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# Preparation, Spectral Characterization, and Single Crystal X-Ray Structures of *Cis* and *Trans* Isomers of 2,4,6-Trifluoroethoxy-1,3,5-triethyl-1,3,5,2$\lambda^5$, 4$\lambda^5$, 6$\lambda^5$-triazatriphosphorinane-2,4,6-trioxide, $[EtNP(O)(OCH_2CF_3)]_3$

Ramaswamy Murugavel, Natesan Thirupathi, Setharampattu S. Krishnamurthy,* and Munirathinam Nethaji

*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India*

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## ABSTRACT

*Oxidation of the cis isomer of the $\lambda^3$-cyclotriphosphazane $[EtNP(OCH_2CF_3)]_3$ with trimethylamine-N-oxide (TMNO) gives the cis isomer of trioxo-$\lambda^5$-cyclotriphosphazane $[EtNP(O)(OCH_2CF_3)]_3$; the trans isomer of $[EtNP(O)(OCH_2CF_3)]_3$ is obtained by the treatment of a cis and trans mixture of $[EtNP(OCH_2CF_3)]_3$ with aqueous $H_2O_2$. The two trioxocyclotriphosphazanes have been characterized by elemental analysis, IR, and NMR ($^1H$, $^{13}C$, $^{19}F$, and $^{31}P$) spectroscopy. The solid state structures of both the isomers have been determined by single crystal X-ray diffraction. The six-membered $P_3N_3$ ring in both the isomers exhibits a twist-boat conformation; in the cis isomer, the trifluoroethoxy substituents lie on the same side of the ring, whereas, in the trans isomer, two trifluoroethoxy groups are on one side of the ring and the third on the other side of the ring. Crystal data for cis-$[EtNP(O)(OCH_2CF_3)]_3$: monoclinic,* **P**$2_1$/**n**, **a** *= 13.593(3),* **b** *= 9.721(2),* **c** *= 17.539(3) Å,* **β** *= 99.49(2)°,* **V** *= 2286(1) Å$^3$,* **Z** *= 4, and Final* **R** *= 0.047. Crystal data for trans-$[EtNP(O)(OCH_2CF_3)]_3$: monoclinic,* **P**$2_1$/**n**, **a** *= 11.685(4),* **b** *= 15.115(5),* **c** *= 13.233(5) Å,* **β** *= 102.21(3)°,* **V** *= 2284(1) Å$^3$,* **Z** *= 4, and Final* **R** *= 0.078.*

## *INTRODUCTION*

The rearrangement of alkoxycyclophosphazenes $[NP(OR)_2]_n$ ($n$ = 3,4) to N-alkyl oxocyclophosphazanes $[RNP(O)(OR)]_n$ was first reported by Fitzsimmons et al. [1,2]. Subsequently, this approach was further developed and exploited in our laboratory to obtain a range of trioxocyclotriphosphazanes [3,4] and mixed cyclic phosphazene-phosphazane derivatives [5] from the thermolysis of a series of alkoxy(aryloxy)cyclotriphosphazenes $N_3P_3(OR)_{6-n}(OC_6H_4Me\text{-}4)_n$ (R = Me, Et, or $CH_2Ph$). Recently, Murray and co-workers reported the preparation of trioxo-N-aryl cyclotriphosphazanes by a direct condensation reaction between $POCl_3$ and an aromatic primary amine hydrochloride [6]. These trioxocyclotriphosphazanes can exist in two different geometrical isomeric forms (*cis* and *trans*). The crystal structures of the *trans* isomers of three compounds, *viz.* $[MeNP(O)(OMe)]_3$ [7], $[MeNP(O)(OC_6H_4Me\text{-}4)]_3$ [4], and $[PhNP(O)Cl]_3$ [6],

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

*To whom correspondence should be addressed.



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have been determined. Murray and Woodward have recently reported in a conference proceedings [8] that the $P_3N_3$ ring of *cis*-$[PhNP(O)Cl]_3$ exists in an almost planar chair or boat conformation in its two independent crystallographic modifications.

We have earlier reported that the *cis* and *trans* isomers of $\lambda^5$-trioxocyclotriphosphazanes are accessible from oxidation reactions of $\lambda^3$-cyclotriphosphazanes with TMNO or $H_2O_2$ [9]. Using this approach, we herein report the preparation, spectroscopic data, and solid state structures of both the *cis* and *trans* isomers of the trioxocyclotriphosphazane, $[EtNP(O)(OCH_2CF_3)]_3$ (**1a**, **1b**). This work is part of our program to obtain structural data on a range of cyclic and acyclic phosphorus–nitrogen compounds with a view to understanding the nature of the P–N bond [10].

## EXPERIMENTAL

### Apparatus and Chemicals

All experimental manipulations were performed under an atmosphere of dry dinitrogen in a vacuum system using the Schlenk apparatus [11]. Solvents, such as petroleum ether (bp 60–80°C), toluene, dichloromethane, chloroform, thf, and methanol, were purified by conventional procedures and freshly distilled prior to use [12]. Trifluoroethanol (Fluka) and trimethylamine-N-oxide (TMNO) (Sigma) were used as purchased. The $^1H$, $^{13}C$ ($Me_4Si$—internal standard), $^{19}F$ ($CFCl_3$—external standard), and $^{31}P$ (85% $H_3PO_4$—external standard) NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400.0, 100.6, 376.3, and 161.9 MHz, respectively. Chemical shifts downfield from the standard were assigned positive values. Infrared spectra were recorded on a Bio-Rad FT-IR Spectrometer.

The *cis-trans* isomeric mixture of $[EtNP(OCH_2CF_3)]_3$ was prepared and purified as described previously [9], and the *cis* isomer was separated from the mixture by fractional crystallization.

