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Molecular Structures of Phosphoryl Fluoride, Phosphoryl Chloride, and Thiophosphoryl Chloride Studied by Gas Electron Diffraction

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The bond lengths and angles for POF_3, $POCl_3$, and $PSCl_3$ have been determined by gas electron diffraction to be $r_g(\text{P–F}) = 1.5240 \pm 0.003$ Å, $r_g(\text{P–O}) = 1.4356 \pm 0.006$ Å, and $\theta_\alpha(\text{F–P–F}) = 101.3 \pm 0.2°$ for POF_3; $r_g(\text{P–Cl}) = 1.9931 \pm 0.003$ Å, $r_g(\text{P–O}) = 1.4487 \pm 0.005$ Å, and $\theta_\alpha(\text{Cl–P–Cl}) = 103.3 \pm 0.2°$ for $POCl_3$; and $r_g(\text{P–Cl}) = 2.0114 \pm 0.003$ Å, $r_g(\text{P–S}) = 1.8851 \pm 0.005$ Å, and $\theta_\alpha(\text{Cl–P–Cl}) = 101.8 \pm 0.2°$ for $PSCl_3$. The uncertainties represent estimated limits of experimental error. For each molecule the structure is found to be consistent with the corresponding rotational constant B_0. The observed bond lengths and angles for these molecules are compared with one another and with those for related molecules. The systematic differences can be accounted for in terms of the Gillespie model. Smooth correlation curves between the bond lengths or angles in PXY_3 and the electronegativities of the atoms coordinated to the phosphorus atom are obtained.

Introduction

The relationship between the structure and bonding in molecules is a classical problem but, in a sense, is a still uncultivated field in chemistry. No theory has been presented to explain it thoroughly, nor are there a sufficient number of accurate data available from experiment.

Some years ago, Gillespie proposed a simple model[1-3] for a systematic interpretation of the stereochemistry of inorganic molecules. His success has stimulated chemists to investigate the structures of molecules, in particular, the halides of group V elements.[4-6] Phosphoryl and thiophosphoryl halides, together with PF_3 which has recently been studied by the present authors,[6] constitute an appropriate model series for such stereochemical studies. The present work aims to answer the following question: How are the P–F (P–Cl) bond length and F–P–F (Cl–P–Cl) angle influenced by the coordination of the oxygen or sulfur atom to the lone pair of PF_3 (PCl_3)?

Electron diffraction by the sector-microphotometer method is one of the most suitable techniques for this purpose because it enables us to determine the structures of the above molecules directly and accurately. Rotational constants obtained from spectroscopy also give independent information on molecular structure. The consistency of the diffraction with spectroscopic results, which should be of primary importance in the structure analysis, has been examined in detail in the present study.

The structures of POF_3, $POCl_3$, and $PSCl_3$ reported so far are listed in Table I. They were first studied by Beach and his coworkers,[7,8] who used the visual method of electron diffraction. Williams, *et al.*,[9] and Hawkins, *et al.*,[10] later determined the rotational constants B_0 from microwave spectroscopy. The latter group derived the structure of POF_3 using the B_0 and the bond angle of 106° obtained in the above diffraction study. The former authors revised the diffraction data for POF_3 and $POCl_3$ using their B_0 constants, while for $PSCl_3$ they determined the structure from their microwave data alone.

After the present work was undertaken, an electron diffraction study of $POCl_3$ and $PSCl_3$ was reported by Vilkov, *et al.*[11] A comparison with their results is discussed in a later section.

Experimental Section

Liquid samples of $POCl_3$ and $PSCl_3$ obtained from commercial sources were purified by fractional distillation. Gaseous POF_3 (bp −39.7° and mp −39.1°)[12] was synthesized by the reaction[13] $2POCl_3 + 3ZnF_2 \rightarrow 2POF_3 + 3ZnCl_2$. The crude product trapped at liquid nitrogen temperature contained POF_2Cl, $POFCl_2$, and SiF_4 as impurities. A considerable difficulty was encountered in preparing pure POF_3, but the impurities were removed by a careful distillation in a still with a head cooled with Dry Ice and acetone as described by Tarbutton, *et al.*[12] The POF_3 gas had a slight tendency to attack glass and produce SiF_4, which was removed by means of a methylcyclohexane slush bath (−126°) just before the electron diffraction experiment. Before and after the photographing, infrared spectra were recorded to check for impurities, which were found to be negligible.

The detail of the electron diffraction instrument and the experimental procedures have been reported elsewhere.[14] Diffraction photographs were taken with an r^3 sector. The accelerating voltage was on the average 40.59 kV, which corresponds to the electron wavelength of 0.05970 Å. This wavelength was later calibrated with reference to the $r_a(\text{C=O})$ bond length (1.1646 Å) of carbon dioxide measured under the same experimental condi-

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TABLE I

STRUCTURAL PARAMETERS IN PREVIOUS REPORTS[a]

