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Preparation and the Crystal and Molecular Structure of 1,2,3,4-Tetramethyl-2,2,4,4-tetrakis(trifluoromethyl)-1,3-diaza-2,4-diphosphetidine, $[CH_3(CF_3)_2PNCH_3]_2$

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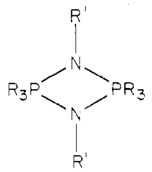
The reaction of excess CH_3NH_2 with $CH_3(CF_3)_3PX$ (X = F or Cl) produced the crystalline dimeric compound $[CH_3(CF_3)_2PNCH_3]_2$ rather than the monomeric monoalkylaminophosphorane $CH_3(CF_3)_3PN(H)CH_3$. Crystals of the diazaphosphetidine are monoclinic, of space group $P2_1/n$ with $a = 7.0932$ (5) Å, $b = 9.2318$ (8) Å, $c = 11.6562$ (14) Å, $\beta = 93.49$ (1)°, and $Z = 2$. The structure, solved by a Patterson function, refined to $R = 0.045$ for 1070 reflections. The molecule is centrosymmetric. The geometry of the atoms bonded to each phosphorus is best described as a trigonal-bipyramid phosphorane unit showing longer axial than equatorial bond lengths: $P-N_{ax} = 1.806$ (2) Å, $P-N_{eq} = 1.633$ (2) Å, $P-CF_{3(ax)} = 1.963$ (3) Å, and $P-CF_{3(eq)} = 1.916$ (3) Å. The presence of a second isomer in solution having gauche orientation of the respective CF_3 and CH_3 equatorial groups was indicated by ^{19}F NMR.

Introduction

Detailed description of the stereochemistry of five-coordinate phosphorus compounds and the relationship to dynamic behavior of this species continues to excite interest as illustrated by a recent review.[1] Structural studies on the diazadiphosphetidine series[2-8] which are characterized by two essentially trigonal-bipyramidal phosphorus atoms incorporated in a four-membered ring show that the nitrogen atoms occupy one axial and one equatorial substituent position at each phosphorus. The most electronegative R substituent occupies the other axial position. Temperature-dependent NMR studies[9] of those compounds where the two equatorial R groups are different have demonstrated the existence of both trans and gauche isomers in solution whereas only the trans isomer is found in the solid state. While attempting to synthesize the aminophosphorane $CH_3(CF_3)_3PN(H)CH_3$ from $CH_3(CF_3)_3PX$ (X = F or Cl) and CH_3NH_2, we isolated a crystalline solid formulated as $[CH_3(CF_3)_2PNCH_3]_2$, the first diazadiphosphetidine having three alkyl groups attached to phosphorus. This compound also provides the first example of crystallographic characterization of CF_3 substituents in axial and equatorial positions of a trigonal-bipyramidal phosphorus center. We report here the synthetic, spectroscopic, and structural characteristics of this compound.



Experimental Section

All reactions were done in evacuated containers and standard vacuum techniques were used throughout for the manipulation of volatile compounds.

Proton and ^{19}F NMR spectra were recorded on solutions of the compound (approximately 10%) in CCl_3F at 100.1 and 94.2 MHz with a Varian HA 100 instrument or at 60 and 56.4 MHz with a Varian A56/60 instrument in continuous-wave mode. Phosphorus-31 NMR spectra were recorded at 36.4 MHz with a Bruker HFX 90 spectrometer or at 80.9 MHz with a Bruker WH 200 spectrometer in the pulsed Fourier-transform mode. Samples were prepared in 5-mm o.d. tubes in CCl_3F solvent including CD_2Cl_2 for heteronuclear reference lock signal.

Fluorine chemical shifts were measured relative to internal CCl_3F solvent; proton shifts are relative to external (capillary) $(CH_3)_4Si$ (as a 5% solution in CCl_3F). Phosphorus-31 shifts were measured with respect to the heteronuclear ^2D lock signal and converted to the P_4O_6[10] scale by means of the appropriate conversion factor.

Preparation of $[CH_3(CF_3)_2PNCH_3]_2$. (a) Excess CH_3NH_2 (0.327 g, 10.5 mmol) was allowed to react with $CH_3(CF_3)_3PCl$[11] (0.946 g, 3.28 mmol) in a gas-phase reactor[12] for 5 h. Vacuum condensation of the volatile components gave CF_3H (0.469 g, 6.70 mmol) trapped at −196 °C, CH_3NH_2 (0.081 g, 2.6 mmol) trapped at −116 °C, and the diazaphosphetidine (0.196 g, 0.575 mmol; 35%; mp 115–116 °C). The diazaphosphetidine, which sublimes slowly under a dynamic vacuum, was trapped at 0 °C.

Anal. Calcd for $C_8H_{12}F_{12}N_2P_2$: C, 22.51; H, 2.78; N, 6.45. Found: C, 22.55; H, 2.84; N, 6.57.