### *Preparation of cis-*$[EtNP(O)(OCH_2CF_3)]_3$ (**1a**)

The *cis* isomer of $[EtNP(OCH_2CF_3)]_3$ (0.5 g, 1 mmol) was stirred with an excess (fivefold) of TMNO (0.53 g, 4.8 mmol) in $CH_2Cl_2$/methanol mixture (50 mL/10 mL) for 7 days at 25°C, and the solvent was removed *in vacuo* to give *cis*-$[EtNP(O)(OCH_2CF_3)]_3$ (**1a**) in almost quantitative yield. The product was recrystallized from toluene. Mp: 90–92°C; CHN anal. [found (calcd)]: C, 25.3 (25.4); H, 3.5 (3.7); N, 6.9 (7.4). IR (KBr pellet): 2990 (m), 1448 (w), 1424 (w), 1388 (w), 1356 (w), 1317 (m); 1290 (s), 1253 (s), 1170 (vs), 1068 (s), 967 (vs), 877 (w), 864 (w), 835 (m), 785 (s), 702 (m), 672 (w), 655 (m), 566 (m), 536 (m), 483 (w), 427 (w) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 1.26 (t, $C\underline{H}_3$, 9H, $^3J_{HH}$ = 7.1 Hz), $\delta$ 3.54–3.66 (br multiplet, $NC\underline{H}_2$, 6H), $\delta$ 4.36–4.39 (br multiplet, $OC\underline{H}_2$, 6H). $^{13}C$ NMR ($CDCl_3$): $\delta$ 16.5 (s, $\underline{C}H_3$, 3C), $\delta$ 42.5 (s, $N\underline{C}H_2$, 3C), $\delta$ 63.4 (q, $O\underline{C}H_2$, 3C, $^2J_{CF}$ = 38.3 Hz), $\delta$ 122.4 (q, $\underline{C}F_3$, 3C, $^1J_{CF}$ = 277.5 Hz). $^{19}F$ NMR ($CDCl_3$): $\delta$ −76.2 (t, $C\underline{F}_3$, 9F, $^3J_{FH}$ = 7.8 Hz). $^{31}P$ NMR ($CDCl_3$): $\delta$ 3.6 (s, 3P).

### *Preparation of trans-*$[EtNP(O)(OCH_2CF_3)]_3$ (**1b**)

The *trans* isomer **1b** was prepared from the *cis-trans* isomeric mixture of the $\lambda^3$-cyclotriphosphazane. To a stirred solution of *cis/trans*-$[EtNP(OCH_2CF_3)]_3$ (1 g, 1.9 mmol) in methanol (50 mL) was added 20% aqueous $H_2O_2$ (10 mL) in drops at 0°C. The reaction mixture was slowly brought to room temperature and stirred for 24 hours, and the solvent and water were removed. The resulting oil was dissolved in chloroform (50 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed and the residue was recrystallized from $CH_2Cl_2$/petroleum ether (1:3) at 0°C to yield *trans*-$[EtNP(O)(OCH_2CF_3)]_3$ in >90%. Mp: 100–102°C, CHN anal. [found (calcd)]: C, 25.4 (25.4); H, 3.5 (3.7); N, 7.0 (7.4). IR (KBr pellet): 2995 (m), 1467 (w), 1431 (w), 1391 (w), 1357 (w), 1323 (m), 1289 (s), 1253 (s), 1167 (vs), 1074 (s), 975 (vs), 868 (w), 844 (w), 782 (m), 713 (w), 699 (w), 658 (w), 566 (m), 553 (w), 535 (w), 492 (w). $^1H$ NMR ($CDCl_3$): $\delta$ 1.26 (t, $C\underline{H}_3$, 3H, $^3J_{HH}$ = 8.3 Hz), $\delta$ 1.28 (t, $C\underline{H}_3$, 6H, $^3J_{HH}$ = 7.2 Hz), $\delta$ 3.41–3.66 (complex multiplet, $NC\underline{H}_2$, 6H), $\delta$ 4.32–4.44 (br complex multiplet, $OC\underline{H}_2$, 6H). $^{13}C$ NMR ($CDCl_3$) $\delta$ 16.2 (s, $\underline{C}H_3$, 2C), $\delta$ 17.1 (s, $\underline{C}H_3$, 1C), $\delta$ 41.8 (s, $N\underline{C}H_2$, 1C), $\delta$ 43.3 (s, $N\underline{C}H_2$, 2C), $\delta$ 62.6 (dq, $O\underline{C}H_2$, 1C, $^2J_{CF}$ = 38.2 Hz, $^2J_{PC}$ = 4.3 Hz), $\delta$ 63.1 (q, $O\underline{C}H_2$, 2C, $^2J_{CF}$ = 38.3 Hz, $^2J_{PC}$ = unresolved), $\delta$ 122.3 (q, $\underline{C}F_3$, 1C, $^1J_{CF}$ = 277 Hz), $\delta$ 122.4 (q, $\underline{C}F_3$, 2C, $^1J_{CF}$ = 278 Hz). $^{19}F$ NMR ($CDCl_3$): $\delta$ −76.0 (t, $C\underline{F}_3$, 3F, $^3J_{FH}$ = 7.9 Hz), $\delta$ −76.3 (t, $C\underline{F}_3$, 6F, $^3J_{FH}$ = 7.9 Hz). $^{31}P$ NMR ($CDCl_3$): $A_2X$ pattern, $\delta_A$ = 4.8 (d), $\delta_X$ = 6.7 (t), $^2J_{PP}$ = 25.7 Hz.

