The higher values for the dispersion are probably due to scattering which raises the base line and therefore the ratios at low pressures.

The bands at 654 + 662, 729, and 1375 cm^{-1} and the pair at 1217 and 1225 cm^{-1} lose some or all their intensity under pressure. The 1375-cm^{-1} band is part of a complex envelope of several bands, and it is difficult to measure its area. Nevertheless, Figures 1 and 2 show clearly that its intensity does decrease with increasing pressure. The band at 654 cm^{-1} cannot be unambiguously separated from the band at 662 cm^{-1}, and so their combined relative intensity is plotted in Figure 5. It drops to about 0.42 of its zero-pressure value in the first 30 kbar, and then it drops slowly to the highest pressure by ~0.02 of its zero-pressure value.

The relative intensity of the band at 729 cm^{-1} drops steadily with increasing pressure by ~20% in the first 20 kbar. It increases back to approximately the zero-pressure value at the I–II phase change, which is the only significant effect of the phase change on the relative intensities, decreases rapidly until 30 kbar, and then falls more slowly. The relative intensity of the split degenerate pair at 1217 and 1225 cm^{-1} decreases to about a quarter of its zero-pressure value in the first 30 kbar and then declines more slowly.

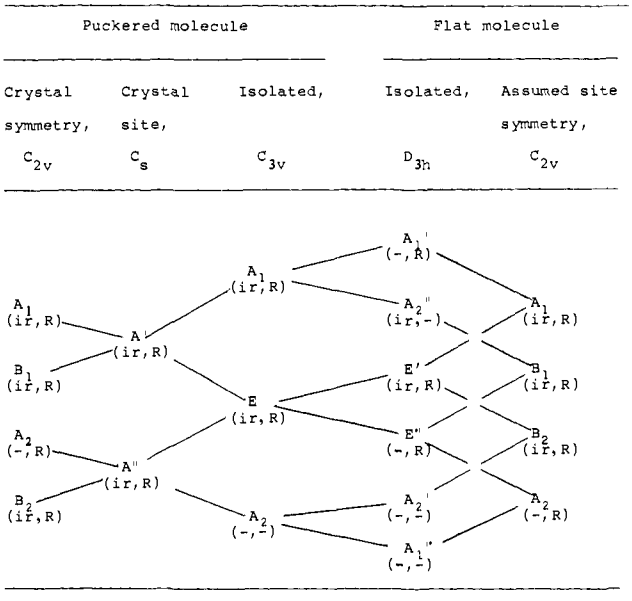
The relative intensity of the band at 796 cm^{-1} increases by about a factor of 4 in 100 kbar, and it is also plotted in Figure 5. The relative intensities of the other bands did not appear to change significantly.

In the C–H stretching region, the A_1 CH_2 symmetric stretch at 2906 cm^{-1} should lose its intensity on flattening, as is shown in section III, but the A_1 and E symmetric stretching bands overlap too much to be sure that this occurs. However, the ratio of the areas of the CH_2 symmetric and asymmetric stretches changes strikingly with pressure, as Figures 1 and 2 show clearly. The ratio is plotted in Figure 6. It decreases from 13 at zero pressure to 2 at about 50 kbar and then remains constant to 100 kbar.

III. Interpretation of the Spectra

Qualitative Spectroscopic Effects of Flattening. Before interpreting the spectra, it is worth reviewing the expected spectroscopic effects of flattening.[1] The isolated trithiane molecule in its puckered conformation has symmetry C_{3v} and vibrations belonging to symmetry species A_1 and E, which are active in both the Raman and infrared spectra, and to species A_2, which are forbidden in both. The planar conformation has symmetry D_{3h}. The A_1 vibrations of the puckered molecule that become symmetric to the horizontal plane in the flat molecule, and so belong to species A_1', and the E vibrations that become antisymmetric to the horizontal plane, and so belong to species E″, lose their infrared activity. These correlations are summarized in Table II.