The involatile white residue left in the reactor proved to be a mixture of $CH_3NH_3^+Cl^-$ and two unidentified phosphorus salt species neither of which had a CF_3 group attached to phosphorus. ($\delta(^{31}P) = +65.9$ and $+80.6$ vs. P_4O_6.[10])

(b) Treating $CH_3(CF_3)_3PCl$ (0.474 g, 1.64 mmol) with a twofold molar ratio of CH_3NH_2 (0.106 g, 3.42 mmol) in a sealed tube for 15 h gave a mixture (0.036 g) of CF_3H (10%) and CH_3NH_2 (90%) trapped at −196 °C and $CH_3(CF_3)_3PN(H)CH_3$ (0.238 g, 0.840 mmol, 51% yield) trapped at −78 °C. An involatile white residue remained in the reaction tube, and NMR spectroscopy indicated the presence of phosphorus-containing CF_3 groups. The residues were not unambiguously identified.

(c) Treatment of $(CF_3)_3CH_3PF$[11] with CH_3NH_2 in a 1:2.5 ratio also in the gas-phase reactor[12] gave the diazadiphosphetidine in low yield, a small amount of $(CF_3)_2F(CH_3)PN(H)CH_3$, which was trapped at −78 °C, and CF_3H.

(d) A mixture of $CH_3(CF_3)_3PN(H)CH_3$ (0.187 g, 0.66 mmol), synthesized[13] from $(CF_3)_3CH_3PF$ and $(CH_3)_3SiN(H)CH_3$, and CH_3NH_2 (0.012 g, 0.32 mmol) reacted within 1 h in a sealed tube to form a solid. Vacuum condensation of the volatile products gave CF_3H (0.086 g, 1.23 mmol), trapped at −196 °C, and $[CH_3(CF_3)_2PNCH_3]_2$ (0.042 g, 0.10 mmol, 30%), trapped at 0 °C. A white involatile residue (0.036 g) remained in the reaction tube.

Collection of X-ray Diffraction Data. A small amount of $[CH_3(CF_3)_2P(NCH_3)]_2$ was loaded into a 12-mm o.d. U-tube and sealed

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(1) Sheldrick, W. S. *Top. Curr. Chem.* **1978**, *73*, 1.
(2) Harris, R. K.; Wazeer, M. I. M.; Schlak, O.; Schmutzler, R.; Sheldrick, W. S., *J. Chem. Soc., Dalton Trans.* **1977**, 517.
(3) Sheldrick, W. S.; Hewson, M. J. C. *Acta Crystallogr., Sect. B* **1975**, *31*, 1209.
(4) Fild, M.; Sheldrick, W. S.; Stankiewicz, T. *Z. Anorg. Allg. Chem.* **1975**, *415*, 43.
(5) Cox, J. W.; Corey, E. R. *Chem. Commun.* **1967**, 123.
(6) Hoard, L. G.; Jacobson, R. A. *J. Chem. Soc.* **1966**, 1203.
(7) Hess, H.; Forst, D. *Z. Anorg. Allg. Chem.* **1966**, *342*, 240.
(8) Almeningen, A.; Andersen, B.; Astrup, E. E. *Acta Chem. Scand.* **1969**, *23*, 2179.
(9) Harris, R. K.; Wazeer, M. I. M.; Schlak, O.; Schmutzler, R. *J. Chem. Soc., Dalton Trans.* **1976**, 17 and references cited therein.
(10) Chapman, A. C.; Homer, J.; Mowthorpe, D. J.; Jones, K. T. *Chem. Commun.* **1965**, 121. The chemical shift of 85% H_3PO_4 is +112 (to high field) ppm vs. P_4O_6.
(11) The, K. I.; Cavell, R. G. *Inorg. Chem.* **1977**, *16*, 2887.
(12) Cavell, R. G. *J. Chem. Soc.* **1964**, 1992.
(13) Cavell, R. G.; Vande Griend, L.; Pirakitigoon, S., unpublished results.

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Table I. Crystal and Intensity Collection Data for $[CH_3(CF_3)_2PNCH_3]_2$

space group	$P2_1/n$ (C_{2h}^5)
extinctions	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$
a	7.0932 (5) Å
b	9.2318 (8) Å
c	11.6562 (14) Å
β	93.49 (1)°
V	761.9 Å^3
Z	2
d(calcd)	1.857 g/cm^3
cryst dimens	0.34 × 0.40 × 0.72 mm
cryst shape	monoclinic prism with faces of the form {001}, {101}, {011}, and {110}
cryst vol	0.0598 mm^3
μ	39.37 cm^{-1} (Cu Kα)
transmission factors applied to F_o	0.492–0.643
radiation	Cu Kα (λ = 1.540 45 Å filtered by 0.5 mil thick Ni foil)
takeoff angle	4.0°
scan speed	2° min^{-1}
scan range	1.0° below Kα_1 to 1.0° above Kα_2
bkgd counts for 2θ ranges	10 s for $3 \leqslant 2\theta \leqslant 88°$; 20 s for $88 \leqslant 2\theta \leqslant 123°$
receiving aperture	5.5 × 3.8 mm; 30 cm from crystal
std reflctns	200, 006, $0\bar{2}0$
final no. of variables	121
no. unique reflctns $F_o^2 \geqslant 3\sigma(F_o^2)$	1070
error in observn of unit wt	2.56 electrons

under vacuum. Under the static vacuum the compound slowly sublimed at room temperature and rectangular-shaped crystals formed in a part of the tube cooled to 0–5 °C in about 3 h. The tube was opened in a drybox, and a crystal was mounted approximately along the b axis in a 0.5-mm Lindemann glass capillary and then sealed under a N_2 atmosphere.

