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Low-Frequency Vibrational Spectra and Ring-Puckering Potential Energy Function of 2-Phospholene and 2-Phospholene-*1-d*

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The far-infrared and low-frequency Raman spectra of 2-phospholene, $CH{=}CHCH_2CH_2PH$, and 2-phospholene-*1-d* have been recorded. Four infrared and three Raman ring-puckering transitions were observed for each isotopic species. Kinetic energy expansions, corresponding to reduced masses of 130.42 and 136.72 au, were calculated for the two species, and these were used to determine the asymmetric potential function for the ring puckering vibration of molecules: $V(\mathrm{cm}^{-1}) = 6.05 \times 10^5x^4 + 3.24 \times 10^5x^3 + 5.43 \times 10^4x^2$, where x is the puckering coordinate in angstroms. The minimum at $x = 0$ corresponds to a puckered (presumably endo) conformation. Inflection points occur in the potential function at $x = -0.08$ Å (where $V = 205$ cm^{-1}) and $x = -0.19$ Å (where $V = 524$ cm^{-1}). It is likely that the less stable planar ring conformation and the less stable puckered conformation (exo) may be associated with these values.

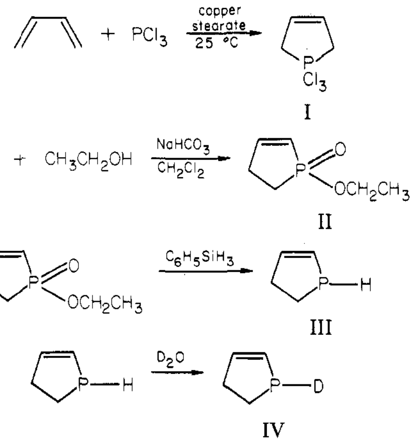
Introduction

Several asymmetrically substituted derivatives of cyclopentene ($CH{=}CHCH_2CH_2M$ for M = O, SiH_2, CH_2, or C=O) have had their ring-puckering potential energy functions determined from low-frequency vibrational spectra.[1-5] However, for the first time we now report the low-frequency spectra and the potential energy function for a molecule of this type with an asymmetric ring-puckering vibration. 2-Phospholene, $CH{=}CHCH_2CH_2PH$, is the asymmetric phosphorous analogoue of cyclopentene. The spectra of the symmetric analogue, 3-phospholene, have been analyzed previously.[6,7]

The equilibrium conformation of $CH{=}CHCH_2CH_2M$ molecules can be influenced not only by the usual torsional and ring strain forces but also by dπ–pπ bonding (M = S, SiH_2, or PH) or conjugation of double bonds (M = C=O). For 2,5-dihydrofuran ($CH_2CH{=}CHCH_2O$) and 2,3-dihydrofuran ($CH{=}CHCH_2CH_2O$), the conformation of the molecule is mainly influenced by the CH_2 torsional forces. 2,3-Dihydrofuran has a double-minimum ring-puckering potential energy function and a nonplanar equilibrium conformation.[1] 2,5-Dihydrofuran, however, has a planar equilibrium structure because there are no CH_2–CH_2 torsional forces in this molecule.[8] For 2,5-dihydrothiophene ($CH_2CH{=}CHCH_2S$) and 2,3-dihydrothiophene ($CH{=}CHCH_2CH_2S$), the same arguments hold as for the oxygen analogues. However, 2,3-dihydrothiophene could have some dπ–pπ bonding between the sulfur atom and the carbon–carbon double bond. This molecule has a nonplanar equilibrium conformation with a reported[1] barrier to planarity of 325 cm^{-1} (or 206 cm^{-1}).[8] From this information we may conclude that the dπ–pπ bonding in 2,3-dihydrothiophene does not overcome the CH_2 torsional forces to cause the ring to have a planar equilibrium structure. Silacyclopent-3-ene ($CH_2CH{=}CHCH_2SiH_2$)[9,10] and silacyclopent-2-ene ($CH{=}CHCH_2CH_2SiH_2$)[4] have been found to be planar. The latter molecule apparently does show substantial dπ–pπ bonding. 2-Cyclopenten-1-one ($CH{=}CH_2CH_2CH_2$-C=O) is also planar,[5] and this results from the conjugation between the carbonyl group and the carbon–carbon double bond.

