

SHORT COMMUNICATIONS

LASER-EXCITED RAMAN SPECTRUM AND VIBRATIONAL ANALYSIS OF THIOPHOSPHORYL DIBROMOFLUORIDE

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THE vibrational spectra of thiophosphoryl trichloride and trifluoride have been extensively studied by many workers¹⁻⁴. Although the infrared spectrum of thiophosphoryl dibromofluoride has been reported, its vibrational assignments are in doubt⁵. In line with the situation in the SPCl_2F molecule, P-S wagging vibration and SPF torsion vibration should assume almost the same frequency. But in the earlier results they differ by 33 cm^{-1} . Further P-F and P=S stretching vibrations are interchanged. The aim of the present work therefore is to reinvestigate the vibrational spectrum of SPBr_2F by laser Raman spectroscopy and to arrive at a satisfactory vibrational assignment for this molecule. Further the vibrational analysis of thiophosphoryl dibromofluoride is also presented.

Thiophosphoryl dibromofluoride was obtained from Prof. S. Gunasekaren of Pachiyappa's College, University of Madras. The polarized laser Raman spectra were recorded on a Cary model 82 grating spectrophotometer using the 488 nm line of Ar^+ from a 4 W argon laser for excitation in the region $100\text{--}4000\text{ cm}^{-1}$. The frequencies for all the sharp bands are accurate to $\pm 1\text{ cm}^{-1}$.

The laser Raman spectrum of thiophosphoryl dibromofluoride is shown in figure 1. The observed frequencies of SPBr_2F along with their relative intensities and probable assignments are presented in table 1. The molecule belongs to point group C_s and has only one plane of symmetry. The symmetry yields nine fundamentals. Out of the nine fundamentals six vibrations are symmetric (A' species) with respect to plane of symmetry and are polarized. The rest are asymmetric vibrations (A'' species) and are depolarized. All the nine vibrations are active in both Raman and infrared absorption.

The observed frequencies are assigned in a satisfactory manner using thiophosphoryl halides

and phosphorus pyramidal halides^{4, 6-8}. The strong polarized line at 377 cm^{-1} is assigned to P-Br symmetric stretch and the strong line at 470 cm^{-1} is assigned to P-Br asymmetric stretch without any doubt^{9, 10}. The P-Br stretch in phosphorus pyramidal halides agrees favourably with this assignment¹¹.

In comparison with the PF_3 stretching frequency in POF_3 ¹², PF_5 ¹³, PBrF_4 ¹⁴ and PF_3Br_2 ¹⁵, the band at 887 cm^{-1} is assigned to P-F stretching frequency. The medium band at 713 cm^{-1} is assigned to P=S stretching, which agrees quite well with the P=S stretching frequency in PSCl_3 and PSBr_3 ^{4, 6}. The band centred at 274 cm^{-1} is assigned to $\text{Br}\hat{\text{P}}\text{Br}$ bending and this agrees quite well with $\text{Br}\hat{\text{P}}\text{Br}$ bending in PSBr_3 . The band at 254 cm^{-1} is assigned to the PBr_2 rocking vibration in the present work. The lowest frequency 129 cm^{-1} is assigned to P-S wagging mode, since the wagging frequency is always low. Further, since it is known that ν_6 and ν_9 cannot differ by more than 15 cm^{-1} , we have assigned the same frequency to SPF torsional mode¹⁶. The remaining strong frequency at 218 cm^{-1} is assigned to PBr_2 wagging vibration. The rest of the observed frequency in table 1 may be accounted for as resulting from allowed combination of the selected nine fundamentals, which give additional support for their choice.