		POF_3		
r(P-F), Å	r(P-O), Å	θ(F-P-F), deg	Method	Ref
1.52 ± 0.02	1.56 ± 0.03	107 ± 2	ED	7
1.52 ± 0.02	1.45 ± 0.03	102.5 ± 2	MW	9
1.52	1.48	106	MW	10
		$POCl_3$		
r(P-Cl), Å	r(P-O), Å	θ(Cl-P-Cl), deg		
2.02 ± 0.03	(1.58)	106 ± 1	ED	7
1.99 ± 0.02	1.45 ± 0.03	103.6 ± 2	MW	9
2.002 ± 0.002	1.434 ± 0.005	103.8 ± 0.35	ED	11
		$PSCl_3$		
r(P-Cl), Å	r(P-S), Å	θ(Cl-P-Cl), deg		
2.01 ± 0.02	1.94 ± 0.03	107 ± 3	ED	8
2.02 ± 0.01	1.85 ± 0.02	100.5 ± 1	MW	9
2.020 ± 0.002	1.908 ± 0.006	101.8 ± 0.35	ED	11

[a] Abbreviations: ED, electron diffraction: MW, microwave spectroscopy.

tions. The gas was introduced into the diffraction chamber through a nozzle of 0.2-mm diameter. The pressure of the chamber was below 6 × 10^{-5} Torr during photographic exposure. The nozzle temperature was 20° and the electron beam current was about 0.40 μA. The sample pressures were 52, 26, and 37 Torr, and the exposure times were 50, 25, and 45 sec for POF_3, $POCl_3$, and $PSCl_3$, respectively. The photographs were recorded on Fuji process hard plates.

Three or four plates taken at the camera length of 10.782 cm for every molecule and two plates at 24.322 cm for POF_3 were used for the following analyses. Optical densities were measured across the plate at intervals of $\Delta q = 1$ Å^{-1} by means of a microphotometer and an integrating digital voltmeter. The observed optical densities (0.13–0.69) were assumed to be proportional to the electron intensities. The background intensity due to extraneous scattering was subtracted by means of an empirical method.[14]

Analysis

The radial distribution curves,[15] calculated from the experimental intensities and smooth empirical backgrounds (Tables II–IV) with an artificial damping factor of $\exp(-0.00016q^2)$, are shown in Figure 1. No significant ghost peaks were found in any case. Though the peaks for POF_3 and $PSCl_3$ overlap so closely as to jeopardize a unique resolution into component peaks, nonoverlapping portions have provided sufficient information to determine all the structure parameters.

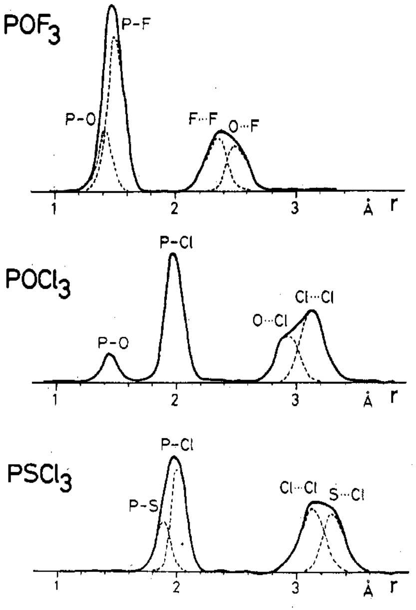

Figure 1.—Experimental radial distribution curves.

TABLE II

INTENSITY AND BACKGROUND DATA FOR POF_3[a]

q	I_t	I_b	q	I_t	I_b	q	I_t	I_b	q	I_t	I_b	q	I_t	I_b
						8	1286	1718	9	1570	1730	10	1484	1737
11	1532	1744	12	1547	1751	13	1571	1755	14	1656	1752	15	1820	1743
16	2007	1734	17	2134	1725	18	2139	1720	19	2003	1718	20	1771	1717
21	1531	1716	22	1374	1713	23	1339	1705	24	1422	1697	25	1571	1691
26	1723	1689	27	1826	1689	28	1867	1691	29	1857	1695	30	1820	1700
31	1786	1705	32	1759	1711	33	1737	1716	34	1705	1722	35	1665	1727
36	1624	1731	37	1599	1737	38	1607	1739	39	1649	1743	40	1726	1748
41	1807	1753	42	1877	1759	43	1907	1767	44	1898	1774	45	1860	1782
46	1809	1790	47	1767	1800	48	1740	1811	49	1736	1826	50	1755	1839
51	1790	1855	52	1836	1871	53	1879	1887	54	1927	1902	55	1966	1918
56	1992	1933	57	2009	1948	58	2007	1964	59	1997	1978	60	1989	1994
61	1981	2010	62	1987	2025	63	2008	2041	64	2039	2056	65	2080	2072
			17	2584		18	2866		19	2826		20	2575	
21	2288		22	2129		23	2075		24	2199		25	2402	
26	2602		27	2712		28	2786		29	2748		30	2698	2568
31	2639	2560	32	2585	2551	33	2538	2542	34	2490	2533	35	2421	2523
36	2347	2513	37	2305	2503	38	2304	2495	39	2352	2488	40	2441	2481
41	2541	2474	42	2619	2469	43	2650	2465	44	2628	2462	45	2565	2459
46	2484	2457	47	2409	2456	48	2343	2455	49	2332	2454	50	2339	2454
51	2366	2454	52	2408	2453	53	2453	2453	54	2497	2453	55	2530	2453
56	2543	2454	57	2541	2454	58	2519	2453	59	2481	2453	60	2441	2453
61	2406	2453	62	2387	2453	63	2379	2452	64	2389	2452	65	2411	2451
66	2438	2451	67	2466	2450	68	2491	2449	69	2509	2448	70	2508	2446
71	2498	2444	72	2468	2442	73	2437	2439	74	2402	2435	75	2379	2432
76	2373	2428	77	2379	2425	78	2397	2421	79	2418	2417	80	2432	2414
81	2445	2411	82	2446	2407	83	2434	2404	84	2420	2401	85	2405	2398
86	2395	2396	87	2382	2393	88	2370	2391	89	2365	2388	90	2365	2385
91	2356	2382	92	2365	2379	93	2378	2375	94	2388	2372	95	2396	2369
96	2396	2365	97	2389	2362	98	2369	2358	99	2349	2355	100	2333	2351
101	2327	2348	102	2322	2345	103	2327	2342	104	2332	2338	105	2337	2336
106	2341	2333	107	2344	2331	108	2341	2328	109	2338	2326	110	2331	2323
111	2325	2320	112	2315	2317	113	2310	2314	114	2299	2310	115	2292	2306
116	2289	2302	117	2296	2299	118	2298	2295	119	2302	2292	120	2304	2290
121	2308		122	2301		123	2291		124	2279		125	2274	
126	2277		127	2274		128	2280		129	2290		130	2298	

