Androstane-2,17-dione.—The reduction of 4.0 g. of the enol tosylate with 2 g. of W-4 Raney nickel catalyst[10] in 400 cc. of ethanol was carried out exactly as described for the analogous reaction in the cholestane series[6] including reoxidation and chromatography; yield 0.88 g. (35%), m. p. 150–154°. The analytical sample was obtained from acetone–pentane with m. p. 152.5–154.5°, $[\alpha]^{20}D$ +119.9°, ultraviolet maximum at 290 mμ (log *E* 1.87).

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 79.03; H, 9.79.

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(10) Adkins and Pavlic, THIS JOURNAL, **69**, 3039 (1947).

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RECEIVED JULY 24, 1950

The Infrared Spectrum of P_4

BY H. S. GUTOWSKY AND C. J. HOFFMAN

Phosphorus in both the liquid and vapor state is known to be tetraatomic.[1] The molecular structure of P_4 has been investigated in electron[2] and X-ray[3] diffraction experiments which eliminate a plane square model in favor of a tetrahedral[2] or near tetrahedral[3] configuration. The Raman spectrum[4] is also compatible[5] with tetrahedral symmetry, T_d, but by itself is not conclusive. This investigation of the infrared spectrum of phosphorus confirms the tetrahedral structure for P_4. In addition, selection rule violations in the infrared spectra of solid yellow phosphorus and carbon disulfide solution are reported.

Experimental

The absorption spectrum of yellow phosphorus was observed from 400 to 1300 cm.$^{-1}$ with a Perkin-Elmer Model 12B spectrometer. Pieces of the solid, from 0.5 to 1.5 mm. thick, were mounted between potassium bromide plates. Carbon disulfide solutions, ranging from 10 to 50% phosphorus by volume, were observed in a 1.6 mm. liquid cell. Considerable difficulty was experienced in obtaining a satisfactory spectrum of the vapor. The results included herein were observed upon heating[6] to 230° a sealed, evacuated 90 cm. Pyrex cell, 4.5 cm. in diameter, with potassium bromide windows, and containing 3.8 g. of solid yellow phosphorus in a side arm. The primary optics of the spectrometer were modified to accommodate this cell and heating jacket by placing a globar at the focus of the 3″ diameter, 6″ focal length, spherical mirror removed from the spectrometer, and passing the reflected parallel light through the cell. A 3″ by 2″ flat mirror and another identical spherical mirror were used to bring the light along the optical axis of the monochromator and focus the image of the source upon the entrance slits. Figure 1 gives a schematic diagram of the arrangement.

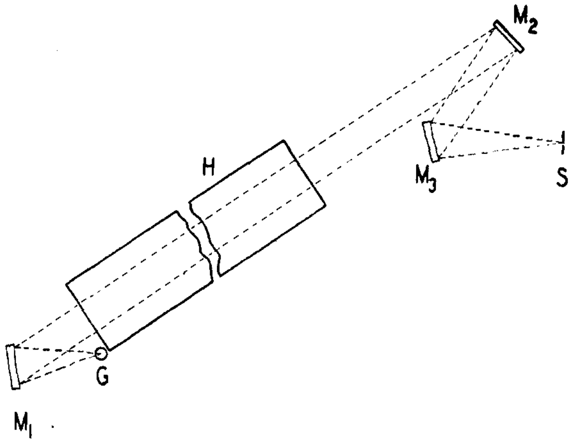

Fig. 1.—Schematic diagram of apparatus: G, globar; H, heater and cell; M_1, spherical mirror; M_2, flat mirror; M_3, spherical mirror; S, entrance slit.

Results and Discussion

The observed spectrum of the vapor is given in Fig. 2 and the spectral data are summarized in Table I, which includes frequency assignments.

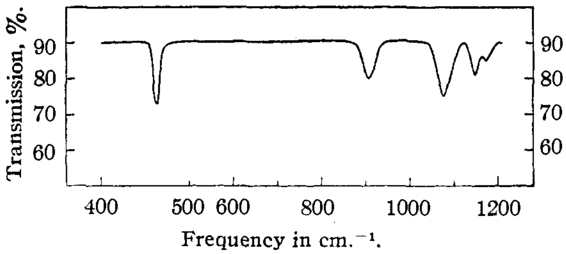

Fig. 2.—The infrared spectrum of P_4 vapor.

In the case of tetrahedral symmetry, P_4 has three fundamentals of species A_1, E and F_2, all of which are Raman active; the A_1 fundamental is polarized. In addition, the F_2 fundamental is infrared active. In all of the infrared spectra there was no indication of absorption at 363 cm.$^{-1}$, the lowest fre-

TABLE I

THE INFRARED AND RAMAN SPECTRA OF P_4

Solid	Infrared CS₂ soln., ν cm.⁻¹	Vapor	Raman[4] Liquid, Δν cm.⁻¹	Assignment
[a]	[a]	[a]	363 (2, 0.85)	ν_2
465 vw?	461 w	464.5 m	465 (6, 0.87)	ν_3
602[b] ms	604[b] m		606 (10, 0.05)	ν_1
811 vw				$\nu_2 + \nu_3$
911 w	916 w	910 mw		$2\nu_3$
959[b] w				$\nu_1 + \nu_2$
1053 m, b		1075 m		$\nu_1 + \nu_3$
		1150 } mw 1173 } mw		$2\nu_2 + \nu_3$

[a] Too low for observation with KBr optics. [b] Should be infrared inactive for tetrahedral symmetry.

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(1) See Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 155 *et seq.*, for a general survey of the data and literature.

(2) Maxwell, Hendricks and Mosley, *J. Chem. Phys.*, **3**, 699 (1935).