### *X-ray Structures of cis and trans-*$[EtNP(O)(OCH_2CF_3)]_3$ (**1a**, **1b**)

Crystals suitable for X-ray diffraction were obtained as colorless needles for **1a** and rectangular plates for **1b**. A suitable crystal of each isomer was mounted on a glass fiber and centered on an Enraf–Nonius diffractometer equipped with a Mo $K_\alpha$ source (graphite monochromator). A total of 25 reflections in the $2\theta$ range 24–35° were used to derive the lattice parameters. Three reflections measured after every 3600 seconds of exposure time showed no decrease in their intensities. The data were corrected for Lorentz and polarization effects; no absorption correction was made as the absorption coefficient $\mu$ was very small.

The structures of both the isomers were solved by direct methods using SHELXS-86 [13]. Full-matrix least-squares refinement was carried out on

**TABLE 1** Details of Crystal Data and Refinement for **1a** and **1b**

| | **1a** | **1b** |
|---|---|---|
| Empirical formula | $C_{12}H_{21}F_9N_3O_6P_3$ | $C_{12}H_{21}F_9N_3O_6P_3$ |
| Formula weight | 567.2 | 567.2 |
| Temperature, K | 290(1) | 290(1) |
| Wavelength, Å | 0.7107 | 0.7107 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| *a*, Å | 13.593(3) | 11.685(4) |
| *b*, Å | 9.721(2) | 15.115(5) |
| *c*, Å | 17.539(3) | 13.233(5) |
| $\beta$, deg | 99.49(2) | 102.21(3) |
| Volume, Å$^3$ | 2286(1) | 2284(1) |
| *Z* | 4 | 4 |
| $D_c$, g/cm$^{-3}$ | 1.648 | 1.649 |
| Radiation | Mo $K_\alpha$ | Mo $K_\alpha$ |
| $\mu$, mm$^{-1}$ | 0.37 | 0.37 |
| *F*(000) | 1152 | 1152 |
| Crystal size, mm | 0.4 × 0.2 × 0.15 | 0.45 × 0.2 × 0.2 |
| $\theta$ range, deg | 1 to 25 | 1 to 22.5 |
| Index ranges | $0 < h < 16$ | $0 < h < 13$ |
| | $0 < k < 11$ | $0 < k < 17$ |
| | $-20 < l < 20$ | $-15 < l < 15$ |
| Reflections, unique | 4014 | 2970 |
| with positive $F^2$ | 3673 | 2611 |
| with $[I > 2\sigma(I)]$ | 3002 | 2036 |
| Final $R_1$[a] | 0.047 | 0.078 |
| $wR_2$[b] | 0.115 | 0.190 |
| Parameters | 301 | 301 |
| *S* on $F^2$[c] | 1.04 | 1.09 |
| Residual peak, $e \cdot$ Å$^{-3}$ | 0.81 | 0.55 |
| Negative peak, $e \cdot$ Å$^{-3}$ | −0.30 | −0.73 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$
[c] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$

**TABLE 2** Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × 10$^3$) for **1a**[a]

| *Atom* | *x/a* | *y/b* | *z/c* | $U_{eq}$ |
|---|---|---|---|---|
| P(1) | 161(1) | 1042(1) | 8644(1) | 44(1) |
| P(2) | 1576(1) | 1636(1) | 7640(1) | 47(1) |
| P(3) | 815(1) | 3835(1) | 8502(1) | 48(1) |
| N(1) | 474(2) | 1054(3) | 7760(1) | 49(1) |
| N(2) | 1757(2) | 2925(3) | 8259(1) | 47(1) |
| N(3) | 140(2) | 2694(3) | 8880(2) | 51(1) |
| C(1) | −38(4) | 104(5) | 7143(3) | 83(1) |
| C(2) | −836(4) | 791(8) | 6660(3) | 133(3) |
| C(3) | 2788(3) | 3188(4) | 8679(2) | 62(1) |
| C(4) | 2991(4) | 2495(6) | 9447(3) | 107(2) |
| C(5) | −482(3) | 3137(4) | 9466(2) | 60(1) |
| C(6) | −1413(3) | 3852(5) | 9106(3) | 86(1) |
| O(1) | −972(2) | 626(2) | 8467(1) | 51(1) |
| O(2) | 1313(2) | 2249(3) | 6795(1) | 57(1) |
| O(3) | 114(2) | 4204(2) | 7719(1) | 54(1) |
| O(4) | 759(2) | 178(3) | 9216(1) | 58(1) |
| O(5) | 2417(2) | 688(3) | 7721(1) | 62(1) |
| O(6) | 1148(2) | 5007(2) | 8989(1) | 61(1) |
| C(11) | −1401(3) | −331(4) | 8934(2) | 59(1) |
| C(12) | −1555(4) | −1673(5) | 8531(3) | 76(1) |
| F(11) | −2014(3) | −2530(3) | 8944(2) | 138(1) |
| F(12) | −705(2) | −2247(3) | 8440(2) | 113(1) |
| F(13) | −2105(2) | −1571(3) | 7841(2) | 102(1) |
| C(21) | 2092(3) | 2587(4) | 6370(2) | 57(1) |
| C(22) | 1605(4) | 2769(5) | 5556(2) | 74(1) |
| F(21) | 904(2) | 3713(4) | 5473(2) | 121(1) |
| F(22) | 1196(3) | 1639(4) | 5259(2) | 124(1) |
| F(23) | 2268(2) | 3139(4) | 5124(2) | 110(1) |
| C(31) | 317(3) | 5377(4) | 7289(2) | 62(1) |
| C(32) | −578(3) | 5678(4) | 6720(2) | 71(1) |
| F(31) | −1371(2) | 5928(3) | 7034(2) | 108(1) |
| F(32) | −409(3) | 6788(3) | 6318(2) | 130(1) |
| F(33) | −841(2) | 4677(3) | 6223(2) | 101(1) |

[a] $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

$F^2$ using SHELXL-93 [14]. All the unique reflections with positive $F^2$ values were used in the refinement. The hydrogen atoms were placed in the calculated positions and were allowed to ride on the attached atoms during refinement. The non-hydrogen atoms were refined with anisotropic thermal parameters. The refinement converged for the *cis* isomer at $R_1 = 0.047$ and $wR_2 = 0.115$, for the *trans* isomer, convergence occurred at $R_1 = 0.078$ and $wR_2 = 0.190$. The weighted *R* factor $wR_2$ is based on $F^2$ and, hence, will be statistically about twice as large as those based on *F*.