[a] Typical experimental leveled intensity $I_t(q)$ and background $I_b(q)$, defined in ref 16, for long (top) and short (bottom) camera lengths: 24.322 and 10.782 cm.

TABLE III

INTENSITY AND BACKGROUND DATA FOR $POCl_3$[a]

q	I_t	I_b	q	I_t	I_b	q	I_t	I_b	q	I_t	I_b	q	I_t	I_b
26	1860		27	1863		28	1892		29	1886		30	1898	1906
31	1928	1899	32	1970	1891	33	1994	1884	34	1972	1877	35	1900	1870
36	1810	1864	37	1758	1859	38	1753	1855	39	1790	1851	40	1842	1848
41	1882	1845	42	1898	1843	43	1900	1842	44	1883	1841	45	1862	1841
46	1834	1841	47	1808	1841	48	1793	1842	49	1797	1842	50	1823	1843
51	1858	1843	52	1885	1844	53	1887	1845	54	1869	1847	55	1845	1849
56	1826	1850	57	1823	1851	58	1830	1853	59	1843	1854	60	1855	1855
61	1867	1856	62	1880	1857	63	1888	1859	64	1885	1860	65	1871	1861
66	1847	1863	67	1830	1864	68	1824	1865	69	1840	1866	70	1865	1867
71	1891	1867	72	1900	1867	73	1899	1867	74	1883	1867	75	1866	1867
76	1856	1866	77	1850	1866	78	1847	1865	79	1849	1865	80	1851	1865
81	1860	1864	82	1874	1863	83	1884	1862	84	1885	1861	85	1874	1861
86	1860	1860	87	1842	1858	88	1837	1857	89	1844	1856	90	1852	1855
91	1858	1853	92	1864	1852	93	1864	1851	94	1855	1849	95	1844	1847
96	1836	1845	97	1836	1844	98	1833	1843	99	1836	1841	100	1838	1839
101	1846	1837	102	1848	1835	103	1846	1834	104	1840	1832	105	1831	1830
106	1818	1828	107	1813	1826	108	1811	1824	109	1812	1822	110	1818	1819
111	1822	1817	112	1824	1815	113	1823	1813	114	1820	1810	115	1811	1808
116	1803	1805	117	1802	1803	118	1793	1801	119	1792	1798	120	1793	1795

[a] Typical experimental leveled intensity $I_t(q)$ and background $I_b(q)$, defined in ref 16, for the short camera length 10.782 cm.

TABLE IV

INTENSITY AND BACKGROUND DATA FOR $PSCl_3$[a]

q	I_t	I_b	q	I_t	I_b	q	I_t	I_b	q	I_t	I_b	q	I_t	I_b
						18	1467		19	1678		20	1854	
21	1919		22	1884		23	1812		24	1790		25	1788	
26	1761		27	1688		28	1606		29	1578		30	1626	1693
31	1717	1683	32	1789	1674	33	1788	1665	34	1727	1658	35	1643	1650
36	1581	1643	37	1566	1637	38	1580	1633	39	1604	1630	40	1625	1627
41	1640	1625	42	1655	1622	43	1667	1621	44	1663	1621	45	1638	1620
46	1605	1620	47	1581	1620	48	1576	1621	49	1590	1621	50	1614	1622
51	1638	1623	52	1655	1624	53	1659	1625	54	1652	1627	55	1634	1629
56	1619	1631	57	1606	1633	58	1604	1634	59	1617	1636	60	1639	1637
61	1653	1638	62	1660	1639	63	1656	1641	64	1649	1642	65	1643	1643
66	1637	1644	67	1637	1646	68	1634	1647	69	1638	1649	70	1644	1651
71	1660	1653	72	1670	1654	73	1672	1656	74	1665	1658	75	1656	1660
76	1647	1662	77	1652	1664	78	1660	1666	79	1673	1668	80	1676	1669
81	1674	1671	82	1673	1672	83	1675	1673	84	1677	1674	85	1676	1676
86	1676	1678	87	1673	1680	88	1675	1682	89	1682	1684	90	1689	1686
91	1696	1688	92	1699	1690	93	1695	1692	94	1694	1694	95	1688	1696
96	1692	1698	97	1694	1699	98	1700	1700	99	1705	1702	100	1707	1704
101	1708	1705	102	1714	1706	103	1710	1708	104	1710	1710	105	1708	1712
106	1708	1714	107	1709	1715	108	1713	1717	109	1721	1719	110	1727	1720
111	1728	1721	112	1728	1723	113	1725	1725	114	1722	1726	115	1723	1727
116	1728	1730	117	1729	1733	118	1734	1735	119	1740	1737	120	1743	1740

[a] Typical experimental leveled intensity $I_t(q)$ and background $I_b(q)$, defined in ref 16, for the short camera length 10.782 cm. For an exact calibration of the scale factor, the listed q values should be divided by 0.9982.

