

according to the line determined by the E CH₂ rock and twist vibrations, and at the rate of $\sim 2.4^\circ$ kbar⁻¹ according to the slope of the A₁ ring stretch line at zero pressure. In 1,2-dichloroethane and 1,2-dibromoethane² it decreases at the rate $\sim 2^\circ$ kbar⁻¹.

These changes in molecular conformation should significantly affect the chemical properties; for example, the axial and equa-

torial 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

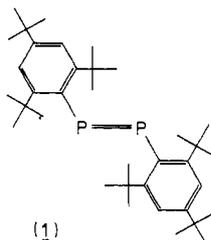
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Abstract: The frequency of the P=P double bond stretching has been obtained for the first time from a resonance Raman study of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene.

I. Introduction

Recent success in the synthesis of bis(2,4,6-tri-*tert*-butylphenyl)diphosphene¹ (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 (C₆H₅P)_n, n = 5, 6. The ultraviolet absorption,¹ ³¹P NMR,^{1,2} and ESCA³ 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.



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_6) of benzene, but the origin of

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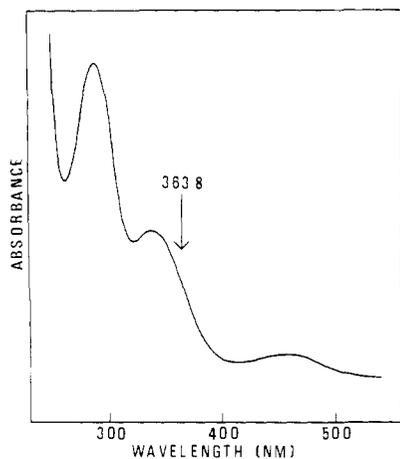


Figure 1. Visible and ultraviolet absorption spectrum of diphosphene **1** in dichloromethane. Absorption peaks are at 284 (ϵ 15 560), 340 (7690), and 460 nm (1360). The wavelength of the exciting line used in the present study is shown by an arrow.

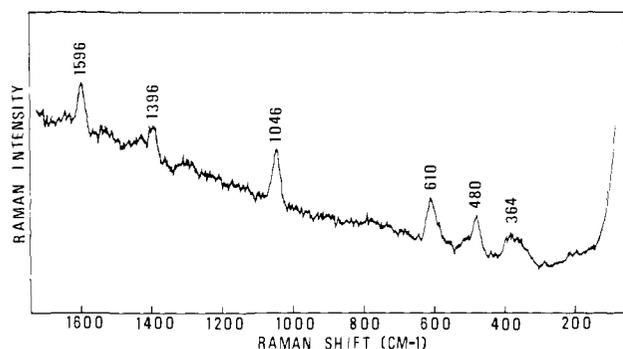


Figure 2. Resonance Raman spectrum of diphosphene **1** in a KBr disk (1:10 in weight) excited at 363.8 nm.

the 1396- cm^{-1} band is not clear. It has been found that the phenyl ring in the diphosphene is distorted to a boat form¹ and this may well cause a considerable change in the frequencies of the ring vibrations.

The remaining three bands should be assigned to the C—P=P—C group. An empirical rule⁶ concerning the P—Ph stretching

frequency locates this vibration at $520 \pm 20 \text{ cm}^{-1}$. Therefore, the 480- cm^{-1} band of diphosphene is reasonably assigned to the symmetric C—P stretching. The 364- cm^{-1} band is much broader than the others and likely to be a bending mode, most probably the symmetric C—P=P bending vibration. It is therefore concluded that the 610- cm^{-1} band is assigned to the P=P double-bond stretching. This assignment accords well with the fact that the frequency of the P=S stretching has been found in the range 580 ~ 620 cm^{-1} in compounds having the Ph—P=S linkage.⁶

In the case of azobenzene,^{7,8} the N=N and symmetric C—N stretching bands were much stronger than the bands due to the phenyl-ring vibrations, when a resonance with the $\pi^* \leftarrow \pi$ transition of the C—N=N—C group was used. The relatively higher intensities of the phenyl-ring bands in the diphosphene can be attributed to the effect of the preresonance from the 284-nm absorption, which is much stronger than the $\pi^* \leftarrow \pi$ transition of the C—P=P—C chromophore.

Since the frequencies of the P=P and C—P stretchings are close to each other, there must be a significant amount of mixing between the P=P and symmetric C—P stretching vibrations. There is also a possibility for a mixing between the C—P=P bending and the two stretching vibrations. The latter type of mixing is much less possible in the case of azobenzene, where the frequency differences between the bending and stretching vibrations are much larger than those in the diphosphene. This may give an explanation to the fact that the bending band is observed only in diphosphene and not in the case of azobenzene. A normal coordinate analysis including extensive analogous compounds will be necessary to establish the force constant of the P=P bond.

The assignment of the 610- cm^{-1} band seems beyond any doubt. Thus, the result presented here affords a highly reliable basis for the characterization of the phosphorus-phosphorus double bond.

Registry No. 1, 83466-54-0.

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(9) **Note Added in Proof:** The resonance Raman spectrum of a dialkyl-diphosphene, which we recently measured, confirmed the present assignment of the P=P stretching band. Hamaguchi, H.; Tasumi, M.; Yoshifuji, M.; Hashida, T.; Inamoto, N., to be published.