

Malaysia for a Visiting Postdoctoral Research Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with packing diagrams of the molecules, have been deposited with the IUCr (Reference: MU1239). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Fun, H. K., Sivakumar, K., Chua, S. O., Ooi, M. F., Anwair, M. A. S., Gan, E. E. & Jackson, W. R. (1996). *Acta Cryst.* **C52**, 2231–2236.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. University of Göttingen, Germany.
- Siemens (1994). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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## Substituted Imidazonaphthyridine Derivatives. III. $C_{24}H_{28}N_4$ , $C_{24}H_{28}N_4O$ and $C_{23}H_{25}BrN_4$

KANDASAMY SIVAKUMAR,<sup>a†</sup> HOONG-KUN FUN,<sup>a</sup> SWEE-ONG CHUA,<sup>b</sup> MUN-FOO OOI,<sup>b</sup> MASSUD ALLAG S. ANWAIR,<sup>b</sup> EE-KIANG GAN<sup>b</sup> AND WILLIAM ROY JACKSON<sup>c</sup>

<sup>a</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, <sup>b</sup>School of Pharmaceutical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and <sup>c</sup>Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia.  
E-mail: hkfun@usm.my

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## Abstract

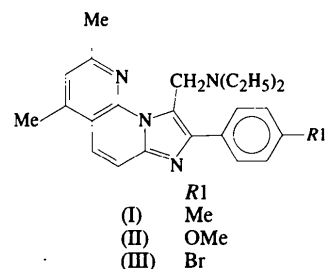
The structures of three 1,2,6,8-tetrasubstituted imidazonaphthyridine derivatives, 1-diethylaminomethyl-6,8-dimethyl-2-(4-methylphenyl)imidazo[1,2-*a*][1,8]naphthyridine, (VII), 1-diethylaminomethyl-2-(4-methoxyphenyl)-6,8-dimethylimidazo[1,2-*a*][1,8]naphthyridine, (VIII), and 2-(4-bromophenyl)-1-diethylaminomethyl-6,8-dimethylimidazo[1,2-*a*][1,8]naphthyridine, (IX), are reported. Two molecules related by a pseudo inversion centre are present in the asymmetric unit of (IX). Intramolecular

† On leave from: Department of Physics, Anna University, Madras-600 025, India.

C—H···N hydrogen bonds are observed in (VII) and (IX) whereas an intermolecular C—H···O hydrogen bond is present in (VIII).

## Comment

We continue our reports of the crystal structures of imidazonaphthyridine compounds (Fun *et al.*, 1996; Sivakumar *et al.*, 1996) with those of three 1,2,6,8-tetra-substituted imidazonaphthyridine compounds, (VII), (VIII) and (IX). All three compounds were prepared by the Mannich reaction (Chua & Jackson, 1995). The bond lengths and angles observed in these structures (Table 2) are normal and comparable with those observed in other imidazonaphthyridine derivatives. However, the orientations of the phenyl rings and of the diethylaminomethyl groups show some differences in the three compounds.



In (IX) two molecules are present in the asymmetric unit and are related by a pseudo inversion centre at (0.22, 0.50, 0.25). The diethylaminomethyl groups in the two molecules (IXA) and (IXB) lie on opposite sides of the imidazonaphthyridine plane (see the relevant torsion angles in Table 2). The dihedral angles between the planes of the imidazonaphthyridine moiety and the phenyl ring are 15.66(4), 29.07(3), 20.6(1) and 17.1(1)° in (VII), (VIII), (IXA) and (IXB), respectively. In (VII), (IXA) and (IXB), the orientation of the diethylaminomethyl group is favourable for intramolecular C12—H12···N4 hydrogen bonding whereas in (VIII) the orientation of this group is entirely different and an intermolecular C—H···O hydrogen bond involving the O1 methoxy atom is observed instead. Hydrogen-bond details: in (VII) C12···N4 3.258(2) Å, C12—H12···N4 151(2)°; in (VIII) C18···O1<sup>i</sup> 3.473(3) Å, C18—H18A···O1<sup>i</sup> 154(3)°; in (IX) C12A···N4 3.258(8) Å, C12A—H12A···N4 154(4)°, C12B···N4B 3.270(8) Å, C12B—H12B···N4B, 152(4)° [symmetry code: (i) 1-x, 1-y, 1-z]. The planar imidazonaphthyridine moieties stack parallel to the (222) planes (spacing 3.412 Å) in (VII), to (202) (spacing 3.351 Å) in (VIII), and to (004) (spacing 3.443 Å) in (IX). In all three structures, the packing involves intermolecular  $\pi$ - $\pi$  interactions.