(3) Thomas and Gingrich, *ibid.*, **6**, 659 (1938).

(4) Venkateswaran, *Proc. Indian Acad. Sci.*, **4A**, 345 (1946), and prior work cited therein.

(5) The details of the discussion are summarized by Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 299.

(6) The general details of the heating arrangement were similar to a shorter cell described by Miller and Koch, THIS JOURNAL, **70**, 1890 (1948). A separately controlled heating coil at each end was necessary to compensate for radiation losses which otherwise caused phosphorus to condense on the windows.

quency observed in the Raman spectrum, though a search was made for it; however, this is considerably below the limit of reliability of the potassium bromide optics used and the apparent absence is suggestive at the very most. The only observed coincidence between the infrared spectrum of the vapor and the Raman spectrum is the 465 cm.$^{-1}$ frequency, which had been assigned previously[5] as the F_2 fundamental on the basis of a force constant analysis. This coincidence confirms both the tetrahedral structure and the frequency assignment.

There also seemed to be weak absorption by P_4 vapor in the region from 1240 to 1290 cm.$^{-1}$; however, it was obscured by erratic general absorption in the region, which became very strong at temperatures above 250° and was caused by red phosphorus sporadically deposited on the windows. There are several allowed combination bands which can account for this weak P_4 absorption.

The appearance of the totally symmetric vibration ν_1 at 602 and 604 cm.$^{-1}$ in the solid and CS_2 solution spectra, respectively, and the presence of weak absorption at 959 cm.$^{-1}$ in the solid are attributed to selection rule violations caused by intermolecular forces. An alternate interpretation in terms of a pyramidal structure, a slightly distorted tetrahedron, was considered in detail prior to obtaining a satisfactory spectrum for the vapor, and was found to be compatible with other available experimental data. However, the conditions under which the vapor spectrum was later obtained were such that the absence of absorption in the vicinity of 605 cm.$^{-1}$ is almost certain evidence that the corresponding vibrational mode is not infrared active in the vapor.

The resolution, stability and general performance of the spectrometer with the modified primary optics and heated cell were comparable to that of the normal instrument used for the spectra of the solid and solutions; a slight decrease in available light was compensated for by increasing slit widths 5 to 10%. When vaporized, the sample was equivalent to a thickness of 1.3 mm. of the solid, about three times that which gives readily detectable absorption at 602 cm.$^{-1}$ in the solid. Spectra were obtained at temperatures up to 280° where all of the phosphorus was vaporized and the pressure in the cell was nearly one atmosphere, without a trace of absorption at 605 or at 959 cm.$^{-1}$. Moreover, at 170° when the vapor pressure is of the order[1] of 6 to 10 cm., all of the bands were clearly present. The resulting conclusion that the selection rules are violated is substantiated by a high value, about[1] 22.8, of Trouton's constant for phosphorus and by the presence of complexes and molecular chains in carbon disulfide solution,[1] both facts indicative of strong intermolecular attraction.

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RECEIVED JULY 13, 1950

Decomposition of Amine Picrates with Ethanolamine

BY IRVING ALLAN KAYE, IRVING C. KOGON AND WILLIAM BURLANT

Amines, especially thermolabile or air-sensitive liquids yielding oily or hygroscopic salts, are frequently purified through their picrates. The recovery of the base, usually accomplished by decomposing the salt with an inorganic base, is complicated by the low water-solubility of sodium, potassium and ammonium picrates. This difficulty may be overcome by using lithium hydroxide.[1]

We have found that the more economical ethanolamine forms a picric acid salt which is extremely soluble in water and have used this base, following previously described directions,[1,2] in recovering numerous amines of varied structure.

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(1) Burger, THIS JOURNAL, **67**, 1615 (1945).

(2) Weiner and Kaye, *J. Org. Chem.*, **14**, 868 (1949).

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RECEIVED JULY 24, 1950

The Lead Tetraacetate Oxidation of Pregnenolone Benzoate

BY O. MANCERA

Recently Giral[1] described the lead tetraacetate oxidation of pregnenolone benzoate to a product, $C_{30}H_{38}O_5$, m. p. 175–176°, $[\alpha]_D$ +161° (chloroform), formulated as Δ^5-pregnen-3β,21-diol-20-one 3-benzoate 21-acetate.

A calculation of the molecular rotation differences yields a value of +628 for the contribution of the benzoyl group of Giral's product (Table I), in complete disagreement with such values reported by Barton.[2]

Some time ago we had investigated the lead tetraacetate oxidation of pregnenolone benzoate and obtained in 39% yield a product, $C_{30}H_{38}O_5$, m. p. 200–201°, $[\alpha]^{20}_D$ +48.95° (chloroform), shown to be Δ^5-pregnen-3β,21-diol-20-one 3-benzoate 21-acetate by comyarison with an authentic specimen prepared by benzoylation of Δ^5-pregen-3β,21-diol-20-one 21-acetate. The molecular rotation differences given in Table I are in good agreement with the values expected on the basis of earlier work.[2]

TABLE I

Substance	$[\alpha]_D$	$[M]_D$	$[M]_D$ contribution of the 3-benzoyl group[a]
Giral's product	+161	+770	+628
Δ^5-Pregnen-3β,21-diol-20-one 3-benzoate 21-acetate	+ 49	+234	+ 92
Δ^5-Pregnen-3β,21-diol-20-one 21-acetate	+ 38	+142	...

[a] Barton (ref. 2) reported +81 ± 16.

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(1) Giral, THIS JOURNAL, **72**, 1913 (1950).

(2) Barton, *J. Chem. Soc.*, 813 (1945).