Experimental Section

Synthesis. The samples of 2-phospholene and 2-phospholene-*1-d* were prepared by using the sequence of reactions shown below.



1. 1,1,1-Trichloro-3-phospholene (I). The preparation of the trichlorophospholene (I) has been reported previously.[11] Sealed tubes containing the butadiene–PCl_3 mixture were left intact for 9 months and then opened under inert conditions and washed with petroleum ether to give 275 g (96% yield) of crude product. The 1,1,1-trichloro-3-phospholene was characterized by proton NMR spectra and was used without further purification.

2. 1-Oxo-1-ethoxy-2-phospholene (II). The procedure previously reported by Hunger et al.[12] was followed. The reaction was carried out at −10 °C. Saturated $NaHCO_3$ solution and sizeable quantities of solid $NaHCO_3$ were added to the mixture, at room temperature, until no further CO_2 evolution was evident. Extraction with CH_2Cl_2, concentration, and distillation under vacuum resulted in a colorless liquid (bp 106–108 °C; 0.5 torr). The compound was characterized by proton NMR and infrared spectroscopy.

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3. 2-Phospholene (III). Reduction of II was accomplished by dropping an equimolar mixture of the 2-phospholene ester and phenylsilane into a flask heated to 170 °C. All transfers were made under N_2, and precautions were taken to exclude both oxygen and water from the reactants and products. Distillation, also under inert conditions, gave a clear, colorless liquid (bp 103–107 °C) that spontaneously burst into flame on contact with air. The product was characterized by infrared and proton NMR spectroscopy. A slight impurity of phenylsilane was removed by redistillation using a 12-in. packed column.

4. 2-Phospholene-1-d (IV). The phosphorous hydrogen of 2-phospholene was replaced with deuterium by performing three successive exchanges with 99.8% D_2O (Aldrich) on a vacuum line. Raman spectra of the deuterated 2-phospholene showed only a minor impurity of III and showed no phenylsilane impurity.

Spectroscopic Measurements. Far-infrared spectra were recorded on a high-resolution vacuum Digilab FTS-20 spectrophotometer. A Perkin-Elmer 4.9-m multireflection cell modified for use on the Digilab instrument and equipped with polyethylene windows was used to record all far-infrared spectra. A mercury arc served as the source of the radiation, and a TGS detector was used. A Mylar beam splitter of 12.5-μm thickness was used in recording the spectra.

For the 2-phospholene-*1-d* molecule the cell was "deuterated" several times with D_2O before the spectra were recorded to reduce the exchange of P–D deuterium with H_2O adsorbed onto the cell walls. The procedures for the cell deuteration and spectroscopic methods were similar to those previously described[6] for the 3-phospholene-*1-d* species.

Gas-phase Raman spectra were recorded with a Cary Model 82 spectrophotometer equipped with standard Cary multipass optics. The 5145-Å line of a Coherent Radiation Model 53 argon ion laser operating at about 2.0 W was used exclusively as the excitation source. Modified gas cells with an independent sample reservoir attached to the cell were used.

Calculation of the Kinetic Energy Expansion

We have recently discussed vector methods for the representation of the ring-puckering in four-membered rings and in symmetrical (1-substituted cyclopent-3-ene) rings[13] and used these methods for determining kinetic energy expansions. Because the ring puckering is a large amplitude motion, the reduced mass for the vibration varies with vibrational coordinate. Consequently, it is not sufficient to simply use the reciprocal of a constant reduced mass as the kinetic energy term. Instead, a kinetic energy expansion as a function of coordinate must be calculated.