In 2,6,8-trisubstituted imidazonaphthyridine derivatives, the molecules readily form dimers through C2—H2···N1 bonds (Fun *et al.*, 1996; Sivakumar *et al.*,

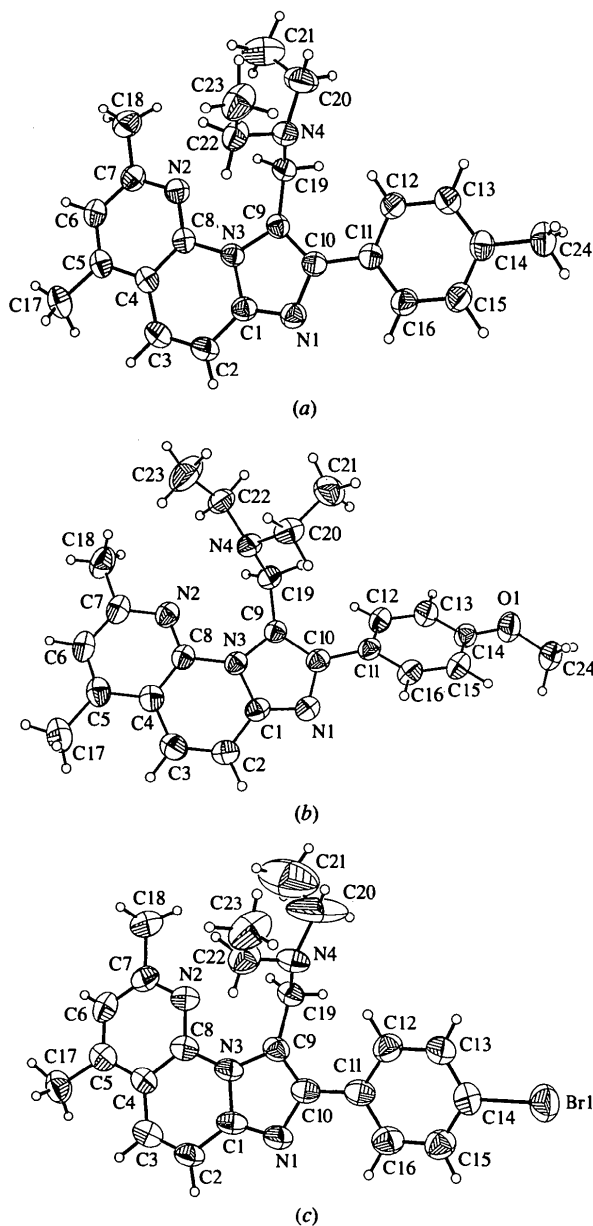


Fig. 1. Views of (a) (VII), (b) (VIII), and (c) a single molecule of (IX), showing numbering schemes; displacement ellipsoids are drawn at the 50% probability level.

1996). The present study shows that the additional substitution of a diethylaminomethyl group at C9 sterically hinders such dimer formation.

### Experimental

Single crystals of (VII), (VIII) and (IX) were obtained by slow evaporation of ethyl acetate solution of the compound.

