Preparation, Spectroscopic Properties, and Molecular Structure, Determined by Electron Diffraction, of Bis(difluorophosphino)carbodi-imide, $F_2P{\cdot}N{:}C{:}N{\cdot}PF_2$

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The title compound has been prepared by the reaction of bromodifluorophosphine with silver cyanamide and shown by i.r., Raman, n.m.r., and mass spectroscopy to be a carbodi-imide, and not a cyanamide derivative. The molecular structure of the compound in the gas phase has been determined by electron diffraction. Principal parameters are: r(P–F) 1·562 + 0·002, r(P–N) 1·680 ± 0·006, r(N=C) 1·240 ± 0·005 Å, and P–N–C 132·8 ± 0·5°. The overall symmetry of the molecule is C_2, the dihedral angle being *ca.* 55°, and the PF_2 groups are *trans* with respect to the carbodi-imide group.

RECENT structural work on a number of fluorophosphine derivatives has suggested that difluorophosphino and silyl groups have very similar stereochemical effects when bonded to oxygen or nitrogen.[1-4] As part of an extension of the work, the possibility of preparing bis(difluorophosphino)carbodi-imide has been investigated.

It is well known that alkyl iodides react with silver cyanamide to give dialkyl cyanamides,[5] and that the preparation of the corresponding carbodi-imides is only possible by a more complicated route.[6] In contrast with this, silyl iodide, when streamed over silver cyanamide, gives entirely the carbodi-imide.[7] In this present work, bromodifluorophosphine has similarly been found to give the carbodi-imide derivative when treated with silver cyanamide.

RESULTS AND DISCUSSION

Bis(difluorophosphino)carbodi-imide can be prepared from bromodifluorophosphine and silver cyanamide either by a gas–solid reaction, streaming the phosphine over the silver salt in a long, fairly narrow tube, or by slowly warming frozen bromodifluorophosphine and allowing the liquid to run onto the silver salt. Yields varied from 25—52% (based on bromodifluorophosphine taken) depending on the precise conditions used, the optimum being for a liquid–solid reaction in which the silver cyanamide was diluted with powdered glass. Care had to be taken to ensure that all traces of water were removed from the reaction vessel, as hydrolysis to bis(difluorophosphino) ether occurred very readily. Similar easy hydrolysis has been noted for digermylcarbodi-imide, and has provided a convenient synthetic route to a number of germyl derivatives.[8]

Spectroscopic methods have been used to characterise the new compound, and to demonstrate that it is a carbodi-imide rather than a cyanamide. The ^{19}F n.m.r. spectrum of bis(difluorophosphino)carbodi-imide (10% solution in trichlorofluoromethane) consists of a doublet [δ +52·8 ± 0·2 p.p.m., ^1J(PF) 1314 ± 8 Hz], with no signs of extra weak lines or further splitting. In compounds with two difluorophosphino-groups on one nitrogen atom, long-range couplings normally lead to complex n.m.r. spectra.[9,10] The spectrum obtained in the present case therefore indicates that more than one atom separates the two phosphorus atoms.

The mass spectra of bis(difluorophosphino)carbodi-imide (Table 1), while confirming the formula of the compound, do not indicate directly whether a carbodi-imide or a cyanamide is present. The presence of $(PF_2)_2N^+$ might be taken as evidence in favour of the cyanamide structure, but the intensity of the peak at *m/e* 152 is small, and skeletal rearrangements of carbodi-imides are not unknown.[8]

Three metastable peaks, at *m/e* 129·8w, 45·5s, and 31·7w, indicate that the following processes are important:

$$PF_2NCNPF^+ \longrightarrow PNCN^+ + PF_3$$

$$PF_2NCNPF_2^+ \longrightarrow PFNCN^+ + PF_3$$

$$PF_2NCNPF_2^+ \longrightarrow PF_2NPF_2^+ + CN$$

Initial breakdown of the parent ion can therefore proceed by at least three distinct routes, involving loss of F, PF_3, or CN. A full study of the processes involved in the formation of positive and negative ions in a number of difluorophosphino-pseudohalides has been undertaken.[11]