The vector representation of the ring-puckering vibration for an asymmetrically substituted derivative of cyclopentene is considerably more complicated than that for the symmetrically substituted derivatives. The vibrational motion is not along a path that bisects the double bond (as it is for symmetrical molecules), since all of the bond lengths between the ring atoms are different. Nonetheless, we have developed methods for analyzing this motion, and these are described elsewhere.[14,15] The kinetic energy expansion, because of the asymmetry arising from the P–H hydrogen lying above (or below) the ring when the ring is in its planar configuration, has the form

$$g_{44}(x) = \sum_{i=0} g_{44}^{(i)} x^i \tag{1}$$

where g_{44} represents the kinetic energy (reciprocal reduced mass) expansion and derives from the 4,4-position of the rotational–vibrational G matrix. The first three subscripts by convention have been reserved for the molecular rotations. The above expansion is determined by evaluating g_{44} at many different x values and then calculating (by using the Newton–Raphson method) the coefficients $g_{44}^{(i)}$ that best fit the numerical data. The kinetic energy expansions through fourth order evaluated in this manner for the 2-phospholene and 2-phospholene-*1-d* molecules are, respectively

$$g_{44}^{H} = 0.766721 \times 10^{-2} - 0.436805 \times 10^{-2}x - 0.261504 \times 10^{-1}x^2 - 0.122632 \times 10^{-1}x^3 - 0.446209 \times 10^{-1}x^4 \tag{2}$$

and

$$g_{44}^{D} = 0.73140 \times 10^{-2} - 0.399017 \times 10^{-2}x - 0.205399 \times 10^{-1}x^2 - 0.142848 \times 10^{-1}x^3 - 0.550612 \times 10^{-1}x^4 \tag{3}$$

The corresponding reduced masses are

$$\mu_H = 130.42 \text{ au} \qquad \mu_D = 136.72 \text{ au} \tag{4}$$

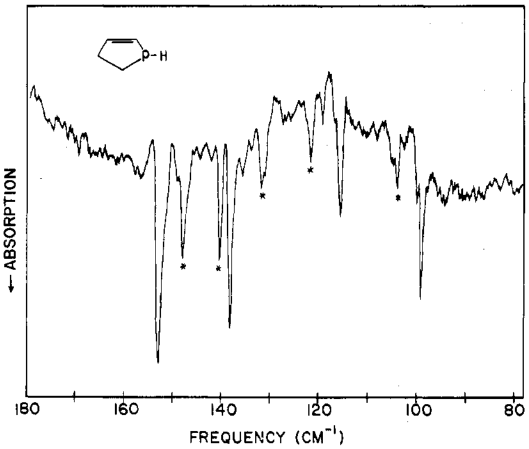

Figure 1. Vapor-phase far-infrared ring-puckering spectrum of 2-phospholene (14-torr vapor pressure; 4.9-m path length; 0.5-cm^{-1} resolution). The starred peaks are due to 3-phospholene.

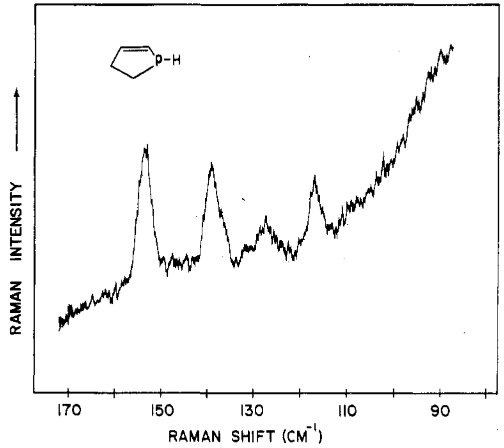

Figure 2. Low-frequency vapor-phase Raman spectrum of 2-phospholene in the ring-puckering region (3-cm^{-1} slit width).