#### Compound (VII)

##### Crystal data

C<sub>24</sub>H<sub>28</sub>N<sub>4</sub>  
M<sub>r</sub> = 372.50

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71073 Å

#### Triclinic

$P\bar{1}$

$a$  = 9.387 (1) Å  
 $b$  = 10.173 (2) Å  
 $c$  = 11.6980 (1) Å  
 $\alpha$  = 110.36 (1)°  
 $\beta$  = 91.83 (1)°  
 $\gamma$  = 103.34 (1)°  
 $V$  = 1011.3 (2) Å<sup>3</sup>  
 $Z$  = 2  
 $D_x$  = 1.223 Mg m<sup>-3</sup>  
 $D_m$  not measured

#### Data collection

Siemens P4 diffractometer  
 $\theta/2\theta$  scans  
Absorption correction:  
none  
5333 measured reflections  
4502 independent reflections  
3645 observed reflections  
[ $I > 2\sigma(I)$ ]  
 $R_{int}$  = 0.0176

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)]$  = 0.0503  
 $wR(F^2)$  = 0.1604  
 $S$  = 1.096  
4502 reflections  
365 parameters  
All H-atom parameters  
refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0951P)^2 + 0.1094P]$   
where  $P = (F_o^2 + 2F_c^2)/3$

#### Compound (VIII)

##### Crystal data

C<sub>24</sub>H<sub>28</sub>N<sub>4</sub>O  
M<sub>r</sub> = 388.50  
Triclinic  
 $P\bar{1}$   
 $a$  = 7.358 (1) Å  
 $b$  = 10.641 (1) Å  
 $c$  = 13.586 (1) Å  
 $\alpha$  = 96.55 (1)°  
 $\beta$  = 95.64 (1)°  
 $\gamma$  = 98.11 (1)°  
 $V$  = 1039.1 (2) Å<sup>3</sup>  
 $Z$  = 2  
 $D_x$  = 1.242 Mg m<sup>-3</sup>  
 $D_m$  not measured

#### Data collection

Siemens P4 diffractometer  
 $\theta/2\theta$  scans  
Absorption correction:  
none

#### Cell parameters from 38 reflections

$\theta$  = 8–25°  
 $\mu$  = 0.074 mm<sup>-1</sup>  
 $T$  = 293 (2) K  
Prism  
0.56 × 0.52 × 0.40 mm  
Colourless

$\theta_{max}$  = 27.50°  
 $h$  = -1 → 12  
 $k$  = -12 → 12  
 $l$  = -15 → 15  
3 standard reflections  
monitored every 97  
reflections  
intensity decay: <3%

$(\Delta/\sigma)_{max}$  = -0.003  
 $\Delta\rho_{max}$  = 0.34 e Å<sup>-3</sup>  
 $\Delta\rho_{min}$  = -0.21 e Å<sup>-3</sup>  
Extinction correction: none  
Atomic scattering factors  
from *International Tables  
for Crystallography* (1992,  
Vol. C, Tables 4.2.6.8 and  
6.1.1.4)

#### Mo K $\alpha$ radiation

$\lambda$  = 0.71073 Å  
Cell parameters from 35  
reflections  
 $\theta$  = 9–25°  
 $\mu$  = 0.078 mm<sup>-1</sup>  
 $T$  = 293 (2) K  
Prism  
0.58 × 0.44 × 0.32 mm  
Colourless

$\theta_{max}$  = 24.99°  
 $h$  = -1 → 8  
 $k$  = -12 → 12  
 $l$  = -16 → 16

4559 measured reflections  
3642 independent reflections  
2749 observed reflections  
 $[I > 2\sigma(I)]$   
 $R_{\text{int}} = 0.0270$

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0383$   
 $wR(F^2) = 0.1050$   
 $S = 0.976$   
3642 reflections  
374 parameters  
All H-atom parameters  
refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0673P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$

**Compound (IX)****Crystal data**

$\text{C}_{23}\text{H}_{25}\text{BrN}_4$   
 $M_r = 437.38$   
Triclinic  
 $P\bar{1}$   
 $a = 12.134 (1) \text{ \AA}$   
 $b = 12.833 (2) \text{ \AA}$   
 $c = 15.250 (2) \text{ \AA}$   
 $\alpha = 113.98 (1)^\circ$   
 $\beta = 91.33 (1)^\circ$   
 $\gamma = 105.68 (1)^\circ$   
 $V = 2064.9 (5) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.407 \text{ Mg m}^{-3}$   
 $D_m$  not measured