The details pertaining to data collection and structure refinement are summarized in Table 1. The final fractional atomic coordinates with the associated equivalent isotropic temperature factors are listed in Tables 2 and 3.

## *RESULTS AND DISCUSSION*

### *Synthesis and Spectra*

The reaction of $[EtNPCl]_3$ with $NaOCH_2CF_3$ in THF yielded a 1:1 *cis-trans* isomeric mixture of $[EtNP(OCH_2CF_3)]_3$. Repeated recrystallization of this mixture yielded pure *cis*-$[EtNP(OCH_2CF_3)]_3$. However, the *trans* isomer of this compound could not be isolated in a pure form. Reaction of *cis*-$[EtNP(OCH_2CF_3)]_3$ with an excess of TMNO (5 equivalents) at ca. 25°C for 7 days yielded *cis*-$[EtNP(O)(OCH_2CF_3)]_3$ (**1a**). The *trans* isomer **1b** was obtained by the oxidation of the *cis-trans* isomeric mixture of $[EtNP(OCH_2CF_3)]_3$ with aqueous $H_2O_2$ at 0°C (Scheme 1).

$$\textit{cis}\text{-}[EtNP(OCH_2CF_3)]_3 \xrightarrow[CH_2Cl_2,\ 25°C,\ 7\ d]{TMNO} \textit{cis}\text{-}[EtNP(O)(OCH_2CF_3)]_3 \quad (\mathbf{1a})$$

$$\textit{cis/trans}\text{-}[EtNP(OCH_2CF_3)]_3 \xrightarrow[methanol,\ 0°C,\ 24\ h]{20\%\ aqueous\ H_2O_2} \textit{trans}\text{-}[EtNP(O)(OCH_2CF_3)]_3 \quad (\mathbf{1b})$$

**SCHEME 1**

Both **1a** and **1b** have been characterized by elemental analysis, IR, and NMR ($^1H$, $^{13}C$, $^{19}F$, and

**TABLE 3** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1b**[a]

| *Atom* | *x/a* | *y/b* | *z/c* | $U_{eq}$ |
|---|---|---|---|---|
| P(1) | 1934(2) | 8314(1) | 6317(1) | 45(1) |
| P(2) | 1220(2) | 6496(1) | 6592(1) | 43(1) |
| P(3) | 113(2) | 7500(1) | 4792(1) | 45(1) |
| N(1) | 2238(4) | 7246(4) | 6542(4) | 46(1) |
| N(2) | 40(4) | 6944(4) | 5852(4) | 44(1) |
| N(3) | 1006(5) | 8345(3) | 5181(4) | 50(1) |
| C(1) | 3482(6) | 6932(6) | 6625(6) | 67(2) |
| C(2) | 3775(8) | 6857(7) | 5622(6) | 86(3) |
| C(3) | −1132(7) | 6655(9) | 6025(8) | 111(4) |
| C(4) | −1562(13) | 7309(10) | 6616(10) | 148(5) |
| C(5) | 1025(8) | 9115(5) | 4465(6) | 79(3) |
| C(6) | 1752(9) | 8975(7) | 3722(7) | 97(3) |
| O(1) | 1141(4) | 8588(3) | 7069(3) | 50(1) |
| O(2) | 898(4) | 6564(3) | 7679(3) | 48(1) |
| O(3) | 866(4) | 6923(3) | 4193(4) | 53(1) |
| O(4) | 2973(4) | 8857(3) | 6382(4) | 58(1) |
| O(5) | 1551(4) | 5608(3) | 6344(4) | 54(1) |
| O(6) | −1047(4) | 7742(4) | 4176(3) | 61(1) |
| C(11) | 1636(6) | 8816(5) | 8120(5) | 52(2) |
| C(12) | 732(7) | 9184(6) | 8602(6) | 61(2) |
| F(11) | 1112(5) | 9389(4) | 9569(4) | 108(2) |
| F(12) | −165(5) | 8627(4) | 8562(4) | 96(2) |
| F(13) | 269(5) | 9917(4) | 8114(4) | 102(2) |
| C(21) | 1544(6) | 6048(4) | 8542(5) | 47(2) |
| C(22) | 1061(7) | 6233(5) | 9429(6) | 56(2) |
| F(21) | 1152(5) | 7069(3) | 9719(3) | 82(2) |
| F(22) | −47(5) | 6026(4) | 9319(4) | 105(2) |
| F(23) | 1642(6) | 5762(4) | 10236(3) | 102(2) |
| C(31) | 411(7) | 6158(5) | 3633(6) | 56(2) |
| C(32) | 1112(8) | 5962(6) | 2886(7) | 74(2) |
| F(31) | 731(5) | 5267(3) | 2311(4) | 94(2) |
| F(32) | 2215(5) | 5821(6) | 3291(6) | 160(4) |
| F(33) | 1095(7) | 6649(5) | 2234(5) | 136(3) |

[a] $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

$^{31}P$) spectroscopy. The IR spectra of **1a** and **1b** show strong absorptions in the region 1250–1290 $cm^{-1}$ attributable to the P=O stretching mode [15].