Results and Discussion

Figure 1 shows the far-infrared ring-puckering spectrum of 2-phospholene. Since the sample has a small amount of the 3-phospholene isomer in it, bands due to the latter species are also present; these are marked with asterisks. Even though there are only a few percent of 3-phospholene in the sample, the impurity bands are nearly half as intense as those of the 2-phospholene. This is because the 3-ene spectrum[6] is substantially more intense than that of the 2-ene. This follows the trend observed previously that the far-infrared spectra of the asymmetrically substituted cyclopentenes are considerably weaker than those of the symmetrical molecules. This is true for the oxygen, sulfur, and silicon ring compounds as well as for the cyclopentenones. Despite the impurity, four bands can be conclusively assigned to 2-phospholene. The lowest frequency band of 2-phospholene is at 99.0 cm^{-1}, and this virtually coincides with the 3-phospholene band at 99.1 cm^{-1}. However, on the basis of the rest of the impurity spectrum, most

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TABLE I: Observed and Calculated Ring-Puckering Transitions (cm^{-1}) for 2-Phospholene and 2-Phospholene-*1-d*

	2-phospholene				2-phospholene-*1-d*			
transition	Raman	infrared	calcd	Δ^a	Raman	infrared	calcd	Δ^a
$0 \rightarrow 1$	153.4	152.7	153.3	−0.6	150.0	148.9	150.1	−1.2
$1 \rightarrow 2$	139.0	138.5	136.3	2.2	136.8	135.3	134.1	1.2
$2 \rightarrow 3$	116.9	115.8	116.1	−0.3	115.9	113.3	115.0	−1.7
$3 \rightarrow 4$		99.0	98.6	0.4		97.8	97.7	0.1

[a] Observed − calculated for far-infrared frequencies.

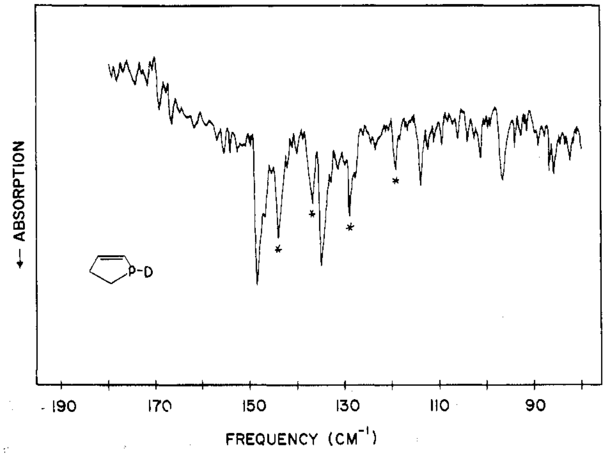

Figure 3. Vapor-phase far-infrared ring-puckering spectrum of 2-phospholene-*1-d* (14-torr vapor pressure; 4.9-m path length; 0.5-cm^{-1} resolution). The starred peaks are due to 3-phospholene-*1-d*.

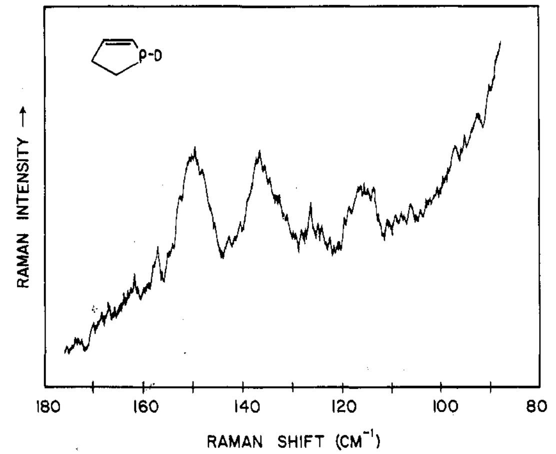

Figure 4. Low-frequency vapor-phase Raman spectrum of 2-phospholene-*1-d* in the ring-puckering region (4-cm^{-1} slit width).

of the intensity of this peak cannot be accounted for by the 3-ene isomer. The somewhat higher than expected intensity at this frequency is nevertheless explained by the overlap.

The Raman spectrum of 2-phospholene is shown in Figure 2. Three frequencies matching the higher frequency infrared transitions were observed. An additional peak at 126 cm^{-1} was also detected, but this is apparently not part of the puckering series since it is not shifted upon deuteration.