Table II. Species and Activities of the Vibrations of the Trithiane Molecule in Various Symmetries



The molecules do not, however, have C_{3v} symmetry in the crystal. Trithiane crystallizes at low pressure in the orthorhombic space group $Pmn2_1$-C_{2v}^{17} [4,5] with two molecules in the unit cell, each having point symmetry m-C_s. The correlation of the vibrations of the isolated C_{3v} molecule with those of the molecule in the crystal is summarized in Table II. The A_1 and A_2 vibrations under C_{3v} symmetry become A′ and A″, respectively, under C_s symmetry, and each degenerate vibration is split by the site symmetry into an A′ and an A″. The A′ vibrations are split by intermolecular coupling into an A_1 and a B_1 vibration under the unit cell group, which is isomorphous with point group C_{2v}, and the A″ vibrations into an A_2 and a B_2. All four species are allowed in the Raman spectrum, and the A_2 vibrations are forbidden in the infrared. The species and activities of the vibrations under C_{2v} symmetry are summarized in Table II.

Only the E vibrations appear to be significantly split in the infrared and Raman spectra of the crystal,[1,6–9,11–13] and so the correlation splitting is much weaker than the site splitting. The vibrations assigned to species A_1 under C_{3v} should, therefore, be assigned to the A′ vibrations of the uncoupled molecule on its site, and the E vibrations are split into an A′ and an A″ vibration. All the A_2 vibrations of the C_{3v} molecule have been assigned to observed features.[9,12,13] They do not double under the crystal symmetry, so these bands can be assigned to the A″ vibrations of the uncoupled molecule on its site, the splitting of the Raman bands into A_2 + B_2 being unobserved at present resolutions.

If the molecule in the low-pressure solid flattens without any other change of crystal structure, its site symmetry may increase from C_s to C_{2v}. Then the A_1' vibrations of the D_{3h} molecule, which are forbidden in the infrared, become A_1 under C_{2v} and are allowed. The A_2'' vibrations become B_1 and acquire Raman activity, and the E′ vibrations split into A_1 + B_2 and retain their infrared and Raman activity. The E″ vibrations that become antisymmetric to the C_2 axis acquire infrared activity, and the A_2' vibrations become B_2 and also acquire infrared activity. The A_1'' vibrations become A_2 and acquire Raman activity. These correlations are summarized in Table II, and their application to vibrations that

Table III. Infrared Bands of Trithiane That Become Inactive in the Flat Molecule under D_{3h} Symmetry

vibration[a]	frequency,[b] cm^{-1}	activity under D_{3h} species	IR, R[c]
A_1 CH_2 asymmetric stretch	2954	A_2''	+, −
A_1 CH_2 symmetric stretch	2906	A_1'	−, +
A_1 CH_2 bend	1375	A_1'	−, +
A_1 ν_1 ring stretch	654	A_1'	−, +
A_1 ν_2 ring deformation	398[d]	A_1'	−, +
A_1 ν_3 internal rotation	309[d]	A_2''	+, −
A_1 CH_2 rock	908	A_2''	+, −
E CH_2 twist	1225, 1217	E″	−, +
E CH_2 rock	729	E″	−, +
E ν_8 internal rotation	79[d]	E″	−, +

[a] The symmetry classification is for the isolated C_{3v} molecule. [b] This paper. [c] IR = infrared. R = Raman, + = active, − = inactive. [d] From the Raman spectrum.[1]

become inactive under D_{3h} symmetry is described in Table III. All these vibrations become active under C_{2v} symmetry, and the A_1'' vibrations acquire Raman activity.

It follows from this that no vibration is expected to lose all its intensity on flattening. Different vibrations will, in general, retain different fractions of their activity and the (unknown) activity in the flat molecule will depend on the vibration.

When the band disappears due to a conformational change, its intensity must be transferred to other vibrations if the derivatives of the dipole moments with respect to the internal coordinates are not affected by the conformational change, which is probably true to a first approximation. The band that loses intensity in the Raman spectrum[1] is weak, and so little intensity is transferred elsewhere. However, the bands that disappear in the infrared spectrum are some of the strongest bands, and so the transfer of intensity must be accounted for. It probably goes mostly into nearby vibrations in which the same bonds and bond angles are distorted.