The $^{31}P$ NMR spectrum of **1a** shows a single resonance at $\delta$ 3.6 indicating the equivalence of the three phosphorus nuclei in the $P_3N_3$ ring; the spectrum of the *trans* isomer **1b** shows an $A_2X$ pattern ($\delta_A = 4.8$, $\delta_X = 6.7$, $J = 25.7$ Hz), revealing the presence of two types of phosphorus nuclei in solution. The phosphorus chemical shifts observed for **1a** and **1b** are comparable with the values reported for other trioxocyclotriphosphazanes [3–6]. The $^2J_{PP}$ value of 25.7 Hz observed for the *trans* isomer **1b** is more than twice that observed for the parent $\lambda^3$-cyclotriphosphazane *trans*-[EtNP($OCH_2CF_3$)]$_3$ (11.7 Hz) [9]. The variable temperature $^{31}P$ NMR spectral studies of the *cis* isomer **1a** between 20 and 50°C did not show any interconversion into the *trans* isomer.

The $^1H$, $^{13}C$, and $^{19}F$ NMR spectra of the *cis* isomer **1a** show the presence of only one type of NEt and $OCH_2CF_3$ groups. On the other hand, the spectra of the trans isomer **1b** show the presence of two sets of NEt and $OCH_2CF_3$ groups with an integral ratio of 2:1. All the methyl protons in **1a** resonate as a triplet at $\delta$ 1.26 with a $^3J_{HH}$ of 7.1 Hz, whereas the $NCH_2$ and $OCH_2$ protons give rise to unresolved multiplets centered at $\delta$ 3.60 and 4.38, respectively. In the case of **1b**, the resonances for $CH_3$, $NCH_2$, and $OCH_2$ protons are observed in a 2:1 ratio at $\delta$ 1.27, 3.54, and 4.38, respectively. The various coupling constants of these resonances remain unresolved even at high field (400 MHz).

The $^{13}C$ NMR spectra of **1a** and **1b** are, how-

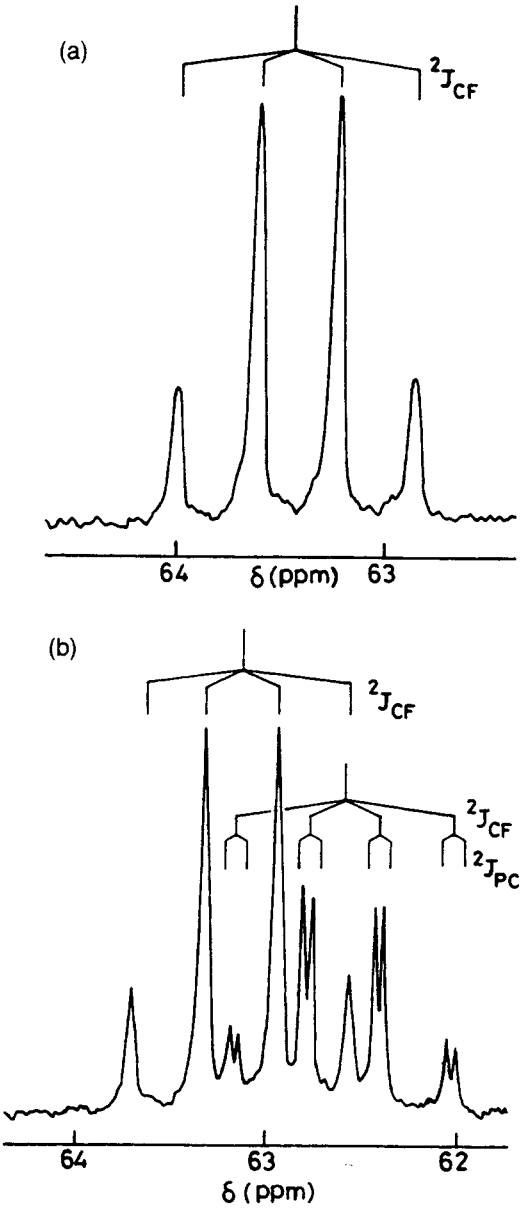


**FIGURE 1** $^{13}C$ NMR spectra (100.6 MHz, $OCH_2$ region only) of (a) *cis*-[EtNP(O)($OCH_2CF_3$)]$_3$ (**1a**) and (b) *trans*-[EtNP(O)($OCH_2CF_3$)]$_3$ (**1b**).

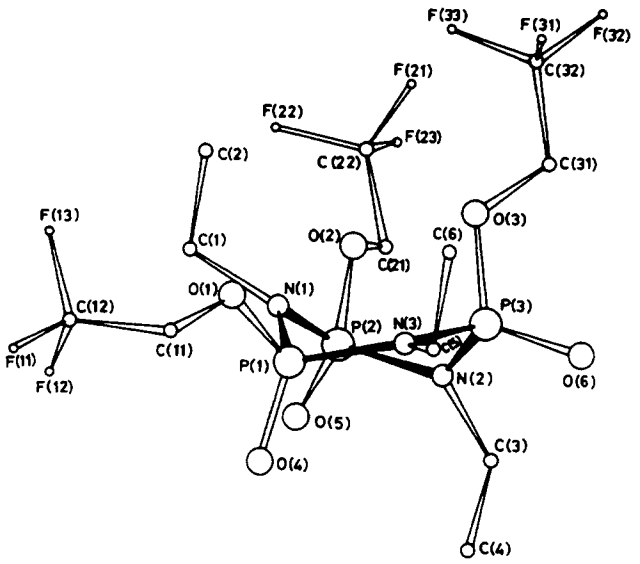


**FIGURE 2** Molecular structure of *cis*-[EtNP(O)($OCH_2CF_3$)]$_3$ (**1a**).

ever, more revealing, and the coupling constants are resolved at room temperature. The $OCH_2$ region of the $^{13}C$ NMR spectra of **1a** and **1b** are shown in Figure 1. The carbon nuclei of $OCH_2$ groups in **1a** resonate as a quartet at $\delta$ 63.4 with $^2J_{CF}$ of 38.3 Hz (Figure 1(a)). Two sets of quartets centered at $\delta$ 62.6 and 63.1 (1:2) are observed for the $OCH_2$