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TABLE V

STRUCTURAL PARAMETERS AND MEAN AMPLITUDES FOR POF_3[a]

	P–F, Å	P–O, Å	F···F, Å	O···F, Å	θ(F–P–F), deg
r_a	1.5229 ± 0.003	1.4347 ± 0.006	2.3535 ± 0.004	2.5200 ± 0.006	
r_g	1.5240 ± 0.003	1.4356 ± 0.006	2.3554 ± 0.004	2.5214 ± 0.006	
r_α	1.5223 ± 0.003	1.4339 ± 0.006	2.3541 + 0.004	2.5202 ± 0.006	101.3 ± 0.2
$r_\alpha{}^0$	1.5226 ± 0.003	1.4338 ± 0.006			101.3 ± 0.2
$r_e{}^a$	1.5191	1.4288			101.3
l_{obsd}	0.0406 ± 0.003	0.0451 ± 0.005	0.0630 ± 0.004	0.0627 ± 0.003	
l_{calcd}	0.0404	0.0355	0.0675	0.0598	

[a] Estimated by an approximate method using the Morse function with an anharmonic constant a_3 of the corresponding diatomic molecule.[18]

TABLE VI

STRUCTURAL PARAMETERS AND MEAN AMPLITUDES FOR $POCl_3$[a]

	P–Cl, Å	P–O, Å	Cl···Cl, Å	O···Cl, Å	θ(Cl–P–Cl), deg
r_a	1.9918 ± 0.003	1.4468 ± 0.005	3.1269 ± 0.006	2.9095 ± 0.008	
r_g	1.9931 ± 0.003	1.4487 ± 0.005	3.1291 ± 0 006	2.9111 ± 0.008	
r_α	1.9910 ± 0.003	1.4460 ± 0.005	3.1281 ± 0.006	2.9091 ± 0.008	103.3 ± 0.2
$r_\alpha{}^0$	1.9906 ± 0.003	1.4465 ± 0.005			103.3 ± 0.2
$r_e{}^a$	1.9885	1.4458			103.3
l_{obsd}	0.0422 ± 0.003	0.0328 ± 0.004	0.0770 ± 0.006	0.0637 ± 0.004	
l_{calcd}	0.0502	0.0356	0.0839	0.0687	

[a] See corresponding footnote in Table V.

TABLE VII

STRUCTURAL PARAMETERS AND MEAN AMPLITUDES FOR $PSCl_3$[a]

	P–Cl, Å	P–S, Å	Cl···Cl, Å	S···Cl, Å	θ(Cl–P–Cl), deg
r_a	2.0101 ± 0.003	1.8840 ± 0.005	3.1160 ± 0.004	3.3112 ± 0.003	
r_g	2.0114 ± 0.003	1.8851 ± 0.005	3.1184 ± 0.004	3.3130 ± 0.003	
r_α	2.0092 ± 0.003	1.8829 ± 0.005	3.1168 ± 0.004	3.3115 ± 0.003	101.8 ± 0.2
$r_\alpha{}^0$	2.0089 ± 0.003	1.8827 ± 0.005			101.8 ± 0.2
$r_e{}^a$	2.0053	1.8815			101.8
l_{obsd}	0.0463 ± 0.003	0.0325 ± 0.005	0.0800 ± 0.005	0.0762 ± 0.004	
l_{calcd}	0.0505	0.0465	0.0863	0.0765	

[a] See corresponding footnote in Table V.

A standard least-squares method was carried out with a diagonal weight matrix[16] to fit the experimental molecular intensity $qM(q)$ to the theoretical expression, using a correction for nonnuclear scattering calculated from the recent data for elastic and inelastic scattering factors.[17] In the final step of the least-squares procedure, the following eight parameters were varied simultaneously: two bond lengths and one bond angle, four mean amplitudes, and the index of resolution. The asymmetry parameters κ for bonded distances were estimated from the a_3 parameters for diatomic molecules,[18] 1.891 (P–F), 2.034 (P–O), 1.67 (P–Cl), and 1.67 $Å^{-1}$ (P–S). The κ parameters for nonbonded distances were ignored. An alternative least-squares analysis with four interatomic distances taken as independent variable parameters gave bond angles consistent to within the uncertainties quoted in Tables V–VII. The ranges of the data used are $15 \leq q \leq 120$, $30 \leq q \leq 120$, and $30 \leq q \leq 120$, and indices of resolution are on the average 0.97, 0.88, and 0.98 for POF_3, $POCl_3$, and $PSCl_3$, respectively. The relatively low index of resolution for $POCl_3$ seems to be due to the correlation with mean amplitudes.[16] The experimental and best fit molecular intensity curves are shown in Figure 2, and the corresponding error matrices[19] are given in Tables