Preliminary film data showed the systematic absences of $k = 2n + 1$ on $0k0$ and $h + l = 2n + 1$ on $h0l$ consistent with the space group $P2_1/n$ ($\beta = 93.49°$) which is the nonstandard setting of $P2_1/c$ ($\beta = 61.25°$). For convenience all data collection as well as the solution and refinement of the structure were done in the $P2_1/n$ setting. Pertinent crystal and intensity collection data are summarized in Table I. Unit cell parameters were determined by a least-squares analysis of the 2θ values of 12 accurately centered high-angle reflections measured on a Picker FACS-1 diffractometer by using Cu Kα radiation. Intensity data were collected on the same diffractometer by using Ni-filtered Cu Kα radiation by the $\theta/2\theta$ scan technique. Stationary-background counts were measured before and after the scan limits. The intensities of three standard reflections were measured after every 100 reflections and showed no signs of systematic decay. The data were corrected for Lorentz and polarization effects and reduced to structure factor amplitudes with standard deviations computed by using a p factor of 0.05.[14] Absorption corrections based on Gaussian integration methods[15] were applied to F_o. A total of 1070 of the 1300 unique measured reflections were judged to be above background when the criterion $F_o^2 > 3\sigma(F_o^2)$ was applied.

Solution and Refinement of the Structure. The position of the unique phosphorus atom was located from a sharpened Patterson map. A Fourier map calculated with the phasing from the phosphorus position revealed the remaining 11 nonhydrogen positions. Several cycles of least-squares refinement on the atom positions using first isotropic temperature factors and finally anisotropic temperature factors for these atoms resulted in R of 0.058. A difference map yielded reasonable positions for the hydrogen atoms. Continued refinement which included the hydrogens of each methyl group as a hindered rotor[16] converged at $R = 0.045$ and $R_w = 0.071$. In the hindered rotor refinement only the position of the center of gravity of the rotor and the angles describing the orientation of the rotor were varied which allows the hydrogen atoms to seek the best plane fitting their positions. The radius of the rotor was fixed at 0.90 Å, which, in an idealized tetrahedral geometry around carbon, corresponds to a C–H distance of 0.95 Å. The barrier to rotation was held at 2.0, and isotropic temperature factors of 6.0 Å^2 were assigned for the hydrogen atoms. This resulted in reasonable distances for the hydrogens bonded to C4, but the geometry of the hydrogens bonded to C3 (Table V), while still acceptable, showed that an extension of the vector P–C3 was not perpendicular to the plane containing the hydrogen atoms. No improvement in the solution resulted when the radius of the hindered rotor was allowed to vary. The largest residual electron density peak in a final difference Fourier map corresponded to a density of 0.4 e/Å^3, about 7% of the height for a typical carbon atom, and was located near the phosphorus atom.

Table II. Final Positional Parameters[a]

atom	x	y	z
P	0.07537 (9)	0.12536 (7)	0.03453 (5)
F11	0.1144 (3)	0.3573 (2)	−0.1096 (2)
F12	0.2758 (3)	0.3832 (2)	0.0511 (2)
F13	0.3809 (3)	0.2489 (3)	−0.0815 (2)
F21	0.4432 (3)	0.1374 (3)	0.1224 (3)
F22	0.2398 (4)	0.1470 (3)	0.2478 (2)
F23	0.2983 (3)	−0.0521 (3)	0.1683 (2)
N	0.0558 (3)	0.0283 (2)	−0.0828 (2)
C1	0.2216 (4)	0.2829 (4)	−0.0300 (3)
C2	0.2764 (5)	0.0881 (4)	0.1480 (3)
C3	−0.0910 (5)	0.2572 (4)	0.0834 (3)
C4	0.1236 (5)	0.0501 (4)	−0.1982 (3)
H31	−0.172 (7)	0.214 (4)	0.107 (6)
H32	−0.024 (6)	0.339 (5)	0.108 (4)
H33	−0.155 (8)	0.310 (6)	−0.002 (4)
H41	0.244 (4)	0.043 (5)	−0.191 (2)
H42	0.062 (6)	−0.029 (4)	−0.246 (4)
H43	0.070 (6)	0.138 (4)	−0.228 (4)

[a] Here and elsewhere the estimated standard deviations are in parentheses.

In the full-matrix least-squares refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(|F_o|)$. R and R_w are defined as $\sum||F_o| - |F_c||/|F_o|$ and $(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. The atomic scattering factors used for P, F, N, and C are from ref 17, those for H are from ref 18, and the anomalous dispersion terms applied to P and F are from ref 19. The major computer programs used were SFLS5 for structure factor and least-squares refinement by C. J. Prewitt, FORDAP for Fourier summation by A. Zalkin, AGNOST the absorption and extinction correction program kindly supplied by Professor J. A. Ibers, ORFFE for calculating bond lengths, angles, and standard deviations by W. Busing and H. A. Levy, and ORTEP for the plotting routine by C. K. Johnson.