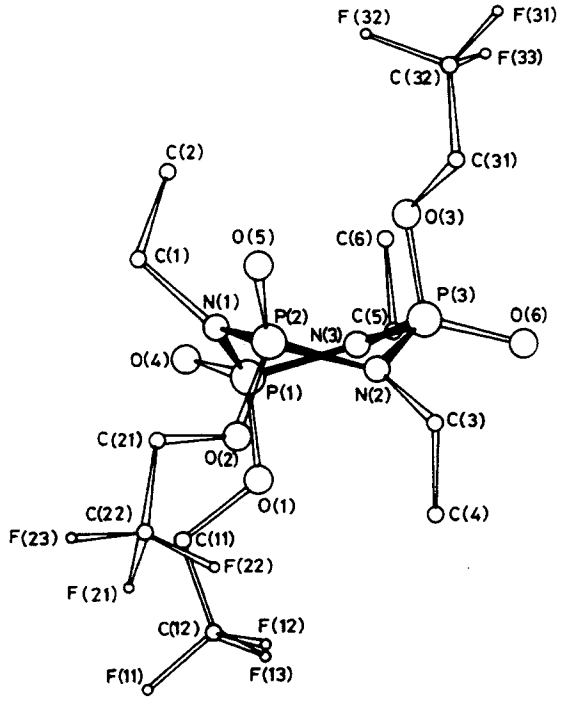


**FIGURE 3** Molecular structure of *trans*-[EtNP(O)-($OCH_2CF_3$)]$_3$ (**1b**).

**TABLE 4** Selected Bond Lengths (Å)

| | *1a* | *1b* |
|---|---|---|
| P(1)–N(1) | 1.673(3) | 1.666(6) |
| P(2)–N(1) | 1.647(3) | 1.655(6) |
| P(2)–N(2) | 1.650(3) | 1.659(5) |
| P(3)–N(2) | 1.668(3) | 1.653(6) |
| P(3)–N(3) | 1.646(3) | 1.661(6) |
| P(1)–N(3) | 1.659(3) | 1.657(6) |
| P(1)–O(1) | 1.573(2) | 1.553(5) |
| P(2)–O(2) | 1.583(2) | 1.566(5) |
| P(3)–O(3) | 1.579(2) | 1.567(5) |
| P(1)–O(4) | 1.450(2) | 1.452(5) |
| P(2)–O(5) | 1.456(3) | 1.453(5) |
| P(3)–O(6) | 1.451(2) | 1.473(5) |
| N(1)–C(1) | 1.504(5) | 1.511(7) |
| N(2)–C(3) | 1.494(4) | 1.500(8) |
| N(3)–C(5) | 1.498(4) | 1.504(8) |
| O(1)–C(11) | 1.425(4) | 1.431(8) |
| O(2)–C(21) | 1.431(4) | 1.455(7) |
| O(3)–C(31) | 1.419(4) | 1.415(8) |

**TABLE 5** Selected Bond Angles (Deg)

| | *1a* | *1b* |
|---|---|---|
| O(4)–P(1)–O(1) | 114.0(1) | 114.6(3) |
| O(4)–P(1)–N(3) | 114.7(2) | 114.7(3) |
| O(1)–P(1)–N(3) | 104.0(1) | 102.0(3) |
| O(4)–P(1)–N(1) | 116.4(2) | 113.1(3) |
| O(1)–P(1)–N(1) | 102.1(1) | 106.1(3) |
| N(3)–P(1)–N(1) | 103.9(1) | 105.3(3) |
| O(5)–P(2)–O(2) | 112.4(1) | 113.4(3) |
| O(5)–P(2)–N(1) | 119.1(2) | 113.3(3) |
| O(2)–P(2)–N(1) | 100.3(1) | 107.8(3) |
| O(5)–P(2)–N(2) | 112.8(2) | 118.2(3) |
| O(2)–P(2)–N(2) | 108.4(1) | 100.6(3) |
| N(1)–P(2)–N(2) | 102.5(1) | 102.2(3) |
| O(6)–P(3)–O(3) | 114.7(1) | 114.1(3) |
| O(6)–P(3)–N(3) | 115.7(1) | 115.1(3) |
| O(3)–P(3)–N(3) | 101.9(1) | 101.7(3) |
| O(6)–P(3)–N(2) | 112.9(2) | 112.9(3) |
| O(3)–P(3)–N(2) | 106.1(1) | 106.4(3) |
| N(3)–P(3)–N(2) | 104.3(1) | 105.6(3) |
| C(1)–N(1)–P(2) | 116.2(2) | 118.0(5) |
| C(1)–N(1)–P(1) | 120.3(2) | 118.8(5) |
| P(2)–N(1)–P(1) | 119.8(2) | 122.9(3) |
| C(3)–N(2)–P(2) | 118.7(2) | 117.6(5) |
| C(3)–N(2)–P(3) | 118.7(2) | 119.4(5) |
| P(2)–N(2)–P(3) | 122.3(2) | 121.5(3) |
| C(5)–N(3)–P(3) | 119.8(2) | 119.5(5) |
| C(5)–N(3)–P(1) | 118.9(2) | 119.9(5) |
| P(3)–N(3)–P(1) | 121.2(2) | 120.5(3) |
| C(2)–C(1)–N(1) | 110.9(5) | 111.7(6) |
| C(4)–C(3)–N(2) | 112.8(3) | 108.9(11) |
| C(6)–C(5)–N(3) | 112.4(3) | 113.9(7) |
| C(11)–O(1)–P(1) | 122.3(2) | 121.0(4) |
| C(21)–O(2)–P(2) | 120.2(2) | 120.0(4) |
| C(31)–O(3)–P(3) | 120.2(2) | 122.1(4) |