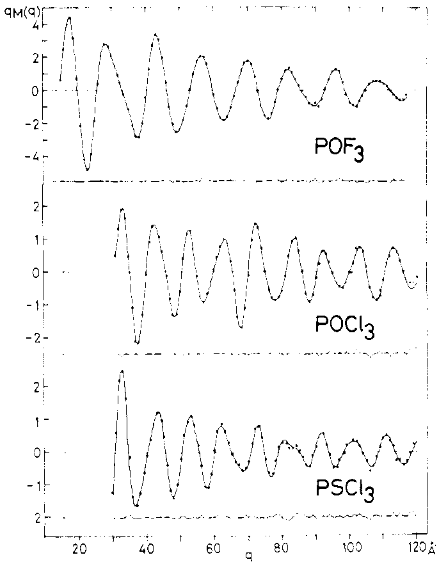

Figure 2.—Experimental and best fit theoretical molecular intensity curves shown in dots and solid curves, respectively. Differences are also shown.

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TABLE VIII

ERROR MATRIX FOR $PSCl_3$[a]

	r(P–Cl)	r(P–S)	r(Cl···Cl)	r(S···Cl)	l(P–Cl)	l(P–S)	l(Cl···Cl)	l(S···Cl)	k
r(P–Cl)	7	9	−4	−4	−4	−4	−3	−3	−14
r(P–S)		17	−5	−8	−8	−11	−6	−7	−39
r(Cl···Cl)			20	16	−2	−3	2	−6	−4
r(S···Cl)				21	7	8	8	4	31
l(P–Cl)					11	15	8	7	39
l(P–S)						24	10	9	50
l(Cl···Cl)							14	11	20
l(S···Cl)								15	32
k									175

[a] The elements are given by $\sigma_{ij} = \text{sgn}[(B^{-1})_{ij}]\,[|(B^{-1})_{ij}| \cdot V^*PV/(n-m)]^{1/2}$ for $n = 91$. The notation corresponds to that of ref 19. The units for the distance r_a and the mean amplitudes l are 10^{-4} Å, while the index of resolution k is given by 10^{-4}.

TABLE IX

ERROR MATRIX FOR $POCl_3$[a]

	r(P–Cl)	r(P–O)	r(Cl···Cl)	r(O···Cl)	l(P–Cl)	l(P–O)	l(Cl···Cl)	l(O···Cl)	k
r(P–Cl)	3	−1	−1	−1	1	1	1	−1	4
r(P–O)		13	0	3	−2	−3	−2	−2	−7
r(Cl···Cl)			13	12	−2	−2	−4	8	−9
r(O···Cl)				20	−4	−4	−9	6	−20
l(P–Cl)					5	4	4	3	20
l(P–O)						16	4	3	22
l(Cl···Cl)							9	4	10
l(O···Cl)								14	13
k									93

[a] See footnote *a* of Table VIII; $n = 91$.

TABLE X

ERROR MATRIX FOR POF_3[a]

	r(P–F)	r(P–O)	r(F···F)	r(O···F)	l(P–F)	l(P–O)	l(F···F)	l(O···F)	k
r(P–F)	6	−8	2	−1	−6	−12	−3	−3	−16
r(P–O)		17	−1	1	10	17	1	1	5
r(F···F)			11	9	−3	−4	−2	−3	−7
r(O···F)				14	2	4	4	1	5
l(P–F)					9	17	4	5	20
l(P–O)						31	8	7	37
l(F···F)							10	8	15
l(O···F)								12	14
k									64

[a] See footnote *a* of Table VIII; $n = 106$.

VIII–X. The interatomic distances and the mean amplitudes determined in the analyses are listed in Tables V–VII, which also contain the mean amplitudes calculated from the force constants reported by Ziomek and Piotrowski.[20] All computer calculations were made with the HITAC-5020E of the Computer Center of the University of Tokyo.

Error Estimation.—Two different estimates of the random errors, σ_1 and σ_2, were obtained from the standard deviations and from the scatter of the parameter values for different plates.[16] In most cases the σ_1 and σ_2 values were comparable with each other, so that the larger of them was taken as the random error σ. The systematic errors for the interatomic distances were estimated from the uncertainty in the scale factor determined by the analysis of carbon dioxide (standard deviation 0.06%). Thus the uncertainties in the interatomic distances were estimated to be $3[(0.0006r)^2 + \sigma^2]^{1/2}$.

The systematic error in the bond angle was estimated to be negligible, because the angle parameter is unaffected by the error in the scale factor. Hence, 3σ was taken as the uncertainty in the bond angles.

On the other hand, the errors in the mean amplitudes were attributed mostly to the extraneous scattering; thus the errors were estimated from the dependence of the results on how extraneous scattering was eliminated in the analytical procedure.

Discussion

Comparison with Rotational Constants.—For a precise determination of molecular structure the results from electron diffraction should be combined with spectroscopic rotational constants, which are directly related to the moments of inertia of the molecule. This comparison displays the credibility of the determined structure and enables us to make the best use of available experimental information.[21] Strictly speaking, the observed values from either source require small corrections for the effects of molecular vibrations, such as shrinkage effects, vibrational anharmonicity, and vibration–rotation interaction. Such effects have been stud-

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(20) J. S. Ziomek and E. A. Piotrowski, *J. Chem. Phys.*, **34**, 1087 (1961).

(21) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1967–1968).

ied in detail[22,23] and a convenient method for comparison by way of the r_z structure has been presented. So far, there are only a few reports on the critical examination of the consistency of diffraction and spectroscopic experiments.