The far-infrared and Raman spectra for 2-phospholene-*1-d* are shown in Figures 3 and 4, respectively, and the observed data for both molecules are summarized in Table I. As can be seen, the far-infrared and Raman data agree within experimental error for the same molecule; the frequencies for the deuteride are shifted down in frequency by 1.2–3.8 cm^{-1}, depending on the transition. The fact that the infrared and Raman frequencies are coincident is characteristic of the fact that the one-dimensional ring-puckering potential energy function is asymmetric. Namely, both the infrared and Raman transitions show puckering quantum number changes of only one, $\Delta v_p = +1$. Similarly, asymmetric potential functions for 3-phospholene, bicyclo[3.1.0]hexane and its analogues,[16] and bicyclo[3.2.0]hept-6-ene and its 2-oxa derivative[17] result in Raman transitions with $\Delta v_p = +1$. However, molecules such as cyclopentene,[18] silacyclobutane,[19] and silacyclopent-3-ene,[19] which have symmetric ring-puckering functions, have Raman transitions with $\Delta v_p = +2$.

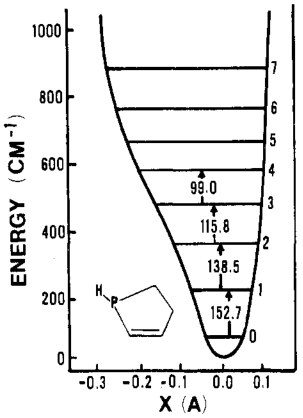

Figure 5. Ring-puckering potential energy function and transitions of 2-phospholene.

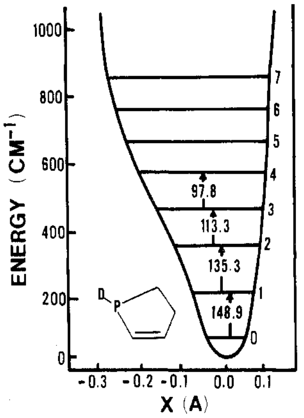

Figure 6. Ring-puckering potential energy function and transitions of 2-phospholene-*1-d*.

The one-dimensional ring-puckering potential energy function for 2-phospholene and its deuterio derivative was determined from the calculated kinetic energy expansions in eq 2 and 3 and the potential energy computer programs previously described.[6,16,17,20,21] Adjustment of the three potential energy parameters resulted in the following function:

$$V(\mathrm{cm^{-1}}) = 6.05 \times 10^5 x^4 + 3.24 \times 10^5 x^3 + 5.43 \times 10^4 x^2 \quad (5)$$

where x is the ring-puckering coordinate in angstroms. Table I shows the calculated frequencies for both isotopic species based on this function. As is evident, good agreement is obtained between the observed and calculated values. This is true even though no

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modifications were made on the simplest puckering model in order to adjust the reduced mass ratio. The kinetic energy expansions were simply used as calculated.

Figures 5 and 6 show this potential function along with the observed infrared transitions for 2-phospholene and 2-phospholene-*1-d*, respectively. As can be seen, the function is asymmetric and single minimum, indicating that only one conformer of the molecule would be stable. This is similar to 3-phospholene,[6] which has a single minimum, corresponding to the endo conformation (both the P–H and ring inverted in the same direction), in its potential function. Without additional (e.g. microwave) data it cannot be ascertained which conformation is more stable for 2-phospholene. However, analogy with 3-phospholene suggests the endo conformation would be at lower energy.