**TABLE 6** Comparative Structural Data for $\lambda^5$-Oxocyclotriphosphazanes

| Property | *cis* $[EtNP(O)(OCH_2CF_3)]_3$ | *trans* $[EtNP(O)(OCH_2CF_3)]_3$ | *trans* $[MeNP(O)(OMe)]_3$ | *trans* $[MeNP(O)(OC_6H_4Me\text{-}4)]_3$ | *trans* $[PhNP(O)(Cl)]_3$ |
|---|---|---|---|---|---|
| Ring Conformation | twist-boat | twist-boat | twist-boat | twist-boat | twist-boat |
| av (P–N), Å | 1.657(3) | 1.659(6) | 1.66(1) | 1.659(2) | 1.661(4) |
| av (P–O), Å | 1.578(2) | 1.562(5) | 1.56(1) | 1.578(3) | 2.000(3)[a] |
| av (P=O), Å | 1.452(2) | 1.459(5) | 1.45(1) | 1.448(5) | 1.446(6) |
| av P–N–P, ° | 121.1(2) | 121.6(3) | 121.6(6) | 123.2(3) | 127.1(2) |
| av N–P–N, ° | 103.9(1) | 104.4(3) | 105.2(6) | 104.8(2) | 103.5(2) |
| $\Sigma N$, ° | 358.6 | 359.4 | 360.0 | 358.5 | 358.6 |
| $\Delta C_2^{(1)}$ | 4.9 | 8.5 | 1.4 | 7.1 | 10.5 |
| $\Delta C_2^{(2)}$ | 8.2 | 12.5 | 6.5 | 11.1 | 13.4 |
| Reference | this work | this work | 7 | 4 | 6 |

[a]P–Cl distance.

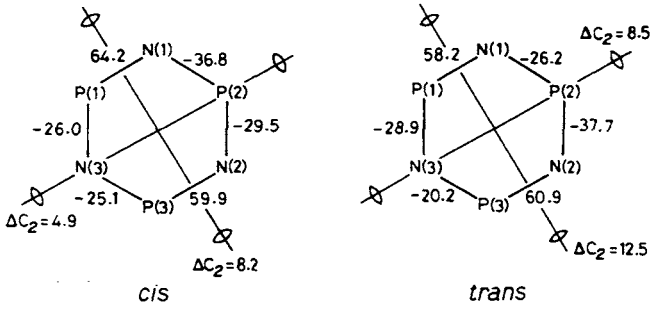


**FIGURE 4** Ring torsional angles and asymmetry parameters calculated for *cis*- and *trans*-$[EtNP(O)(OCH_2CF_3)]_3$ (**1a** and **1b**).

**TABLE 8** Selected Dihedral Angles (Deg) for **1a** and **1b**

| | ***1a*** | ***1b*** |
|---|---|---|
| O(1)–P(1)–N(1)–C(1) | −30.5(3) | −135.4(5) |
| O(2)–P(2)–N(1)–C(1) | 53.2(3) | 105.6(5) |
| O(2)–P(2)–N(2)–C(3) | −110.7(3) | −45.5(7) |
| O(3)–P(3)–N(2)–C(3) | 139.4(3) | −119.0(7) |
| O(1)–P(1)–N(3)–C(5) | 49.4(3) | 102.5(6) |
| O(3)–P(3)–N(3)–C(5) | −96.8(3) | 85.1(6) |
| O(4)–P(1)–N(1)–C(1) | 94.3(3) | −9.0(6) |
| O(5)–P(2)–N(1)–C(1) | −69.8(3) | −20.7(6) |
| O(5)–P(2)–N(2)–C(3) | 14.5(3) | 78.4(7) |
| O(6)–P(3)–N(2)–C(3) | 13.0(3) | 6.9(8) |
| O(6)–P(3)–N(3)–C(5) | 28.3(3) | −38.7(6) |
| O(4)–P(1)–N(3)–C(5) | −75.9(3) | −21.9(7) |

groups in **1b** as a result of the coupling with the adjacent $CF_3$ group. The signal at $\delta$ 62.6 corresponding to the carbon nucleus of the unique $OCH_2$ group further splits into a doublet of quartets ($^2J_{PC}$ = 4.3 Hz) (Figure 1(b)). Likewise, the carbon nuclei of the $CF_3$ groups in **1a** give rise to a quartet at 122.4 with a large $^1J_{CF}$ of 277.5 Hz; in the case of **1b**, two sets of quartets are observed at $\delta$ 122.3 and 122.4 (1:2) with $^1J_{CF}$ of 277 and 278 Hz, respectively.

The NMR spectral data clearly indicate that the *cis*-isomer **1a** will have a structure with an approximate $\underline{C}_3$ symmetry in solution. On the other hand, the data for **1b** suggest that this isomer will have an approximate $\underline{C}_s$ symmetry.

**TABLE 7** Deviations from the Mean Plane for the $P_3N_3$ Ring in **1a** and **1b**

| | *Deviation (Å)* | |
|---|---|---|
| *Atoms* | *cis* | *trans* |
| P1[a] | 0.169(1) | 0.201(2) |
| P2[a] | −0.174(1) | −0.206(2) |
| N2[a] | 0.191(1) | 0.229(5) |
| N3[a] | −0.187(1) | −0.224(6) |
| P3 | −0.552(3) | −0.514(2) |
| N1 | −0.623(3) | −0.510(5) |

[a]Atoms used to calculate the mean plane.