The final atomic positional and thermal parameters are given in Tables II and III, respectively. The observed and calculated structure factors ($10|F_o|$ and $10|F_c|$) in electrons have been tabulated.[20]

Results and Discussion

A. Synthetic Considerations. Symmetrical diazadiphosphetidines have been made previously by means of the reaction of dihalogenophosphoranes (X = F, Cl) with either substituted disilizanes[21] $[(CH_3)_3Si]_2NR'$ (R′ = CH_3, C_2H_5, and C_6H_5), according to eq 1, or methylamine,[22] according to eq 2. All

$$2R_3PX_2 + 2[(CH_3)_3Si]_2NR' \rightarrow [R_3PNR']_2 + 2(CH_3)_3SiX \quad (1)$$

$$2R_3PX_2 + 4CH_3NH_2 \rightarrow [R_3PNCH_3]_2 + 2CH_3NH_3^+X^- \quad (2)$$

previously known examples of diazaphophetidines have at least one F or Cl attached to phosphorus. Unsymmetrical diaza-

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(14) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

(15) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.

(16) Bennett, M. J.; Hutcheon, W. L.; Foxman, B. M. *Acta Crystallogr., Sect. A* **1975**, *31*, 488.

(17) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.

(18) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *Chem. Phys.* **1965**, *42*, 3175.

(19) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(20) Supplementary material.

(21) Schmutzler, R. *J. Chem. Soc., Dalton Trans.* **1973**, 2687.

(22) Harris, J. J.; Rudner, B. *J. Org. Chem.* **1968**, *33*, 1392. Haasemann, P.; Goubeau, J. *Z. Anorg. Allg. Chem.* **1974**, *408*, 293.

Table III. Thermal Parameters (Å^2)[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B[b]
P	0.0409 (5)	0.0365 (5)	0.0366 (5)	0.0004 (3)	0.0019 (3)	−0.0016 (3)	3.01
F11	0.090 (2)	0.058 (1)	0.080 (1)	−0.007 (1)	−0.002 (1)	0.024 (1)	6.03
F12	0.099 (2)	0.058 (1)	0.088 (2)	−0.027 (1)	0.001 (1)	−0.014 (1)	6.46
F13	0.063 (1)	0.081 (2)	0.086 (1)	−0.016 (1)	0.020 (1)	0.008 (1)	6.03
F21	0.053 (1)	0.126 (2)	0.111 (2)	−0.021 (1)	−0.018 (1)	0.035 (2)	7.68
F22	0.115 (2)	0.141 (2)	0.056 (1)	0.008 (2)	−0.021 (1)	−0.028 (2)	8.27
F23	0.077 (1)	0.069 (2)	0.119 (2)	0.009 (1)	−0.035 (1)	0.022 (1)	7.07
N	0.047 (1)	0.040 (1)	0.033 (1)	−0.005 (1)	0.005 (1)	−0.001 (1)	3.14
C1	0.059 (2)	0.049 (2)	0.059 (2)	−0.009 (2)	0.002 (2)	0.001 (1)	4.43
C2	0.054 (2)	0.058 (2)	0.053 (2)	−0.007 (1)	−0.011 (1)	0.005 (2)	4.36
C3	0.064 (2)	0.044 (2)	0.071 (2)	0.005 (1)	0.018 (2)	−0.008 (2)	4.70
C4	0.064 (2)	0.066 (2)	0.037 (1)	−0.001 (2)	0.013 (1)	0.001 (1)	4.37

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. [b] Equivalent isotropic thermal parameter.

Table IV. NMR Data for $[CH_3(CF_3)_2PNCH_3]_2$

	equatorial CF_3				axial CF_3				
isomer	$\delta(^{31}P)$[a]	$\phi(F)$[b]	$^2J_{PF}$, Hz	$^4J_{HF}$, Hz	$\phi(F)$[b]	$^2J_{PF}$, Hz	$^4J_{HF}$, Hz	$\tau(CH_3)$[c]	$\tau(NCH_3)$[c]
A	193.7	61.8	108	10	64.6	32	14	1.95[d]	2.65[e]
B	[g]	60.3	112	10	64.8	[f]	[f]	[g]	[g]

[a] Ppm vs. P_4O_6,[10] recorded at 0 °C with $CD_3CN-CFCl_3$ as solvent, positive value indicating resonance to high field. Only one isomer was detected by NMR even at 161.7 MHz. The shift is assigned to the dominant isomer A. [b] Ppm vs. $CFCl_3$, recorded at −25 °C with $CFCl_3$ as solvent, positive value indicating resonance to high field. [c] Ppm vs. $(CH_3)_4Si$ (τ 10.0) with $CFCl_3$ as solvent at 0 °C. [d] Doublet, $^2J_{PF} =$ 12.5 Hz. [e] Pseudoquartet (spacing of 9 Hz) with equal-intensity peaks. [f] Broadened lines. [g] Presence masked by dominant isomer A.