The potential function of 2-phospholene has inflection points at –0.08 Å, where V = 205 cm^{-1}, and at –0.19 Å, where V = 524 cm^{-1}. Most likely, then, the less stable planar structure and the less stable puckered conformation (exo) correspond approximately to these values. For the 3-phospholene molecule, for which microwave data were also available,[22] the planar and exo conformations occurred at –0.11 and –0.23 Å, respectively. The potential energies for these conformations are 331 and 785 cm^{-1}, respectively. In comparison, then, 2-phospholene appears to have a somewhat less puckered conformation and the energy of the planar form is only about 205 cm^{-1} higher, as compared to 331 cm^{-1} for the 3-ene. A lower energy for the planar ring conformation of 2-phospholene may well be an indication of some dπ–pπ bonding between the phosphorous and the olefinic double bond. Moreover, the quartic constant of 6.05 × 10^5 cm^{-1}/Å^4 in eq 5 is considerably higher than for 3-phospholene (2.86 × 10^5 cm^{-1}/Å^4). Since the quartic constant is a measure of angle strain and ring rigidity,[9] this also suggests additional forces are present in 2-phospholene that are lowering the energy of the planar structure. Nonetheless, the molecule has only one stable conformation and this is puckered. The lower C=C stretching frequency of 1560 cm^{-1} for 2-phospholene vs. 1626 cm^{-1} for 3-phospholene further suggests some dπ–pπ bonding for the 2-ene. Each of these observations parallels the comparisons made for 1-silacyclopent-3-ene and 1-silacyclopent-2-ene, where the latter molecule is believed to show substantial dπ–pπ bonding between silicon d orbitals and the carbon–carbon double bond. Both of these silicon compounds are planar, but the 2-ene is considerably more rigid. The quartic constant for the 2-ene is approximately 18.5 × 10^5 vs. 1.99 × 10^5 cm^{-1}/Å^4 for the 3-ene, and the carbon–carbon stretching frequency for the former is 1560 vs. 1610 cm^{-1} for the 3-ene.

Comparison of the 2-phospholene potential energy function to those of other asymmetric ring molecules is more difficult because reliable kinetic energy expressions for the other molecules have not been published. However, preliminary calculations in our laboratory[14] indicate that the quartic constant of 6.05 (× 10^5 cm^{-1}/Å) is similar to that in the sulfur compound (6.40) but substantially less than for the silicon compound (18.5) with its substantial dπ–pπ bonding. This x^4 coefficient is generally higher when M in $\overline{CH{=}CHCH_2CH_2M}$ involves a first-row element (with higher ring strain). Thus, values of about 7.1 and 10.0 have been found for M = CH$_2$ and O, respectively. Except for M = SiH$_2$ and C=O, where π bonding for M to the C=C occurs, the quadratic constant, which reflects primarily torsional interaction between adjacent CH$_2$ groups, is negative. For 2-phospholene, however, the quadratic term is small and positive, reflecting the fact that it is dominated by the x^3 coefficient. The latter gives rise to the asymmetry resulting from the phosphine hydrogen lying off of the molecular ring plane.

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Registry No. I, 69220-51-5; II, 695-63-6; III, 1769-52-4; IV, 88766-64-7; PCl$_3$, 7719-12-2; C$_6$H$_5$SiH$_3$, 694-53-1; butadiene, 106-99-0.

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Mass-Spectrometric Investigation of the Kinetics and the Deactivation of $C_4H_8^+$ and $(C_4H_8)_2^+$ Ions Formed by Photoionization of Isobutene in Nonpolar Gas Mixtures

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Ion/molecule reactions of isobutene leading to $C_4H_9^+(C_4H_8)_n$ and $C_8H_{14}^+(C_4H_8)_m$ species formation were investigated in a high-pressure photoionization (10.03 eV) mass spectrometer. The kinetics and the deactivation by nonpolar gases of the precursor ions, $C_4H_8^{+*}$ and $(C_4H_8)_2^*$, were evaluated. Some relationships between the deactivation efficiency and some molecular parameters were examined.

Introduction

The ion/molecule reactions in gaseous isobutene have been investigated on several occasions by different mass-spectrometric techniques.[1–8] At low pressure (<10^{-4} torr) the mass-spectrometric results from different laboratories agree fairly well and most discrepancies can be rationalized by taking into account the influence of the kinetic energy of the parent and/or their fragmentary ions on reactions with isobutene neutral molecules.[7] High-pressure mass spectrometry using a photoionization source (krypton resonance line at 10.03 eV or Lyman α hydrogen line at 10.2 eV) has the advantage over electron impact sources in that it leads to the appearance of the parent ion, i-$C_4H_8^+$, only; therefore, one can follow without ambiguities its subsequent reaction sequence.[5,6,8] The second krypton resonance line at 10.63

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