The interatomic distances r_g were converted into r_α distances using the quadratic force constants reported by Ziomek and Piotrowski.[20] Small corrections were made[6] for the extrapolation from r_α to $r_\alpha{}^0$, which represents the average structure for the ground vibrational state,[22] by the use of the a_3 parameters for diatomic molecules.[18] For the bonded distances the decrease due to vibrational anharmonicity and the apparent increase due to the perpendicular vibrations were estimated, whereas the zero-point bond angles $\theta_\alpha{}^0$ were assumed to be equal to θ_α.[6]

On the other hand, the rotational constants B_0 have been determined[9] from microwave spectroscopy, whereas the C_0 constants are yet unknown for these symmetric-top molecules. The B_0 constants for POF_3, $POCl_3$, and $PSCl_3$, 4594.25, 2015.20, and 1402.64 MHz, gave the values of B_z, 4589, 2013, and 1402 MHz, respectively, by adding the harmonic vibration–rotation constants calculated from normal-coordinate analyses. Since the above $r_\alpha{}^0$ structure from electron diffraction should be essentially equal to the r_z structure, the rotational constant B_z(ED) calculated from $r_\alpha{}^0$ should correspond to the above B_z(MW) obtained from microwave spectroscopy. The agreements between the data from the two independent experiments, summarized in Table XI, are within 0.1–0.2% in all cases.

TABLE XI

COMPARISON OF STRUCTURE AND ROTATIONAL CONSTANTS

	This study	Ref 11
	POF_3	
B_z(ED),[a] MHz	4600	
B_z(MW),[b] MHz	4589	
	$POCl_3$	
r_a(P–Cl), Å	1.992 ± 0.003	2.002 ± 0.002
r_a(P–O), Å	1.447 ± 0.005	1.434 ± 0.005
θ_α(Cl–P–Cl), deg	103.3 ± 0.2	103.8 ± 0.35
B_z(ED), MHz	2018	2004
B_z(MW), MHz	2013	
	$PSCl_3$	
r_a(P–Cl), Å	2.010 ± 0.003	2.020 ± 0.002
r_a(P–S), Å	1.884 ± 0.005	1.908 ± 0.006
θ_α(Cl–P–Cl), deg	101.8 ± 0.2	101.8 ± 0.35
B_z(ED), MHz	1403	1381
B_z(MW), MHZ	1402	

[a] Calculated from electron diffraction structures. [b] Calculated from the microwave B_0 constants given in ref 9.

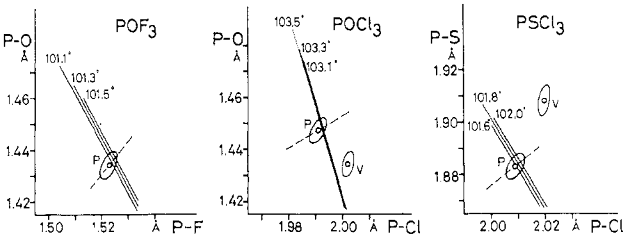

Figure 3.—Diagrams of average structures: *P*, parameters determined in the present study with limits of error indicated by ellipses; *V*, parameters reported by Vilkov, *et al.*[11] Solid lines indicate the conditions set by the rotational constants[9] obtained from microwave spectroscopy for the bond angles given in the diagrams. The parameters determined by electron diffraction vary with the scale factor as indicated by broken lines; see text.

This comparison may be visualized in a more direct way. The geometry of a PXY_3-type molecule is described by three parameters: for instance, r(P–Y), r(P–X), and θ(Y–P–Y). In other words, the structure may be represented by a certain point in a three-dimensional space, the coordinates of which are the three parameters given above. Such a space is shown in Figure 3, where the angle coordinate is taken perpendicular to the paper. The rotational constant B_z(MW) provides one relation among the three parameters or a surface in that space. Three sections of the surface are shown for each molecule in the figure by a set of nearly straight lines in the neighborhood of the most probable angle determined by electron diffraction. Actually, such a surface turns out to be essentially a plane, which is so parallel to the angle coordinate that the section line is hardly displaced by the uncertainty in the angle parameter. This tendency typically appears in the $POCl_3$ case, where the B_z constant is shown to be insensitive to the angle parameter.

The most probable $r_\alpha{}^0$ ($\approx r_z$) parameters determined from the present analysis are shown by *P* with the estimated uncertainty indicated by an ellipse. This uncertainty is larger in the direction of the scale factor variation[24] shown by a broken line. Since the error ellipsoid overlaps with the surface in each case, the consistency between the two independent experimental results within their uncertainties has been confirmed.

Upon closer examination, however, the diffraction points are displaced in the same direction from the B_z lines in all cases. This suggests the presence of an unknown systematic error in the conversion of the structure, although the displacements (about 0.08%) are smaller than the uncertainty due to the scale factor ($3\sigma \approx 0.18\%$).

Provided that this small deviation is ascribed to the systematic error in the scale factor, then the most probable r_z structure should correspond to the point where the B_z line and the scale factor line cross each other.[24] On the other hand, the neglect of the interactions between the bending and stretching vibrations, on which the estimation of $r_\alpha{}^0$ from r_α is based,[6] may cause a small systematic uncertainty in $r_\alpha{}^0$ for those molecules which have relatively low vibrational frequencies.