phosphetidines have been obtained previously from the fluorine-containing diazaphosphetidines and organometallic reagents such as RLi (R = CH_3,[23] OCH_3,[24] o-$C_6H_4O_2Li$[24]) and CH_3MgI.[23]

We have found that methylamine, in parallel to eq 2, produces the diazaphosphetidine from the tetraalkylhalogenophosphoranes $CH_3(CF_3)_3PX$ (X = F, Cl) by removal of the single halogen and one of the CF_3 groups (eq 3), the latter

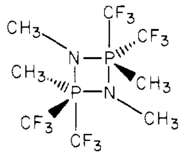
$$2CH_3(CF_3)_3PX + 4CH_3NH_2 \rightarrow [CH_3(CF_3)_2PNCH_3]_2 + 2CF_3H + 2CH_3NH_3^+X^- \quad (3)$$

as CF_3H. While aminolysis of a CF_3 group has been previously observed,[25] the occurrence of sufficient reactivity is rare. The reaction is more complex than suggested by eq 3 because more than the stoichiometric amount of CF_3H was observed and the residues contained phosphorus species which had been stripped of CF_3 substituents indicating that the aminolysis reaction proceeded beyond the removal of one CF_3 group.

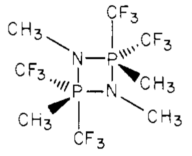
The most likely route of this reaction, preliminary formation of the expected monoalkylamino derivative $CH_3(CF_3)_3PN(H)CH_3$ followed by amine-assisted elimination of CF_3H and ring formation, is supported by the observations that pure $CH_3(CF_3)_3PN(H)CH_3$ (a) reacts with CH_3NH_2 to produce the diazadiphosphetidine, (b) is stable with respect to ring formation by self-condensation and elimination of CF_3H up to 115 °C,[13] and (c) is produced in modest yield when the reaction of $CH_3(CF_3)_3PCl$ is carried out with a limited quantity of CH_3NH_2. Excess amine is therefore essential to the formation of the diazaphosphetidine.

Limitation of the quantity of amine produced different results dependent on the halogen. The chloride $CH_3(CF_3)_3PCl$ gave a modest yield of $CH_3(CF_3)PN(H)CH_3$ and complex CF_3–P salts whereas the fluoride gave a low yield of the diazadiphosphetidine, CF_3H and $(CF_3)_2F(CH_3)PN(H)CH_3$. The latter product may arise from preferential aminolysis of a CF_3 group in competition with the expected aminolysis of the fluorine substituent.

B. NMR Spectroscopy. A summary of the NMR parameters is presented in Table IV. The presence of trans and gauche isomeric forms



trans



gauche

each showing the distinct equatorial and axial CF_3 environments is shown by ^{19}F NMR while the very high-field ^{31}P chemical shifts (the highest yet observed for diazadiphosphetidines) of the complicated multiplets are indicative of the five-coordinate nature of the phosphorus atom. The assignment of the axial and equatorial CF_3 groups is based on earlier observations[26] that $^2J_{PCF_{eq}}$ is greater than $^2J_{PCF_{ax}}$. Integration of the ^{19}F NMR spectrum shows that A accounts for 85% of the total. Although definite assignment of the isomeric forms to A and B cannot be made, it is probable that the major form, A, is the trans isomer since NMR studies on the series $[(Cl_xH_{z-x}C)F_2PNCH_3]_2$[27] and $[RF_2PNCH_3]_2$[28] (R = Me, Et, i-Pr, t-Bu) have shown that the trans isomer usually predominates, accounting for 50% or more of the total. It was also concluded[27,28] that the proportion of trans isomer becomes larger with bulkier substituents.

The ^{19}F NMR spectrum of the CF_3 region at the highest recorded temperature (+48 °C) which continues to show distinct equatorial and axial environments for both the gauche

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(23) Harris, R. K.; Wazeer, M. I. M.; Schlak, O.; Schmutzler, R. *J. Chem. Soc., Dalton Trans.* **1974**, 1912.

(24) Harris, R. K.; Wazeer, M. I. M.; Schlak, O.; Schmutzler, R. *J. Chem. Soc., Dalton Trans.* **1976**, 306.

(25) Poulin, D. D.; Tomlinson, A. J.; Cavell, R. G. *Inorg. Chem.* **1977**, *16*, 24. Cavell, R. G.; Leary, R. D.; Sanger, A. R.; Tomlinson, A. J. *Ibid.* **1973**, *12*, 1374. Burg, A. B.; Sarkis, A. J. *J. Am. Chem. Soc.* **1965**, *87*, 238.

(26) Cavell, R. G.; Gibson, J. A.; The, K. I. *J. Am. Chem. Soc.* **1977**, *99*, 7841.

(27) Harris, R. K.; Lewellyn, M.; Wazeer, M. I. M.; Woplin, J. R.; Dunmur, R. E.; Hewson, M. J. C.; Schmutzler, R. *J. Chem. Soc., Dalton Trans.* **1975**, 61.

(28) Harris, R. K.; Wazeer, M. I. M.; Schlak, O.; Schmutzler, R. *J. Chem. Soc., Dalton Trans.* **1976**, 17.