Of the seven bands that are expected to disappear in the infrared on flattening to a D_{3h} molecule, the A_1 ν_2 ring deformation and E ν_8 internal rotation are below our frequency range, and the A_1 CH_2 symmetric stretch cannot be resolved well enough from the E band. The four remaining bands, the A_1 ν_1 ring stretch at 654 cm^{-1}, E CH_2 rock at 729 cm^{-1}, E CH_2 twist at 1217 and 1225 cm^{-1}, and A_1 CH_2 bend at 1375 cm^{-1}, decrease strongly in intensity with increasing pressure. Of these, the 1375-cm^{-1} band is overlapped by too many bands for any quantitative study.

It is qualitatively clear, therefore, that the molecule flattens under pressure. Asai and Noda[12] assigned the E CH_2 wag to the 1218-cm^{-1} band and the E CH_2 twist to the 1172-cm^{-1} band. The disappearance of the 1217- and 1225-cm^{-1} bands under pressure shows that this assignment must be reversed.

All the bands that lose intensity lose most of it in the first 50 kbar or so, and so it seems likely that the molecule largely flattens in this range. However, all the bands retain some intensity even at the highest pressures of 101 kbar, no doubt because the molecule has a lower symmetry than D_{3h}, as has already been discussed.

The intensity that is apparently lost on flattening was obtained by extrapolating linearly the line of intensity against pressure from well above 50 kbar to lower pressures and measuring the difference between this curve and the actual curve. The ratio of the values of this difference at pressures p and zero is the important quantity and is denoted by R. The extrapolations are indicated in Figure 5. This extrapolation is not strictly accurate because the intensity of the A_1 CH_2 rock probably increases with the flattening, as described below. But the residual intensity is relatively small, and the error introduced should be unimportant. In any case, it would only affect slightly the apparent course of the flattening, but not the pressure at which the molecule becomes flat.

In the paper on the effect of pressure on the Raman intensities[1] an empirical equation was obtained for the intensity of the ring-flattening vibration by noting that its intensity would be zero in both the flat and the fully puckered conformations. For vibrations whose normal coordinate is reasonably well known, a better model can be obtained by calculating the appropriate dipole-moment or polarizability derivatives by using a bond-dipole-moment or bond-polarizability model. For the calculation of the dipole-moment derivatives, the C–S and C–H bonds were assumed to be cylindrically symmetric.

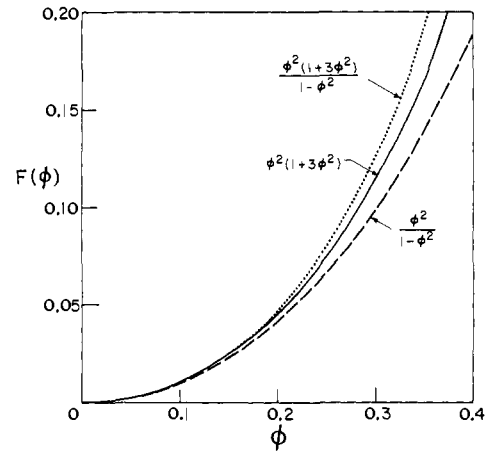


Figure 7. Graphs of three functions of ϕ.

A_1 CH_2 Rock. If the A_1 CH_2 rock is to be used as a reference band, its change of intensity with pressure must be allowed for. It has nearly the same frequency in trioxane (927 cm^{-1} according to the Raman spectrum,[14] 918 cm^{-1} according to the infrared spectrum[15,16]), trithiane (908 cm^{-1} in the infrared and 910 cm^{-1} in the Raman[1]), and triselenane (817 cm^{-1} [17] in the infrared). It is therefore largely uncoupled from other vibrations.