Using Wilson's F-G matrix method, the normal

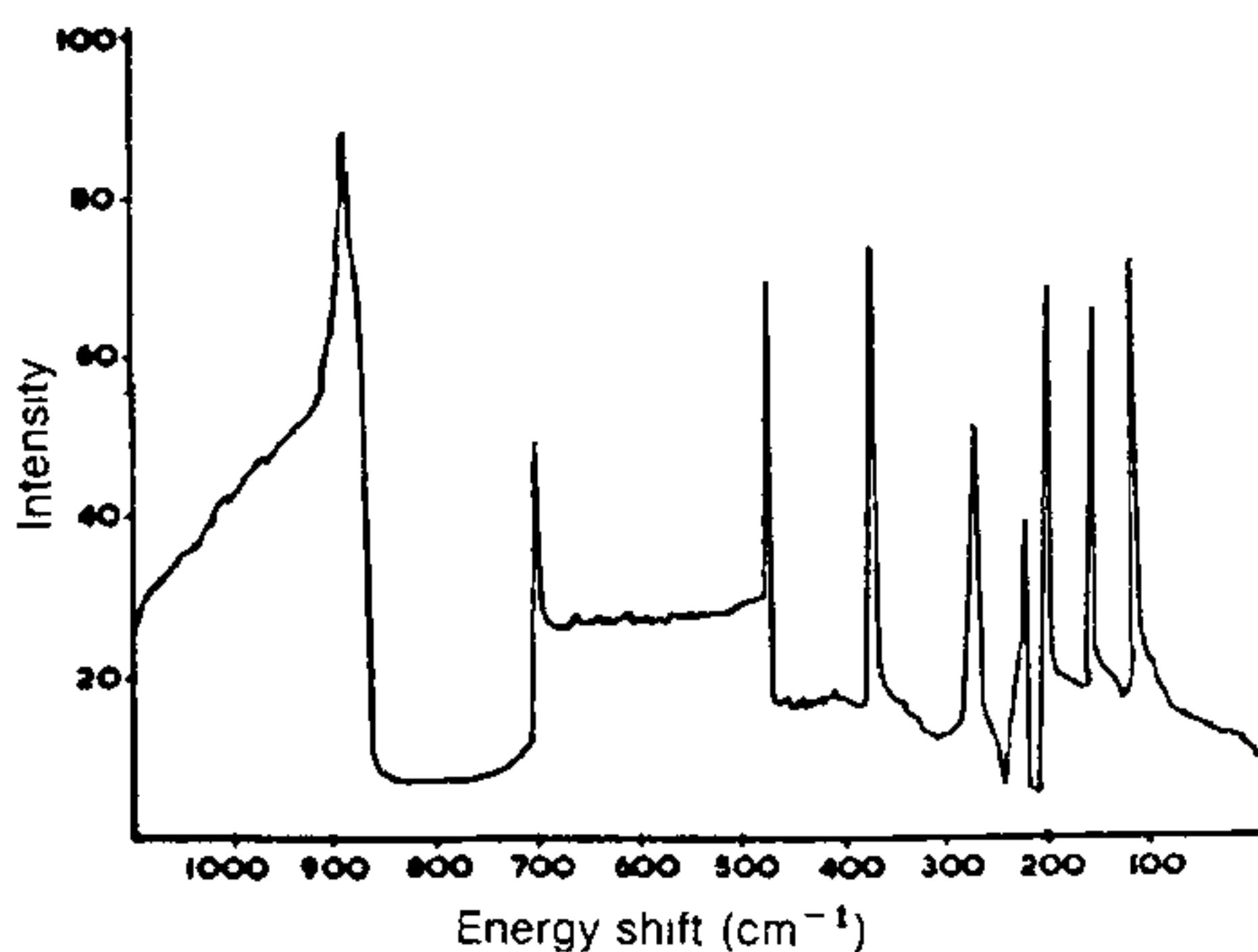


Figure 1. Laser Raman spectrum of thiophosphoryl dibromofluoride.