Table V. Interatomic Distances and Angles

Bond Distances (Å)			
P-N	1.633 (2)	C1-F11	1.351 (4)
P-N′	1.806 (2)	C1-F12	1.362 (4)
P-C1	1.963 (3)	C1-F13	1.349 (4)
P-C2	1.916 (3)	C2-F21	1.319 (4)
N-C4	1.470 (3)	C2-F22	1.324 (5)
		C2-F23	1.323 (4)
C3-H31	0.77 (4)		
C3-H32	0.92 (4)	C4-H41	0.86 (3)
C3-H33	1.17 (3)	C4-H42	0.95 (3)
		C4-H43	1.00 (3)
Nonbonded Intramolecular Distances (Å)			
P-P′	2.654 (1)		
N-N′	2.193 (4)		
F21-F12	2.670 (4)	N-F21	3.671 (3)
F21-F13	2.603 (4)	N-F23	3.385 (3)
C4-F11	3.020 (4)	N-F11	3.083 (3)
C4-F13	2.871 (4)	N-F13	3.075 (3)
C4′-F22	3.179 (5)	N′-F22	3.198 (4)
C4′-F23	3.034 (5)	N′-F23	2.655 (3)
Bond Angles (Deg)			
N-P-N′	79.1 (1)	F11-C1-F12	104.8 (3)
N-P-C1	96.0 (1)	F11-C1-F13	105.3 (3)
N-P-C2	120.1 (1)	F12-C1-F12	105.0 (3)
N-P-C3	127.5 (2)	F21-C2-F22	106.5 (3)
N′-P-C1	175.0 (1)	F21-C2-F23	106.3 (3)
N′-P-C2	91.2 (1)	F22-C2-F23	105.7 (3)
N′-P-C3	94.1 (1)		
C1-P-C2	90.5 (1)	P-C1-F11	110.6 (2)
C1-P-C3	89.6 (2)	P-C1-F12	111.8 (2)
C2-P-C3	112.0 (2)	P-C1-F13	118.3 (2)
P-N-P′	100.9 (1)	P-C2-F21	115.0 (2)
P-N-C4	132.5 (2)	P-C2-F22	110.8 (3)
P′-N-C4	126.6 (2)	P-C2-F23	111.9 (2)
Nonbonded Intermolecular Distances[a] Less Than 3.10 Å			
$F21\cdots H31^{I}$	2.83 (5)	$F12\cdots H33^{IV}$	3.00 (5)
$F21\cdots H43^{II}$	2.82 (4)	$F22\cdots H33^{II}$	3.00 (3)
$F21\cdots H41^{III}$	2.85 (4)	$F11\cdots F22^{VII}$	3.047 (3)
$F11\cdots H32^{IV}$	2.88 (5)	$F22\cdots H43^{II}$	3.07 (3)
$F13\cdots H42^{V}$	2.91 (4)	$H31\cdots H43^{VIII}$	3.06 (6)
$F22\cdots F23^{VI}$	2.963 (4)		

[a] The symmetry transformations are as follows: (I) $1 + x, y, z$; (II) $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; (III) $1 - x, -y, -z$; (IV) $-x, 1 - y, -z$; (V) $^1/_2 - x, {}^1/_2 + y, -{}^1/_2 - z$; (VI) $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; (VII) $-{}^1/_2 + x, {}^1/_2 - y, -{}^1/_2 + z$; (VIII) $-{}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$.

Table VI

Least-Squares Plane Calculations[a]

plane	atoms defining plane	*A*	*B*	*C*	*D*
1	P, N, P′, N′, C4, C4′	−0.8407	0.4662	−0.2755	0.0000
2	P, N, C2, C3	0.5630	0.6957	−0.4462	0.9052

Distances of Atoms from Planes (Å)

plane 1		plane 2	
P	−0.000 (1)	P	0.008 (1)
N	0.005 (2)	N	−0.037 (2)
P′	0.000 (1)	C2	−0.063 (4)
N′	−0.005 (2)	C3	−0.083 (4)
C4	−0.005 (4)		
C4′	0.005 (4)		
C1	−0.026 (3)		
C1′	0.026 (3)		

Dihedral Angle between Plane 1 and Plane 2: 91.5°

[a] The equations of the planes are of the form $AX + BY + CZ = D$ where X, Y, and Z are orthogonal coordinates.

Table VII. Selected Dihedral Angles (Deg)

C1-C2-F21/F12-C1-F13	96.9 (1)
F11-C1-P/F21-C2-P	22.1 (3)
F11-C1-P/P-N-C4	68.0 (2)
F13-C1-P/P-N-C4	53.6 (3)
F22-C2-P/C2-P-C3	10.5 (3)
F23-C2-P/P-N-C4	113.8 (2)
C4-N-C1/F11-C1-F13	91.0 (1)