In order for an approximate formula for its intensity to be derived, the CH_2 group is assumed to have a C_{2v} local symmetry. Then the dipole-moment derivative of the rocking vibration is perpendicular to the bisector of the S–C–S angle, and its projection parallel to the molecular axis is proportional to cos ϵ, where ϵ is the angle between the bisector of the S–C–S angle and its projection in the plane of the sulfur atoms. If the magnitudes of the derivative and the effective mass of the vibration are independent of the degree of flattening, the intensity is proportional to $\cos^2 \epsilon$. Now,

$$\cos^2 \epsilon = 1 - \sin^2 \epsilon = 1 - x^2/a^2 \cos^2 \tfrac{1}{2}\alpha \qquad (1)$$

where x is the distance between the carbon and sulfur planes, a is the C–S bond length, and α is the S–C–S angle. In part 1 of this series of papers,[1] the difference of the cosines of the C–S–C and S–C–S angles, which differ by $\sim 15°$,[4,5] was assumed to be independent of the pressure. For the present paper, it is more convenient to assume that the C–S–C and S–C–S angles have the same value. This will have a small effect on the apparent course of the flattening as a function of pressure but little effect on the actual pressure it occurs at. Then, from eq 1, the intensity of the CH_2 rock is proportional to $(1 - \phi^2)/(1 + 3\phi^2)$, where

$$\phi = x/a$$

At the equilibrium conformation at zero pressure, $\phi = \phi_0$ is 0.359 as calculated from the data of Fleming and Lynton.[4] Then the quantity $(1 - \phi_0^2)/(1 + 3\phi_0^2)$ has the value 0.628. For the flat conformation, it has the value 1 and so the intensity is predicted to increase by 60% on flattening.

A_1 CH_2 Bend and E CH_2 Rock. If the local symmetry of the CH_2 group is effectively C_{2v}, the intensity of both the A_1 CH_2 bend and E CH_2 rock is proportional to $\sin^2 \epsilon$, i.e., to $4\phi^2/(1 + 3\phi^2)$. Their intensities relative to the A_1 CH_2 rock are therefore

(14) M. Nakahara, P. T. T. Wong, and E. Whalley, *Can. J. Chem.*, **57**, 711 (1979).
(15) M. Kobayashi, R. Iwamoto, and H. Tadokoro, *J. Chem. Phys.*, **44**, 922 (1966).
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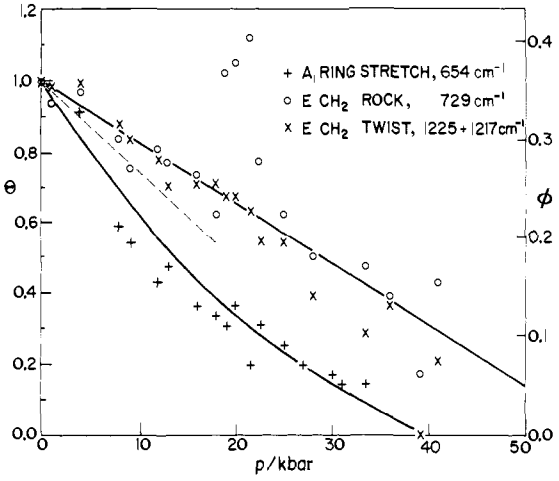

Figure 8. Graph of ϕ and $\theta = \phi/\phi_0 = x/x_0$, where x is the distance between the carbon and sulfur planes of trithiane and x_0 is the equilibrium value at zero pressure. The dashed line was obtained from the Raman spectrum up to 17.8 kbar.[1]

predicted to be proportional to $\phi^2/(1-\phi^2)$. The ratio R of relative intensities at pressures p and zero is, therefore,

$$R(\text{E CH}_2\text{ rock}) = [\phi^2/(1-\phi^2)]/[\phi_0^2/(1-\phi_0^2)] = 6.759\phi^2/(1-\phi^2) \quad (2)$$

As was mentioned earlier, the A_1 CH_2 bend is too much overlapped by other bands to be used. A graph of $\phi^2/(1-\phi^2)$ against ϕ is plotted in Figure 7. It allows the value of ϕ and $\theta = \phi/\phi_0 = x/x_0$, where x_0 is the distance between the carbon and sulfur planes at zero pressure, as a function of pressure to be obtained from the curves in Figure 5. The values obtained from the E CH_2 rock are plotted in Figure 8. They are on a reasonably good straight line, although three points at ~22 kbar are well above it.