Final confirmation of the carbodi-imide structure comes from the vibrational spectra. Observed bands in the i.r. spectrum of the gas phase and in the Raman spectrum of the liquid phase are listed in Table 2. The overall symmetry of the molecule, as determined in the electron diffraction study, is C_2, but with other conformations of the PF_2 groups, the symmetry could be C_{2h},

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C_{2v}, C_s, or C_1. However, the vibrational spectra cannot be used to distinguish between these possibilities for, just as the selection rules for digermylcarbodi-imide are those of point group D_{3d},[8] whereas its symmetry is C_2,[12] so in the present case the selection rules that appear to hold are those of the highest possible point-group, C_{2h}. This state of affairs must arise because the dipole changes for the symmetric modes, and the changes in polarisability in the asymmetric modes, are small, and so the appropriate bands in the i.r. and Raman spectra are of very low intensity. What is certain, in this present case, is that no cyanamide is present, as the characteristic C–N stretching mode at *ca.* 1200 cm^{-1} is absent.[13]

TABLE 1

Mass spectra of bis(difluorophosphino)carbodi-imide

m/e	Ion intensities * +ve, 70 eV	+ve, 22 eV	−ve, 70 eV	Assignment
179	1	1		$F_2PN^{13}CNPF_2^+$
178	47	100		$F_2PNCNPF_2^+$
160	0·1			$F_2PN^{13}CNPF^+$
159	6	6		$F_2PNCNPF^+$
152	0·2			$F_2PNPF_2^+$
140	0·1			$FPNCNPF^+$
109	0·2			F_2PNCN^+
			100	F_2PNCN^-
91	0·5			$FPN^{13}CN^+$
90	24	21		$FPNCN^+$
88	3	3		F_3P^+
83	0·4			F_2PN^+
			<0·1	F_2PN^-
72	0·1			$PN^{13}CN^+$
71	8	3		$PNCN^+$
69	100	37		F_2P^+
			<0·1	F_2P^-
64			0·5	FPN^-
62	1	2		P_2^+
59	0·3			PN_2^+, $NCNF^+$
57	0·4			PNC^+
50	10			FP^+
45	1			PN^+, CNF^+
43	0·4			PC^+
40	0·2			NCN^+
38			3	F_2^-
31	2			P^+
			0·1	P^-
26	0·8			CN^+
			2	CN^-
19	1			F^+
			6	F^-
12			<0·1	C^-

* Intensities <1 are not included in the 22 eV spectrum. Metastable peaks were observed at 129·8, 45·5, and 31·7 mass units.

Assuming the point group to be C_2, as found in the electron diffraction study, there should be two PF stretching modes, a PN stretch, three PF_2N deformations, an NCN stretch and a deformation, a PNC deformation, and a torsion about PN bonds, all of type *B*, and an exactly similar set of modes, plus a torsion about the NCN axis, of type *A*. Of these, any *A* type mode involving the PF_2 groups will probably have a frequency very similar to that of the corresponding *B* mode. However, the symmetric and asymmetric modes of vibration of the PNCNP skeleton have different frequencies, and so the effects of the C_{2h} selection rules become apparent. Thus the asymmetric NCN stretching mode is seen only in the i.r. spectrum, at 2199 cm^{-1}, while the symmetric mode (1498 cm^{-1}) is strong in the Raman spectrum, and very weak in the i.r., if present at all. The other skeletal modes which can be seen in the region studied lie between 800 and 500 cm^{-1}, and the assignments given in Table 2 were made by comparing frequencies with those for similar modes in other fluorophosphine pseudohalides [2] or carbodi-imides.[8,14]

The determination of the molecular structure of bis(difluorophosphino)carbodi-imide by electron diffraction was made unusually simple by the fact that the molecules, although possessing only nine atoms, are over 7 Å-long, and so very few of the peaks in the radial distribution curve (Figure 1) overlap. It was necessary to assume that the molecule has either a two-fold axis or a mirror plane, as small differences between two F_2PNC groups cannot be detected by electron diffraction. Consequently, the molecular model used in the refinements allowed C_2 or C_s symmetry, with C_{2v} or C_{2h} in certain special cases. The geometry is defined by three