The present result may be compared with the recent electron diffraction study of $POCl_3$ and $PSCl_3$ by Vilkov, *et al.*[11] Their bond angles agree with ours, whereas their bond lengths (presumably r_a) differ by about

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(22) Y. Morino, K. Kuchitsu, and T. Oka, *J. Chem. Phys.*, **36**, 1108 (1962); K. Kuchitsu and S. Konaka, *ibid.*, **45**, 4342 (1966).

(23) K. Kuchitsu, *ibid.*, **49**, 4456 (1968).

(24) Y. Morino, K. Kuchitsu, Y. Hori, and M. Tanimoto, *Bull. Chem. Soc. Jap.*, **41**, 2349 (1968).

0.01–0.02 Å, exceeding the estimated uncertainties. They made their experiments at higher temperatures (at 140° for POCl$_3$ and at 120° for PSCl$_3$) than ours (20°). Nevertheless, the above discrepancy cannot be explained even if the temperature difference is taken into account, because the "thermal expansion" of the P–Cl bond length by the temperature difference of about 120° is estimated to be[6,25] at most 0.002 Å and even smaller for those of P–O and P–S.

A calculation of B_z from their structure, shown in Table XI, results in the differences of 0.5 and 1.6% for POCl$_3$ and PSCl$_3$, respectively, from the corresponding spectroscopic B_z. This situation is also demonstrated in Figure 3, where the point V represents the parameters obtained by them with their reported uncertainty indicated by an ellipse. Their results thus appear to be inconsistent with the spectroscopic constants.

Bonding and Structure.—Now let us compare the bond lengths and angles determined above with those in related molecules. Such comparisons should ultimately be made for the equilibrium structures r_e, but the r_e structure is not readily accessible from experiment except for diatomic and some triatomic molecules. Instead, r_g and θ_α are equally reasonable and more convenient quantities for this comparison;[28] r_g has a clear physical meaning, and $r_g - r_e$ is estimated to be essentially constant for bonds with the same atom pair and similar bond nature. On the other hand, θ_α retains the symmetry of the molecule and is essentially equal to θ_e.[6,26]

Observed variations in the structures of phosphorus halides (Figure 4), including PF$_3$,[6] PCl$_3$,[25] PSF$_3$,[9] PF$_3$-BH$_3$,[27] PF$_5$,[4] and PCl$_5$,[28] may be summarized as follows. (A) Coordination of an oxygen or sulfur atom to the lone pair of PF$_3$ (PCl$_3$) makes the P–F (P–Cl) bond decrease and the bond angle F–P–F (Cl–P–Cl) increase. This is also the case for BH$_3$ coordination. (B) The above tendency is stronger for oxygen than for sulfur. (C) Similar bond shortening has been observed for the equatorial P–F (P–Cl) bond in PF$_5$ (PCl$_5$) as compared with PF$_3$ (PCl$_3$).[4,28] (D) The P–O and P–S bond lengths in the fluorides are shorter than those in the corresponding chlorides. (E) The Y–P–Y bond angles for the fluorides (Y = F) are smaller than those in the corresponding chlorides (Y = Cl).

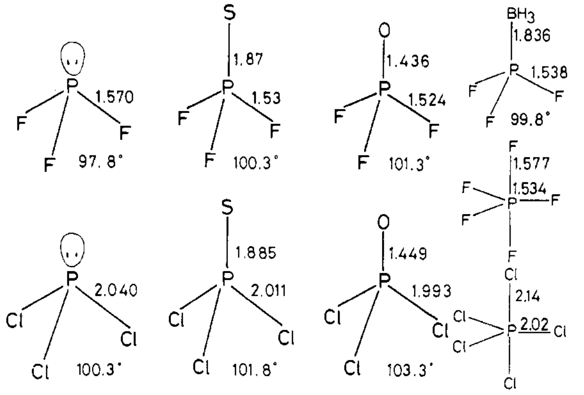

Figure 4.—Structures of phosphorus halides.

The above-mentioned systematic features, which are similar to those observed for (CH$_3$)$_n$PF$_{5-n}$ and discussed by Bartell and Hansen[3,4] and by Gillespie,[1,2] may be accounted for in terms of Gillespie's electron-pair repulsion theory. According to his model, the electrons in the lone pair are drawn away from the phosphorus atom by the coordination or bonding of an electronegative atom so as to alleviate the "repulsion" caused by the lone pair; thus the bond angle should increase and the bond length decrease (trends A–C). Trends D and E may also be understood by a similar argument.

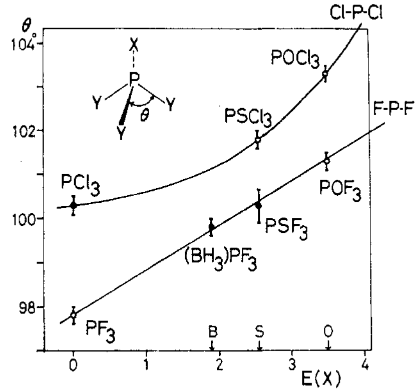

Figure 5.—Variations of the phosphorus bond angles Y–P–Y in PXY$_3$ with the electronegativity E of the atom X. For PY$_3$ the parameter E is arbitrarily set equal to zero. Data with open circles belong to our studies, while those with solid circles are taken from the literature.