A_1 ν_1 Ring Stretch. The integrated intensity of the A_1 ν_1 ring stretch is proportional to ϕ^2 for the bond-dipole model. Consequently, the ratio of its intensity to that of the CH_2 rock is proportional to $\phi^2(1+3\phi^2)/(1-\phi^2)$. The ratio R of intensities at pressures p and zero is then

$$R(\text{A}_1\text{ ring stretch}) = \frac{\phi^2(1+3\phi^2)}{1-\phi^2} \Big/ \frac{\phi_0^2(1+3\phi_0^2)}{1-\phi_0^2} = 4.874\phi^2(1+3\phi^2)/(1-\phi^2) \quad (3)$$

A graph of $\phi^2(1+3\phi^2)/(1-\phi^2)$ against ϕ is plotted in Figure 7 and allows the measurements of R_p/R_0 to be converted to values of ϕ and θ as a function of pressure. The values of θ are plotted as a function of pressure in Figure 8. The best line through the points is curved, having an initial slope of about 0.05 $kbar^{-1}$, and extrapolates to $\theta = 0$ at about 40 kbar. According to Figure 5 the E′ ring stretch gains in intensity under pressure and perhaps some of the intensity lost by the A_1 ν_1 ring stretch goes there.

E CH_2 Twist. The E CH_2 twist has finite intensity in the equilibrium conformation because the equatorial and axial hydrogens differ. They become equivalent in both the planar and the fully puckered conformations, and so the first term in a power series of the intensity as a function of ϕ is proportional to $\phi^2(1-\phi^2)$. It is assumed to be the dominant term. The ratio of the relative intensities of the E CH_2 twist and the A_1 CH_2 rock is, therefore, proportional to $\phi^2(1+3\phi^2)$, and the ratio of the relative intensities R at pressures p and zero is

$$R(\text{E CH}_2\text{ twist}) = \frac{\phi^2(1+3\phi^2)}{\phi_0^2(1+3\phi_0^2)} = 5.596\phi^2(1+3\phi^2) \quad (4)$$

A graph of $\phi^2(1+3\phi^2)$ against ϕ is plotted in Figure 7. The values of ϕ obtained from eq 4 and the relative intensities in Figure 5 are plotted in Figure 8. The points obtained from the E CH_2 rock and twist coincide within their uncertainties and can be represented within their scatter by a straight line that intercepts the pressure axis at 58 kbar. Its slope is 0.0172 $kbar^{-1}$.

The intensities of the A_1 ring stretch and of the E CH_2 rock and twist agree in implying that the ring becomes flat in the range 40–60 kbar. This is somewhat higher than the value of 37 kbar that was deduced from the effect of pressure on the Raman intensity of the A_1 ν_3 internal rotational vibration. However, at low pressure the Raman line in Figure 8 falls about halfway between the two infrared lines. The difference in the shapes of the two infrared lines and the Raman line in Figure 8 shows that the simple models of the intensities that were assumed are not exact. They should be correct at $\theta = 1$ and 0, but they clearly differ at intermediate values of θ. The three curves could give consistent pressures for complete flattening if the Raman line for the A_1 ν_3 internal rotation were suitably curved. There seems little doubt that the molecules are essentially flat by about 60 kbar.