TABLE 2

Vibrational spectra of bis(difluorophosphino)carbodi-imide

I.r. (gas)	Raman (liquid)	Assignment
ca. 3660sh		2199 + 1495
3628mw		2 × 1495 + 644
2858mw		2199 + 2 × 341, 2199 + 644
2620w		2199 + 430
2448mw		2199 + ? *ca.* 250
2199vvs		ν_{asym}(NCN)
	2072m	1495 + 556
1949vw		1495 + 465
1715w		858 + 845
1685w		858 + 816, 845 + 830
1498vw	1495m	ν_{sym}(NCN), 2 × 748
1450w		830 + 644
	1283w	816 + 476
	1161ms	816 + 341
923w		2 × 465
858vs	*ca.* 845sh	ν(PF)
ca. 830sh	816vs	ν(PF)
748vs		ν(PN)
ca. 680m,sh	668m,sh	2 × 341, 341 + 328
	644ms	ν(PN)
599sh		328 + 285
570s		δ(NCN)
	556ms	δ(NCN)
	485ms	$\delta(PF_2)$
465ms	471ms	
430sh	418s	
	402m,sh	
341ms		
328sh		
	285m	

s = Strong, m = medium, w = weak, v = very, sh = shoulder.

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different bonded distances, angles F–P–F, F–P–N, and P–N–C, and by dihedral angles for the P–N and N–C–N bonds; linearity of the latter group was assumed. The P–N dihedral angle was taken to be zero when the PF_2 bisectors were *trans* with respect to the NCN group, and the N–C–N dihedral angles was taken to be zero when the two phosphorus atoms were mutually *cis*.

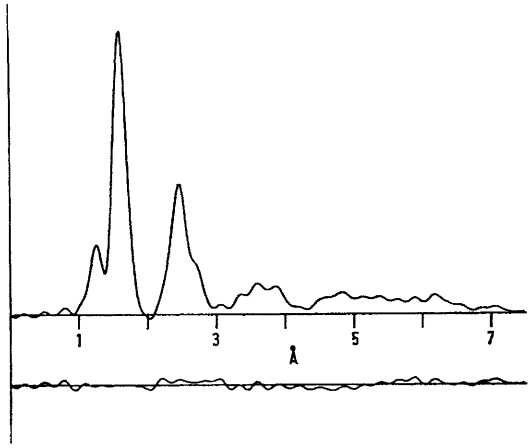

FIGURE 1 Radial distribution curve, P(*r*)/*r*, for bis(difluorophosphino)carbodi-imide. Before Fourier inversion the data were multiplied by $s\,.\,\exp(-0{\cdot}0015\,s^2)/(z_P - f_P)(z_F - f_F)$.