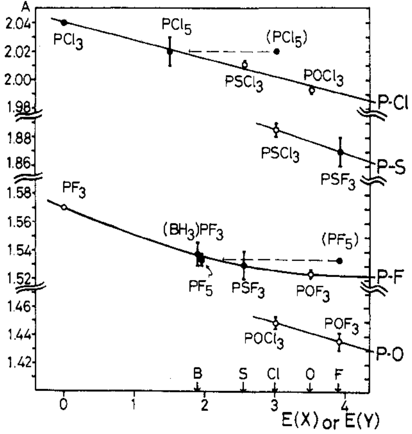

Figure 6.—Variations of the P–Y and P–X bond lengths in PXY$_3$ with the electronegativity E of the atoms X and Y, respectively. For PF$_5$ and PCl$_5$ the equatorial P–F and P–Cl bond lengths are plotted against E(F) and E(Cl), respectively (represented in parentheses), and do not fall on the regular curves, whereas better fits result if $^1/_2E$(F) and $^1/_2E$(Cl) are plotted. See Figure 5 for other comments.

In order to summarize the trends in a semiquantitative way, the Y–P–Y angles and the P–Y (P–X) bond lengths in the PXY$_3$ molecules are plotted against the

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electronegativities[29] E of the X (Y) atoms. For PF_3 and PCl_3, where the atom X is missing, the electronegativities are regarded as zero. Regular curves are obtained for the bond angles (Figure 5) and also for the bond lengths (Figure 6). In addition, the equatorial P–F and P–Cl bond lengths in PF_5 and PCl_5 apparently fit in the curves if they are, rather arbitrarily, plotted against $^1/_2E(F)$ and $^1/_2E(Cl)$, respectively.

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The Molecular Structures of 1,2-, 1,7-, and 1,12-Dicarba-*closo*-dodecaborane(12), $B_{10}C_2H_{12}$[1]

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The molecular structures of 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane(12), $B_{10}C_2H_{12}$, *o*-, *m*-, and *p*-carborane, respectively, have been determined from electron diffraction studies of their vapors. Each structure is a slightly distorted icosahedron. The structure of *p*-carborane with D_{5d} symmetry was characterized most precisely with the following parameter values: B–C = 1.710 ± 0.011 Å, B2–B3 = 1.792 ± 0.007 Å, B2–B7 = 1.772 ± 0.013 Å, B–H = 1.22 ± 0.02 Å, and C–H = 1.15 ± 0.09 Å. Each error limit is the geometric mean of 3 times the least-squares standard deviation and 3 times an estimated 0.1% standard deviation in the scale factor. A "diameter" along the C···C axis is about 10% shorter than a "diameter" along a B···B axis. *o*- and *m*-carborane have much lower symmetry, C_{2v}, and unique structures could not be determined. In *o*-carborane, C–C = 1.65 ± 0.05 Å, B–C (av) = 1.711 ± 0.014 Å, and B–B(av) = 1.793 ± 0.010 Å. In *m*-carborane, B–C(av) = 1.726 ± 0.010 Å and B–B(av) = 1.805 ± 0.008 Å. The B–B bond lengths in the icosahedral carboranes suggest the trend that B–B bonds nearer carbon atoms are longer.

Introduction

Three isomers of the icosahedral carborane[2] $B_{10}C_2H_{12}$ are known.[3–6] The isomers, 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane(12), will be called *o*-, *m*-, and *p*-carborane, respectively. Crystal structures of a variety of derivatives of *o*- and *m*-carborane have been determined. In each the structure of the boron carbon cage is a slightly distorted icosahedron. Since the carboranes are nearly spherical, crystals of the compounds are disordered with a statistical population of borons and carbons at each site. Even in crystals of many of the substituted carboranes there is some disorder. Therefore, not much precise structural information is known. Russian electron diffraction workers have reported results on *o*-[7] and *m*-carborane,[8] *C,C'*-dimethyl-*o*-carborane,[9] and a *C,C'*- and a *B,B'*-diiodo-*m*-carborane.[10] These reports confirm the icosahedral structures of the ortho and meta isomers and report average bond lengths. We undertook electron diffraction studies of the three unsubstituted carboranes to determine the structure of *p*-carborane, to characterize the distortions from icosahedral symmetry, and to deduce structural relationships among the isomers.

Experimental Section and Data Analysis

Samples of the three carborane isomers were purified by preparative vapor phase chromatography and were obtained from Dr. H. A. Schroeder of Olin Corp. The electron diffraction patterns were recorded on the University of Oslo apparatus with a nozzle temperature of 70°. Exposures were taken at two nozzle to plate distances, 48 and 19 cm, which covered the scattering ranges $1.5 \leq s \leq 20$ Å^{-1} and $7 \leq s \leq 45$ Å^{-1}, respectively. The electron wavelength was 0.064606 Å. Four plates from each range were studies for each compound. These were photometered and converted into molecular scattering intensity curves by correcting for nonlinearity of response of the photographic emulsion, for plate flatness, and for the shape of the rotating sector and by subtracting a background intensity.[11] The intensity and background values are given in Tables IA and IB. A theoretical intensity curve was calculated according to

$$sM(s) = \sum_{i}\sum_{\substack{j \\ (i>j)}} A_{ij} \exp(-l_{ij}^2 s^2/2) \sin (sr_{ij})/r_{ij}$$

where $A_{ij} = Z_iZ_j/(1 - F_B/Z_B)^2$. Z_i and F_i are the atomic

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