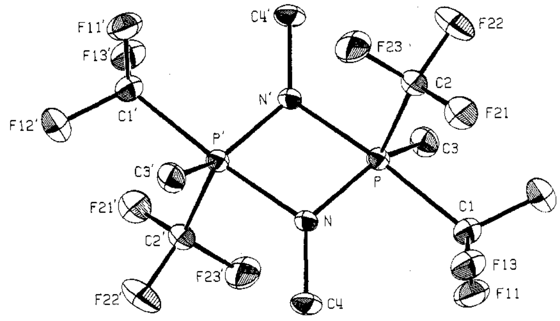

Figure 1. Molecular structure of $[CH_3(CF_3)_2PNCH_3]_2$, showing 20% probability ellipsoids for all atoms other than hydrogen. The primed and unprimed atoms are related by an inversion center.

and trans isomers demonstrates that neither axial ⇌ equatorial exchange nor trans ⇌ gauche interconversion occurs. Earlier NMR studies on $[F_2CH_3PNCH_3]_2$,[23] $[(Cl_xH_{3-x}C)F_2PNCH_3]_2$,[27] and $[RF_2PNCH_3]_2$[28] (R = Me, Et, *i*-Pr *t*-Bu) showed that the concerted pseudorotation of phosphorus substituents could only be stopped at temperatures lower than +10 °C for the first example and lower than −40 °C for the remainder. Our results suggest a higher axial ⇌ equatorial exchange barrier for the present compound (although it is dangerous to assign barriers on the basis of qualitative temperature data)[29] and also exclude the trans ⇌ gauche interconversion up to 50 °C since this has been found[27] to be a higher energy process than axial ⇌ equatorial exchange.

C. Description of the Molecular Structure. Bond distances, bond angles, selected nonbonded intramolecular distances, and the closest intermolecular contacts are tabulated in Table V. The results of least-squares plane calculation and selected dihedral angles are found in Tables VI and VII, respectively. The molecular structure of $[CH_3(CF_3)_2PNCH_3]_2$ is shown in Figure 1. Only one isomer is found in the crystalline solid, the trans isomer, which is presumably the most stable form of the molecule. The molecule also has a center of symmetry.

The geometry of the atoms bonded to phosphorus is best described as a trigonal bipyramid. The largest distortions arise from the ring structure which has forced the N′-P-C1 angle (175.0 (1)°) and the N-P-N′ angle (79.1 (1)°) to be smaller than their idealized angles of 180 and 90°, respectively. A least-squares plane through the equatorial atoms and the phosphorus shows only small deviation of these atoms from this plane. As found in other structures of this type of compound, the coplanarity of the atoms in plane 1 (Table VI) shows that both the geometry around N and the $\overline{\text{P-N-P'-N'}}$ ring system are planar. Furthermore, both C1 and C1′ are very close to this plane. Inspection of the dihedral angles (Table VII), the nonbonded intramolecular contacts, and the C2-P-C1 angle (90.5 (1)°) shows that the CF_3 groups are arranged so as to maximize intramolecular distances between themselves and the methyl groups. Thus, as found[30] in the structure of $CH_3(CF_3)_3PO_2CN(CH_3)_2$, which has a six-coordinate phosphorus center, the CF_3 groups do not contribute to distortions by steric crowding.

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(29) Cavell, R. G.; The, K. I.; Gibson, J. A.; Yap, N. T. *Inorg. Chem.* **1979**, *18*, 3400.

(30) The, K. I.; Vande Griend, L.; Whitla, W. A.; Cavell, R. G. *Inorg. Chem.* **1977**, *99*, 7379.

All of the bond distances (Table V) appear to be within normal ranges. As expected, the axial bond lengths ($P–N_{ax}$ = 1.806 (2) Å and $P–C_{ax}F_3$ = 1.963 (3) Å) are longer than the equatorial bond lengths ($P–N_{eq}$ = 1.633 (2) Å and $P–C_{eq}F_3$ = 1.916 (3) Å). Also the C–F bond lengths for the axial CF_3 (1.354 Å, average) are longer compared to the C–F bond lengths for the equatorial CF_3 (1.322 Å, average).

The closest nonbonded intermolecular contacts (Table V) show that none are longer than the sum of the respective van der Waals radii.

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Registry No. $[CH_3(CF_3)_2PNCH_3]_2$, 73506-03-3; $CH_3(CF_3)_3PCl$, 56420-21-4; CH_3NH_2, 74-89-5; $CH_3(CF_3)_3PN(H)CH_3$, 73506-04-4; $(CF_3)_3CH_3PF$, 57572-93-7; $(CH_3)_3SiN(H)CH_3$, 16513-17-0; $(CF_3)_2F(CH_3)PN(H)CH_3$, 73506-05-5.