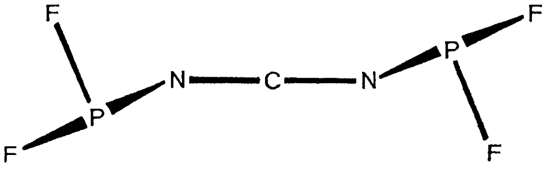

FIGURE 2 Bis(difluorophosphino)carbodi-imide, viewed along the C_2 axis

TABLE 3

Molecular parameters for bis(difluorophosphino)carbodi-imide

	Distance (Å)	Amplitude (Å)
(*a*) Independent distances		
r_1(P–F)	1·562 ± 0·002	0·056 ± 0·003
r_2(P–N)	1·680 ± 0·006	0·060 (tied to u_1)
r_3(N–C)	1·240 ± 0·005	0·050 ± 0·006
(*b*) Dependent distances		
d_4(F · · · F)	2·451 ± 0·011	0·065 ± 0·010
d_5(F · · · N)	2·378 ± 0·013	0·092 (tied to u_4)
d_6(F · · · C)	3·374 ± 0·011	0·191 ± 0·027
d_7(F · · · C)	3·530 ± 0·012	0·191 (tied to u_6)
d_8(F · · · N)	4·493 ± 0·014	0·197 ± 0·031
d_9(F · · · N)	4·727 ± 0·018	0·197 (tied to u_8)
d_{10}(F · · · P)	5·329 ± 0·019	0·244 ± 0·020
d_{11}(F · · · P)	6·076 ± 0·023	0·244 (tied to u_{10})
d_{12}(F · · · F)	6·099 ± 0·019	0·282 (fixed)
d_{13}(F · · · F)	6·461 ± 0·027	0·282 (fixed)
d_{14}(F · · · F)	7·060 ± 0·024	0·282 (fixed)
d_{15}(P · · · C)	2·682 ± 0·009	0·075 ± 0·008
d_{16}(P · · · N)	3·826 ± 0·014	0·154 ± 0·021
d_{17}(P · · · P)	4·898 ± 0·015	0·249 (fixed)
d_{18}(N · · · N)	2·481 ± 0·011	0·043 (fixed)
(*c*) Angles		
∠1 (F–P–F)	103·4 ± 0·8	
∠2 (F–P–N)	94·4 ± 0·7	
∠3 (P–N–C)	132·8 ± 0·5	
P–N Dihedral	14 (fixed)	
N–C–N Dihedral	55 (fixed)	

TABLE 4

Least-squares correlation matrix ×1000

r_1	r_2	r_3	<1	<2	<3	u_1	u_3	u_4	u_6	u_8	u_{10}	u_{15}	u_{16}	k_1	k_2	k_3	
1000	−144	57	−37	−70	146	211	−40	−68	−6	23	7	−20	−13	−59	−6	24	r_1
	1000	152	105	−140	−437	−633	369	207	73	−56	35	100	61	201	126	80	r_2
		1000	69	−19	−510	−105	70	−135	−31	−82	−52	−63	13	62	−37	−61	r_3
			1000	−950	−266	−68	43	−833	52	−436	248	−376	33	2	45	64	<1
				1000	79	41	−50	780	−40	410	−265	331	−24	−53	−111	−112	<2
					1000	418	−185	125	−31	112	−9	24	−18	87	127	77	<3
						1000	−337	−19	28	55	7	−42	24	440	155	34	u_1
							1000	56	17	−27	8	20	15	22	−30	12	u_3
								1000	14	377	−187	477	13	236	87	7	u_4
									1000	−198	32	−81	688	123	143	139	u_6
										1000	−136	188	−309	20	−7	−3	u_8
											1000	−75	31	37	63	49	u_{10}
												1000	−47	40	16	26	u_{15}
													1000	109	130	98	u_{16}
														1000	286	109	k_1
															1000	88	k_2
																1000	k_3

Determination of the principle geometrical parameters, and of vibrational amplitudes for most atom pairs, was straightforward. The biggest problem involved finding the conformation which best fitted the experimental data, as this depends only on the very long P · · · P, P · · · F, and F · · · F distances. The solution was found by fixing the dihedral angles at various values (between 0—20° for the P–N, and 0—360° for the N–C–N dihedral) and comparing *R* factors in the various refinements. In this way it was found that the PF_2 groups appeared each to be twisted 14° away from the *trans* position, and that the PNCNP dihedral angle was 55°. However, variations in *R* as the latter angle was changed were small, and there is an estimated standard deviation of *ca.* 15° in the value quoted. Variations in other geometrical parameters as the dihedral angles were varied near to the optimum values were small, but some amplitudes of vibration were affected. Allowances for all constraints in the final refinements have been included in the quoted estimated standard deviations. Final geometrical parameters and amplitudes of vibration are listed in Table 3, and the structure is also shown in Figure 2.

The extreme similarity of the bond lengths of the F_2PNC groups in this compound and in difluoroisocyanatophosphine and difluoroisothiocyanatophosphine[2] is quite remarkable, although the F–P–F and F–P–N angles in the present case are significantly different from those in the other compounds. This latter difference may be caused by the large correlation between the two angles (see Table 4), caused by the proximity of the F · · · F and F · · · N peaks in the radial distribution curve. When the F–P–F angle was fixed at 100°, the F–P–N angle refined to 96·8°, but R was 0·112, compared with 0·095 for the best refinement.