Table 1 Assignment of fundamental vibrational frequencies (cm^{-1}) of thiophosphoryl dibromofluoride

| Observed frequency (cm^{-1}) | Intensity | Description | Calculated freq. (cm^{-1}) | PED (%) |
|---|-----------|--|---------------------------------------|--------------------|
| 887 | VS(P) | ν_2 (A') P-F stretching | 885 | 99 S ₂ |
| 713 | M(P) | ν_3 (A') P=S stretching | 714 | 100 S ₃ |
| 470 | S | ν_7 (A'') P-Br asymmetric stretch | 470 | 100 S ₇ |
| 377 | S(P) | ν_1 (A') P-Br symmetric stretch | 375 | 100 S ₁ |
| 274 | M | ν_4 (A') Br-P-Br bending | 270 | 94 S ₄ |
| 254 | M | ν_8 (A'') PBr ₂ rocking | 249 | 90 S ₈ |
| 218 | S | ν_5 (A') PBr ₂ wagging | 211 | 92 S ₅ |
| 162 | S | $\nu_1 - \nu_5$ Fermi resonance | | |
| 129 | S | ν_6 (A') P-S wagging | 119 | 88 S ₆ |
| | | ν_9 (A'') SPF torsion | 121 | 91 S ₉ |

VS, Very strong; M, Medium; S, Strong; P, Polarized. PED is the contribution of the i th symmetry coordinate (S _{i}) to the potential energy of the vibration whose frequency is ν_k .

coordinate analysis of thiophosphoryl dibromofluoride has been carried out assuming C_s point group symmetry using a general quadratic valence force field. The structural parameters employed in the present work are P-S 1.86 Å, P-F 1.52 Å, P-Br 2.13 Å and Br-P-Br 106°. The molecular constants of the molecule are given in tables 2 and 3.

1. The evaluated major potential constants agree well with earlier results¹⁷⁻¹⁹.
2. The decrease of force constants from P-F to P-S

Table 2 Valence potential constants (10^2 Nm^{-1}) for SPBr₂F molecule

| | | | |
|---------------------|--------|---------------|--------|
| f_R (P-F) | 5.5394 | f_{DR} | 0.2857 |
| f_D (P-S) | 6.8265 | f_{Dd} | 0.3258 |
| f_d (P-Br) | 2.6041 | f_{Rd} | 0.4856 |
| f_a (Br-P-Br) | 0.0354 | f_{dd} | 0.3654 |
| f_β (F-P-S) | 0.2812 | f_{da} | 0.5124 |
| f_γ (F-P-Br) | 0.8957 | $f_{R\beta}$ | 0.1865 |
| f_δ (Br-P-S) | 0.5112 | $f_{D\beta}$ | 0.1892 |
| | | $f_{R\gamma}$ | 0.2167 |
| | | $f_{D\delta}$ | 0.3581 |
| | | $f_{d\gamma}$ | 0.4127 |
| | | $f_{d\delta}$ | 0.3589 |

Table 3 Vibrational mean amplitudes (pm) for SPBr₂F molecule at 298.18 K

| | |
|-------------------------|---------|
| 1 (P-F) | 4.2216 |
| 1 (P-S) | 3.7127 |
| 1 (P-Br) | 5.1021 |
| 1 _p (Br...F) | 12.1218 |
| 1 _q (Br...S) | 9.5279 |
| 1 _r (F...S) | 6.4911 |

may be attributed to the increase of electronegativity of the halogen atom.

3. Although electron diffraction data are not available for this molecule, the vibrational mean amplitudes for non-bonded atoms are characteristic. They also agree well with Muller's values^{17,18}.

The evaluated molecular constants, which are in the expected range, confirm the correctness of our assignment for this molecule. To check whether the chosen set of vibrational frequencies contributes the maximum to the potential energy associated with normal coordinates of the molecule, the potential energy distribution has been calculated using the relation, P.E. = $\sum F_{ik} L_{ik}^2 / \lambda_k$. The calculated frequencies are also listed along with the observed vibrational frequencies in table 1.

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1-Aroyl-2-[3-*n*-butoxy-5-oxo-4-phenyl-2(5H)-furylidene) phenyl acetyl hydrazines(III) were the products when the reaction was conducted in *n*-butanol due to the etherification of enolic hydroxyl in the presence of a base. All the products were adequately characterized by IR, NMR and high resolution mass spectral data. A few of the new derivatives showed promising activity against some bacterial strains.