Supplementary Material Available: A listing of observed ($10|F_o|$) and calculated $10|F_c|$) structure amplitudes (5 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Magnetism of Sodium Bis(oxalato)cuprate(II) Dihydrate, $Na_2Cu(C_2O_4)_2·2H_2O$. A Deductive Proposal for the Structure of Copper Oxalate, $CuC_2O_4·xH_2O$ $(0 \le x \le 1)$[1]

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Sodium bis(oxalato)cuprate(II) dihydrate, $Na_2Cu(C_2O_4)_2·2H_2O$, was synthesized from aqueous solutions of sodium oxalate and copper oxalate. It crystallizes in the triclinic system (space group $P\bar{1}$) with one formula unit in a cell of dimensions a = 7.536 (3) Å, b = 9.473 (4) Å, c = 3.576 (2) Å, α = 81.90 (6)°, β = 103.77 (5)°, and γ = 108.08 (4)°. The structure has been refined by full-matrix least-squares methods using 1734 independent observations to a final R factor of 0.027. It consists of columnar stacks of quasi-planar units $[(C_2O_4)Cu(C_2O_4)]^{2-}$ along the c axis, with Cu–Cu separation of 3.576 (2) Å and a tilt angle of 129.2 (5)° with respect to the stacking direction. Sodium atoms and water molecules develop independent chains running in the same c direction. This structure is markedly different from that of the potassium and ammonium derivatives. Derived models for ribbon-like structures of hydrated copper oxalate, $CuC_2O_4·xH_2O$ $(0 \le x \le 1)$ are proposed. A weak antiferromagnetic intrastack coupling, brought to evidence from measurements of the magnetic susceptibility in the temperature range 4–300 K, is discussed in the light of the structural features of $Na_2Cu(C_2O_4)_2·2H_2O$.

Introduction

In their review on one-dimensional inorganic compounds, Miller and Epstein[2] have pointed out that "the crystal structures of various complexes which exhibit antiferromagnetic behavior reveal a chain structure formed through intermolecular bridging ligands and not through direct metal–metal bonding....An exception to this trend is α-Cu(msal)$_2$ which has a collinear array of Cu(II) atoms, with metal–metal spacings too large, 3.3 Å, for strong metal–metal bonding".

The study of sodium bis(oxalato)cuprate(II) dihydrate, $Na_2Cu(C_2O_4)_2·2H_2O$, was undertaken in the course of our investigations on compounds likely to have structures build from columnar stacks of nearly planar complex ions such as $Ni(S_2C_2O_2)_2{}^{2-1}$ or $Cu(C_2O_4)_2{}^{2-}$. This latter anion has long been known as its potassium and ammonium salts[3] whose structures[4] and magnetism[5] have been investigated. On the other hand, its sodium salt was not known. We report here on the synthesis, crystal structure, and magnetic behavior of this compound which, unlike the potassium and ammonium derivatives, has a crystal structure made of columnar stacks of anions $Cu(C_2O_4)_2{}^{2-}$.

Table I. Experimental Crystallographic Data

(1) Physical and Crystallographic Data

formula: $Na_2Cu(C_2O_4)_2·2H_2O$
cryst system: triclinic
space group: $P\bar{1}$
a = 7.536 (3) Å
b = 9.473 (4) Å
c = 3.576 (2) Å
α = 81.90 (6)°
β = 103.77 (5)°
γ = 108.09 (4)°
mol wt: 321.6
V = 235 Å^3
$\rho_m = 2.24 \pm 0.03$ g/cm^3
$\rho_x = 2.27 \pm 0.02$ g/cm^3
Z = 1
abs factor: $\mu_{MoK\alpha}$ = 24.58 cm^{-1}
morphology: parallelogram, 0.004 × 0.005 × 0.05 cm

(2) Data Collection

temp: 293 K
radiation: λ (Mo Kα) = 0.710 69 Å
crystal-detector distance: 208 mm
detector window: height = 4 mm; width = 4 mm
scan mode: θ–2θ
maximum Bragg angle: 37°
scan angle: $\Delta\theta = \Delta\theta_0 + B \tan\theta$; $\Delta\theta_0{}^a = 1°$, $B^a = 0.347$
values determining scan speed: SIGPRE^a = 0.66; SIGMA^a = 0.018; VPRE^a = 10°/min; TMAX^a = 80 s
std intensity reflctns: $22\bar{1}$, 300, $0\bar{1}1$ measured every 3600 s

[a] These parameters have been described in: Mosset, A.; Bonnet, J. J.; Galy, J. *Acta Crystallogr., Sect. B* 1977, *33*, 2633.

Experimental Section

Synthesis and Characterization. Copper oxalate was prepared as described in ref 6 and dissolved in an aqueous solution of sodium

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(1) Presented at the 5th European Crystallographic Meeting, Cophenhagen (Abstract No. 15-P3-2), along with studies on bis(dithiooxalato)nickelates(II) of alkali elements. A study of $K_2Ni(S_2C_2O_2)_2$ has been published: Gleizes, A.; Cléry, F; Bruniquel, M.-F.; Cassoux, P. *Inorg. Chim. Acta* **1979**, *37*(1), 19. Results concerning the compounds $M_2Ni(S_2C_2O_2)_2·2H_2O$ with M = Li and Na, which are isostructural with $Na_2Cu(C_2O_4)_2·2H_2O$, are to be published in *Inorg. Chim. Acta*.

(2) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 127.

(3) von Groth, P. *Chem. Krist.* **1910**, *3*, 158.

(4) Viswamitra, M. A. *J. Chem. Phys.* **1962**, *37*, 1408. Viswamitra, M. A. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1962**, *117*, 437.

(5) Jeter, D. Y.; Hatfield, W. E. *Inorg. Chim. Acta* **1972**, *6*(3), 523.

0020-1669/80/1319-2074$01.00/0