Also similar are the vibrational amplitudes which have been determined, and the valence angles at nitrogen. The angles in the isocyanate and isothiocyanate, found by electron diffraction, are 130·6 and 140·5° respectively, and after application of shrinkage corrections, these are *ca.* 135 and 144°. Thus it is likely that the mean P–N–C angle, θ_α, in the carbodi-imide is *ca.* 137°. This compares with an (uncorrected) angle of 138° in digermylcarbodi-imide,[12] the only other carbodi-imide whose gas-phase structure has been determined.

The P–N–C–N–P dihedral angle of 55° (75° in digermylcarbodi-imide) is rather smaller than would be expected for an allene-type structure. The sizes of the shrinkages caused by the torsion about the N–C bonds are unknown, and it may be that if the torsion has a very low frequency, then the mean structure has a dihedral angle, θ_α, close to 90°. The other dihedral angle, at 14°, is exactly the same as those found in the two other difluorophosphinopseudohalides studied. In this case the deviation from the more symmetrical structure (with the P–N dihedral angle 0°) is almost certainly due to the torsional oscillations about the P–N bonds, the frequencies for similar modes in the isocyanate and isothiocyanate[2] probably being about 45—50 cm^{-1}. Thus in these three pseudohalides, the dihedral angles between the nitrogen and phosphorus lone-pairs are 180°, whereas in some aminodifluorophosphines[1,4] the corresponding angles are *ca.* 90°. It may be, therefore, that in the pseudohalides, the conformations of the PF_2 groups are controlled by interactions between the phosphorus lone-pairs and the pseudohalide π-systems, which lie in planes perpendicular to the axes of the nitrogen lone pairs, whereas in the amines, the predominant interactions are between phosphorus and nitrogen lone-pairs.

EXPERIMENTAL

All volatile compounds were handled by use of a Pyrex glass vacuum line, with Apiezon N grease on stop-cocks and ground-glass joints. Bromodifluorophosphine was prepared by the reaction of hydrogen bromide and difluoro(dimethylamino)phosphine.[15] The latter compound was obtained by fluorination (with antimony trifluoride) of the products of the reaction of dimethylamine and phosphorus trichloride.[16]