CH_2 Stretching Bands. Both the symmetric and the asymmetric bands are composed of a strong and a weak peak and a shoulder between them that was not reported in the Raman spectrum.[1] The polarization[9] picks the 2904-cm^{-1} Raman band as the A_1 symmetric stretch and the 2961-cm^{-1} band as the E asymmetric stretch. If the CH_2 angle is tetrahedral and the changes of dipole moment when the bonds are stretched separately are along the bonds, the relative integrated areas of the A_1 and E bands in the puckered conformation should be 2 for the asymmetric stretches and $^1/_2$ for the symmetric stretches.[14] The A_1 and E bands cannot be unambiguously resolved without using single crystals, but as far as can be told they are consistent with the prediction. All the E vibrations that are not overlapped are split by the crystal field and the E symmetric stretch is probably split. Perhaps the E symmetric stretch has one component at 2893 cm^{-1} and the other overlaps the A_1 symmetric stretch. If the molecule flattens at high pressures, the A_1 band should disappear, and the spectra are qualitatively consistent with this.

The most dramatic effect in this region is a large decrease in the ratio of the integrated intensities of the A_1 and E asymmetric to the A_1 and E symmetric bands. Their ratio, which is plotted in Figure 6, changes from ~12 for dispersions in sodium bromide and ~7.3 for pressed films at zero pressure to 1.7 at 100 kbar. If the change of dipole moment when a C–H bond is stretched has the same magnitude for both bonds of a CH_2 group and is directed along the bond and if the H–C–H angle is tetrahedral, the predicted ratio of the asymmetric to the symmetric integrated intensities is 2.[14] Clearly, these assumptions are strongly violated at zero pressure, but at high pressure they agree with experiment. The ratio of intensities is $\tan^2 \gamma/2$ where γ is the angle between the directions of the changes of dipole moment when the two bonds are stretched independently. A ratio of 13 implies that $\gamma = 150°$. It appears that γ falls to nearly the tetrahedral angle at ~50 kbar, i.e., where the molecule appears to become flat.

IV. Conclusion

It is clear from the analysis of the spectra, which is summarized in Figure 8, that the three infrared bands that could be analyzed quantitatively agree that trithiane is in effect flat above ~60 kbar. These findings agree reasonably well with the analysis of the Raman spectrum[1] and with the qualitative observation that the 1375-cm^{-1} band declines greatly in intensity under pressure.

Similar effects should occur in other ring compounds. The effect of pressure on the infrared and Raman spectra of triselenane[17] clearly shows that the molecules flatten, but trioxane shows no sign of flattening at 25 kbar according to the Raman spectrum[18] or at ~55 kbar according to the infrared spectrum.[19] Nevertheless, trioxane, cyclohexane, and other six-membered-ring compounds should flatten at high enough pressures.

The flattening occurs by changes of the internal rotation angle. In trithiane at zero pressure, this angle decreases at the rate ~1.3° $kbar^{-1}$ according to the Raman spectrum,[1] at the rate 0.9° $kbar^{-1}$

(17) P. G. Sim, D. D. Klug, and E. Whalley: Effect of Pressure on Molecular Conformations. 5. The Flattening of Triselenane, to be published.
(18) M. Nakahara, P. T. T. Wong, G. J. Lewis, and E. Whalley, *Can. J. Chem.*, **57**, 2869 (1979).
(19) D. D. Klug and E. Whalley, unpublished results.

according to the line determined by the E CH_2 rock and twist vibrations, and at the rate of ~2.4° $kbar^{-1}$ according to the slope of the A_1 ring stretch line at zero pressure. In 1,2-dichloroethane and 1,2-dibromoethane[2] it decreases at the rate ~2° $kbar^{-1}$.

These changes in molecular conformation should significantly affect the chemical properties; for example, the axial and equatorial positions in a six-membered-ring molecule are identical when it is flat. The changes may be significant in some examples of reaction rates under pressure and may be relevant to chemical synthesis.

Registry No. 1,3,5-Trithiane, 291-21-4.

The P=P Stretching Frequency Observed in the Resonance Raman Spectrum of Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene

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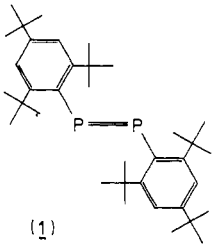
Abstract: The frequency of the P=P double bond stretching has been obtained for the first time from a resonance Raman study of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene.