## *Crystal Structures of* **1a** *and* **1b**

In order to further ascertain the molecular geometry, $P_3N_3$ ring conformations, and disposition of exocyclic phosphorus substituents, the structures of both the *cis* and *trans* isomers **1a** and **1b** have been determined by single crystal X-ray diffraction. Perspective views of the molecules [16] are shown in Figures 2 and 3; selected structural parameters are listed in Tables 4 and 5. The structural features of **1a** and **1b** are compared with those reported for other $\lambda^5$-trioxocyclotriphosphazanes in Table 6.

Both mean plane calculations and torsional angles [17] are used to establish the stereochemistry of the $P_3N_3$-phosphazane ring in **1a** and **1b**. The observed torsional angles of the phosphazane rings in **1a** and **1b** are shown in Figure 4. These torsional angles suggest the presence of two orthogonal $C_2$ axes in structures **1a** and **1b**, indicat-

ing a twist-boat conformation for the $P_3N_3$ rings. However, in the ring systems formed by heteroatoms, there are deviations from the ideal conformations; the degree of departure from the ideal twofold symmetry (known as an asymmetry parameter, $\Delta C_2$) will give an estimate of the distortion from the idealized twist-boat conformation. The asymmetry parameters $\Delta C_2$ calculated for **1a** and **1b** are shown in Figure 4; the $\Delta C_2$ for the other known structures are listed in Table 6. These values suggest that the deviation of the *cis* isomer **1a** ($\Delta C_2$ = 4.9 and 8.2) from the ideal twist-boat conformation is less than that for the *trans* isomer ($\Delta C_2$ = 8.5 and 12.5).

Mean plane calculations indicate that, in both the isomers, P(1), P(2), N(2), and N(3) define the bottom of the twist-boat, and the "prow" and "stern" positions are occupied by P(3) and N(1), respectively. There are considerable deviations from the mean plane for the atoms defining prow and stern positions. The observed deviations for **1a** are larger than those for **1b** (Table 7). The ring conformations observed in **1a** and **1b** are different from those for $\lambda^3$-cyclotriphosphazanes. The $P_3N_3$ ring in *cis*-[EtNP($OC_6H_4$Br-4)]$_3$ adopts a chair conformation, while in the *trans* isomer, the ring is in a regular boat conformation [9]. In the *cis* isomer **1a**, all of the trifluoroethoxy groups lie on the same side of the ring while the oxo groups are on the other side of the ring (**2α**, **4α**, **6α**). On the other hand, in **1b** (**2α**, **4β**, **6α**), two of the trifluoroethoxy groups on the phosphorus atoms P(1) and P(2) are on one side of the ring while the third $-OCH_2CF_3$ group on P(3) occupies the flagpole position, as observed in the case of *trans*-$\lambda^3$-cyclotriphosphazanes [EtNP($OC_6H_4$Br-4)]$_3$ and [EtNP($OC_6H_3Me_2$-2,6)]$_3$ [17] and also in other *trans*-$\lambda^5$-trioxocyclotriphosphazanes [4,6,7].

The ring P–N distances fall in the ranges 1.646(3)–1.673(3) Å for **1a** and 1.653(6)–1.666(6) Å for **1b**, with the average values of 1.657(3) and 1.659(6) Å, respectively. These values are in the range observed for $\lambda^5$-trioxocyclotriphosphazanes (Table 6) and bicyclic tetraphosphapentazane, [$(EtN)_5P_4O_4(OC_6H_3Me_2$-2,6$)_2$] (1.647(4) Å) [19]. The average P–N distances on the whole are significantly shorter than the normal P–N single bond distance of 1.75–1.80 Å, indicating P–N multiple bond character in these molecules. The average P–N–P angles for **1a** and **1b** are 121.1(2) and 121.6(3)°, respectively. These are considerably lower than the values observed for $\lambda^3$-cyclotriphosphazanes [9,18] (e.g., the av P–N–P angles for *cis* and *trans* isomers of [EtNP($OC_6H_4$Br-4)]$_3$ are 131° and 133°). The average N–P–N values for **1a** and **1b** are 103.9(1)° and 104.4(3)°, respectively. The sum of angles around the ring nitrogen atoms are close to 360°, as observed in many of the acyclic and cyclic P–N compounds [20].

### *Factors Governing Ring Conformations and P–N Distances*

On the basis of structural data and theoretical studies, we had earlier proposed that the observed $P_3N_3$ ring conformations and short ring P–N distances in the *cis* and *trans* isomers of $\lambda^3$-cyclotriphosphazanes result from (1) minimization of vicinal P–N lone pair and dipolar repulsions and (2) maximization of negative hyperconjugative interactions [21] between the nitrogen lone pair and an adjacent P–X $\sigma^*$ orbital [9]. Unlike in $\lambda^3$-cyclotriphosphazanes, the vicinal lone pair repulsions (between P and N) are absent as the oxo groups substitute lone pairs on phosphorus in **1a** and **1b**. However, dipolar repulsions cannot be ruled out in the *cis* isomer **1a** as all the OR groups are on the same side of the ring. For negative hyperconjugative interactions to be effective, the nitrogen lone pair should have a parallel orientation with either P–O or P=O bonds, i.e., l.p.–N–P–X (X = –O or =O) torsional angle should have a value close to 0 or 180°. In terms of the C–N–P–X torsional angle, a value close to 90° is preferred for maximum negative hyperconjugation. The C–N–P–X (X = –O or =O) torsional angles for **1a** and **1b** are listed in Table 8 and indicate that each of the nitrogen lone pairs has a parallel orientation with a P–O or P=O bond. However, there is a strong preference for the nitrogen lone pair to be oriented parallel with a P–O bond rather than a P=O bond. This is consistent with our observation in the related P–N systems such as bicyclic phosphazane tetraoxides [19] and bisphosphinimines [22].

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