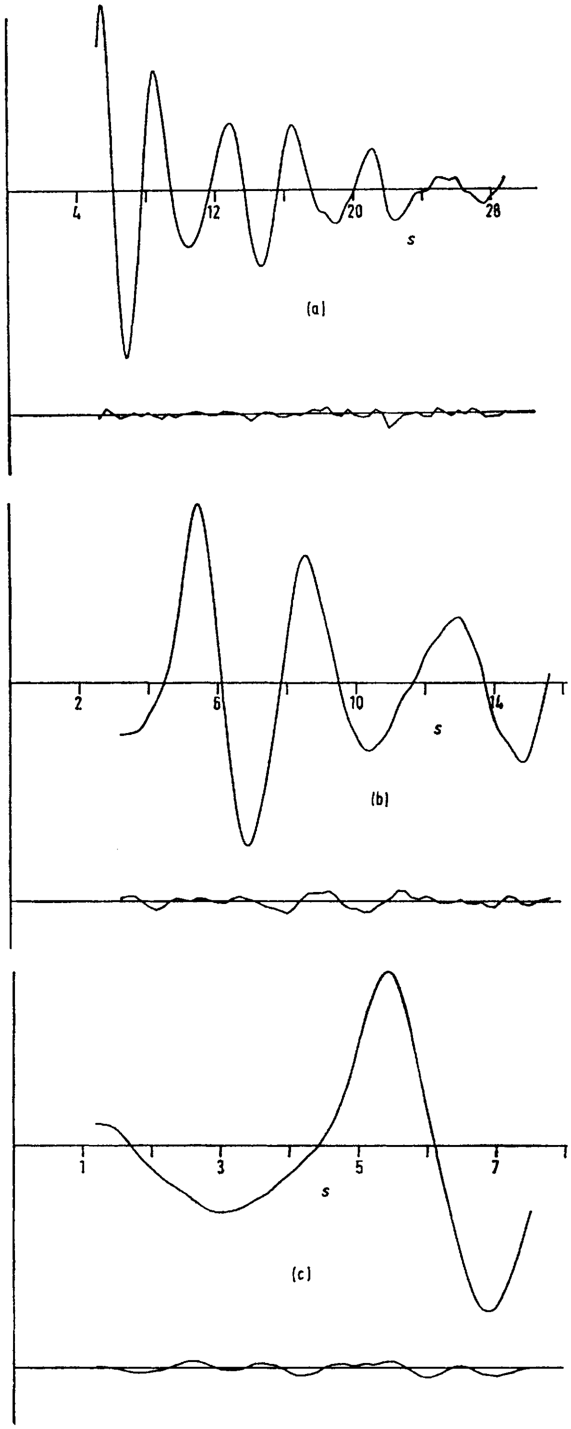

FIGURE 3 Observed and weighted difference molecular insities at nozzle-to-plate distances of (a) 250, (b) 500, and (c) 1000 mm

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Preparation of bis(difluorophosphino)carbodi-imide.—In the most successful preparation of the compound bromodifluorophosphine (5 mmol) was condensed onto silver cyanamide (2 g, 8 mmol) mixed with *ca.* three times its bulk of powdered glass, and was allowed to warm to room temperature. The volatile products were condensed into an adjacent trap. Fractional condensation yielded bis(difluorophosphino)carbodi-imide (1·3 mmol, 52% based on PF_2Br taken), retained at 177 K.

Spectra.—I.r. spectra were recorded on a Perkin-Elmer 225 grating spectrometer in the range 4000—200 cm^{-1} using cells equipped with caesium iodide windows. Raman spectra were recorded in the range 2500—200 cm^{-1} on a Coderg PH 1 laser instrument. ^{19}F n.m.r. spectra were obtained on a Varian Associates HA 100 instrument operating at 94·1 MHz. Positive-ion mass spectra were recorded on an AEI MS 9 spectrometer with ionising potentials of 22 and 70 eV, and negative-ion spectra were recorded using a Bendix model 3015 time-of-flight spectrometer operating at 70 eV.

Electron Diffraction.—Electron diffraction data were recorded by use of a Balzer's KD G2 gas diffraction apparatus.[17] Three plates (Ilford N 60) were used, the nozzle-to-plate distances being 250, 500, and 1000 mm, giving a range of 1·2—28·8 $Å^{-1}$ in the scattering variable, *s*. The sample of compound was maintained at 273 K during the exposures, and the nozzle at 333 K, and the gas temperature may be taken to be near the mean of these. The electron wavelength used, determined from the diffraction pattern of powdered thallium(I) chloride and by direct measurement of the accelerating voltage, was 0·05659 ± 0·00003 Å. The data were reduced to digital form by use of a Joyce–Loebl automatic microdensitometer, and subsequent data reduction and least-squares refinements used programs described earlier.[1,18] The complex scattering factors of Cox and Bonham [19] were used throughout. All calculations were carried out on the Edinburgh Regional Computing Centre's IBM 360/50 computer.

Weighting functions (defined as in ref. 18) used to set up the off-diagonal weight matrix, scale-factors, and correlation parameters [20] are listed in Table 5, and observed and final weighted difference molecular scattering intensities are shown in Figure 3. Uphill curves may be obtained from the author on request.

TABLE 5

Weighting functions, correlation parameters, and scale-factors

Camera height/mm	Δs	$s_{min.}$	s_1	s_2	$s_{max.}$	p/h	Scale-factor
250	0·40	5·20	8·00	26·00	28·80	0·2151	1·354 ± 0·019
500	0·20	3·20	5·20	13·40	15·60	0·4850	0·983 ± 0·020
1000	0·10	1·20	2·50	6·50	7·50	0·4979	0·954 ± 0·035

I thank Professor D. W. J. Cruickshank, Dr. B. Beagley, Dr. M. J. Mays, Dr. G. M. Sheldrick, and Dr. M. J. Smyth for the provision of experimental facilities, Mr. P. W. Harland for running negative-ion mass spectra, and Imperial Chemical Industries Ltd. for a research fellowship.

[1/1810 *Received*, *4th October*, 1971]

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