Pulvinic dilactone reacted with substituted acid hydrazides in boiling dry xylene containing a small amount of pyridine to form 1-aryol-2-[(3-hydroxy-5-oxo-4-phenyl-2(5H)-furylidene)-phenyl-acetyl] hydrazines(II). IR spectra of all the products displayed two strong carbonyl absorptions, at 1730 and 1650 cm^{-1} for lactone and amide group respectively. The 200 MHz PMR of II_a confirmed this by showing two complex multiplets at 7.3–7.7 and 7.9–8.1 for aromatic hydrogens and two D₂O washable signals at 10.6 and 11 respectively for amide and enolic hydroxyl protons.

In the mass spectrum, molecular ion did not appear owing to weak amide linkage in II_a. On the other hand, the spectrum presents all the signals due to pulvinic dilactone and benzoic hydrazide due to reversal of the reaction. The prominent signals are at *m/z* 290, 234, 178, 117, 89 and 63 for pulvinic dilactone¹, 136 and 105 due to benzoic hydrazide and at 264 for pulvinone.

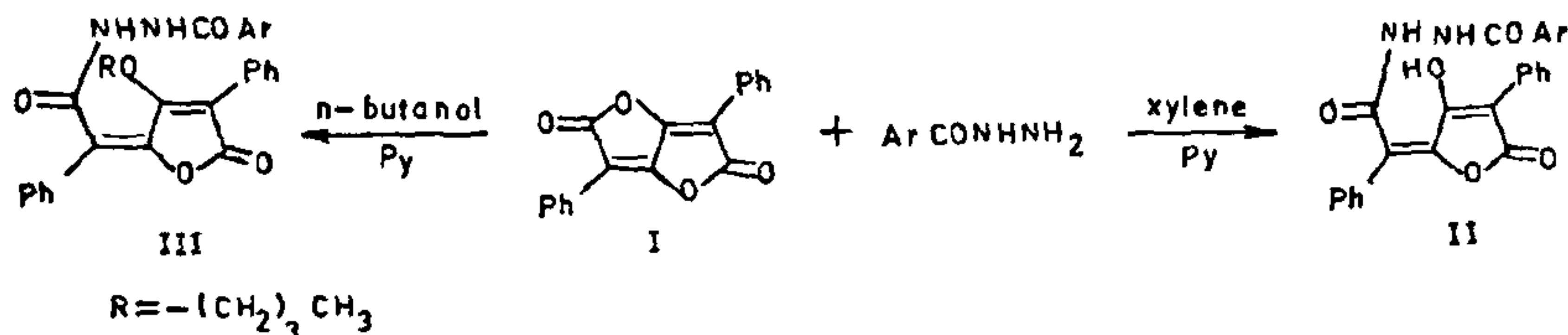
In *n*-butanol, pulvinic dilactone condensed with aroyl hydrazide in the presence of a few drops of pyridine to give 1-aryol-[3-*n*-butoxy-5-oxo-4-phenyl-2(5H) furylidene phenyl acetyl] hydrazines(III) (scheme 1). In acidic medium the enolic hydroxyl underwent etherification with the solvent. In addition to lactone and amide carbonyls appearing at 1710 and 1640, aliphatic vinyl ether stretchings are observed at 1320 and 1040. Aliphatic signals at 0.8, 1.4 and 4.1 for *n*-butoxy group and a neat singlet at 2.5 for aromatic methyl function presented a strong evidence to the structure of III_b. A complex

CHEMISTRY OF LICHEN PRODUCTS: PART VII: SOME NEW AMIDE DERIVATIVES FROM THE REACTION OF ACID HYDRAZIDES WITH PULVINIC DILACTONE

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PULVINIC dilactone (I) reacts with acid hydrazides in dry xylene containing catalytic amount of dry pyridine to afford 1-aryol-2-[(3-hydroxy-5-oxo-4-phenyl-2(5H)-furylidene)-phenyl-acetyl] hydrazines(II).



Scheme 1.