I. Introduction

Recent success in the synthesis of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene[1] (**1**) has raised a wide range of interest in the physicochemical properties of the phosphorus–phosphorus double bond. The X-ray analysis has revealed that this compound takes a trans configuration with regard to the P=P bond, and the observed P=P distance (2.03 Å)[1] is much shorter than the P—P single-bond distances (~2.2 Å) in cyclopolyphosphines $(C_6H_5P)_n$, $n = 5, 6$. The ultraviolet absorption,[1] ^{31}P NMR,[1,2] and ESCA[3] spectra of (**1**) have also been reported. It is thus of vital importance to know the frequency of the P=P stretching vibration, which is a direct measure of the bond character.



(1)

In the present paper, we report the resonance Raman spectrum of the diphosphene in the title. To obtain vibrational information on the P=P bond, resonance Raman spectroscopy is more advantageous than the infrared for the following reasons. It is unlikely that the P=P stretching band appears strongly in the infrared, since this vibration is symmetric with regard to the C—P=P—C linkage. In fact, the observed infrared spectrum showed a number of weak bands in the 500–700-cm^{-1} region, making the identification of the P=P stretching band extremely difficult. On the other hand, only the skeletal vibrations of the chromophore are strongly observed in the resonance Raman spectrum,[4] and this should make the assignment straightforward.

II. Experimental

The title compound (**1**) was prepared from (2,4,6-tri-*tert*-butylphenyl)phosphonous dichloride with magnesium in tetrahydrofuran (mp 175–176 °C dec).[1]

The resonance Raman spectrum was observed with the 363.8-nm line from an NEC GLG-2018 Ar^+ laser (5 mW at sample), a Spex 1401 double monochromator, an HTV R-649 photomultiplier, and a photon counter. The wavenumber calibration was carried out with standard lines from a neon lamp. On account of low signal intensities, the slit had to be opened to 20 cm^{-1}, resulting in the estimated wavenumber accuracy of ±5 cm^{-1}. The crystalline sample of the diphosphene was pressed into a pellet with KBr (1:10 in weight) and used for the Raman spectroscopic measurement. The sample-rotating technique was adopted to avoid the thermal decomposition of the sample. Measurements with visible (514.5, 488.0 nm) and ultraviolet (257.3 nm) lasers were tried but no Raman signal could be detected.

The visible and ultraviolet absorption spectrum was recorded on a Hitachi 340 spectrophotometer.

III. Results and Discussion

Figure 1 shows the visible and ultraviolet absorption spectrum of the diphosphene (**1**) in dichloromethane. By analogy with the N-analogue of diphosphene, i.e., azobenzene,[5] the absorption at 340 nm can be assigned to a $\pi^* \leftarrow \pi$ transition involving the C—P=P—C group. The stronger absorption at 284 nm is characteristic of mono-substituted benzenes and the weak one at 460 nm is assignable to a $\pi^* \leftarrow$ n type forbidden transition. It is therefore most effective to use a resonance with the 340-nm absorption to obtain vibrational information on the P=P bond. Although the 363.8-nm line is slightly off-resonant from the peak of the absorption, we can expect a resonance Raman spectrum that is dominated by the vibrations of the C—P=P—C chromophore.

The obtained resonance Raman spectrum is shown in Figure 2. Six bands are observed at 1596, 1396, 1046, 610, 480, and 364 cm^{-1}. The three frequencies above 1000 cm^{-1} are too high to be assigned to any vibration of the C—P=P—C group and can be attributed to phenyl-ring vibrations. The 1046- and 1596-cm^{-1} bands probably correspond to the ring breathing (ν_1) and degenerate ring stretching (ν_8) of benzene, but the origin of

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(2) Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Matsushita, T.; Nishimoto, K. *J. Am. Chem. Soc.* **1983**, *105*, 2495.
(3) Yoshifuji, M.; Shima, I.; Inamoto, N.; Yamada, M.; Kuroda, H. *Phosphorus Sulfur* **1983**, *16*, 157.
(4) See, for example: Spiro, T. G.; Stein, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 501 and references cited therein.
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