**Data collection**

Siemens P4 diffractometer  
 $\theta/2\theta$  scans  
Absorption correction:  
none  
7970 measured reflections  
6902 independent reflections  
3889 observed reflections  
 $[I > 2\sigma(I)]$   
 $R_{\text{int}} = 0.0248$

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0580$   
 $wR(F^2) = 0.1829$   
 $S = 1.029$   
6876 reflections  
651 parameters  
All H-atom parameters  
refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0973P)^2 + 0.0325P]$   
where  $P = (F_o^2 + 2F_c^2)/3$

3 standard reflections  
monitored every 97  
reflections  
intensity decay: <3%

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.15 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$   
Extinction correction: none  
Atomic scattering factors  
from *International Tables*  
for *Crystallography* (1992),  
Vol. C, Tables 4.2.6.8 and  
6.1.1.4)

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
Cell parameters from 36  
reflections  
 $\theta = 8\text{--}25^\circ$   
 $\mu = 2.007 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
Prism  
 $0.54 \times 0.42 \times 0.32 \text{ mm}$   
Colourless

$\theta_{\text{max}} = 25.00^\circ$   
 $h = -1 \rightarrow 14$   
 $k = -13 \rightarrow 13$   
 $l = -18 \rightarrow 18$   
3 standard reflections  
monitored every 97  
reflections  
intensity decay: <3%

$(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.69 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$   
Extinction correction: none  
Atomic scattering factors  
from *International Tables*  
for *Crystallography* (1992),  
Vol. C, Tables 4.2.6.8 and  
6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$			
	x	y	z	$U_{\text{eq}}$
(VII)				
N1	−0.15401 (13)	−0.00247 (13)	0.90788 (11)	0.0440 (3)
N2	0.21096 (13)	0.38444 (13)	0.90756 (11)	0.0433 (3)
N3	0.02384 (12)	0.19183 (12)	0.91572 (10)	0.0372 (3)
N4	0.23655 (13)	0.03219 (13)	0.69347 (11)	0.0451 (3)
C1	−0.08436 (15)	0.13230 (15)	0.97561 (13)	0.0408 (3)
C2	−0.1062 (2)	0.2166 (2)	1.09554 (14)	0.0471 (3)
C3	−0.0252 (2)	0.3539 (2)	1.15057 (13)	0.0464 (3)
C4	0.0850 (2)	0.41791 (15)	1.08990 (12)	0.0398 (3)
C5	0.1713 (2)	0.5628 (2)	1.14177 (13)	0.0435 (3)
C6	0.2738 (2)	0.6124 (2)	1.07497 (15)	0.0481 (4)
C7	0.2919 (2)	0.5211 (2)	0.95891 (15)	0.0468 (3)
C8	0.11036 (14)	0.33551 (14)	0.97144 (12)	0.0375 (3)
C9	0.02042 (14)	0.08298 (14)	0.80128 (12)	0.0375 (3)
C10	−0.08983 (15)	−0.03349 (15)	0.80051 (13)	0.0396 (3)
C11	−0.14262 (15)	−0.17958 (15)	0.70409 (13)	0.0409 (3)
C12	−0.0621 (2)	−0.2337 (2)	0.60819 (15)	0.0474 (3)
C13	−0.1138 (2)	−0.3729 (2)	0.52197 (14)	0.0493 (4)
C14	−0.2451 (2)	−0.4651 (2)	0.52805 (14)	0.0455 (3)
C15	−0.3240 (2)	−0.4116 (2)	0.6243 (2)	0.0508 (4)
C16	−0.2747 (2)	−0.2718 (2)	0.7102 (2)	0.0482 (3)
C17	0.1521 (2)	0.6618 (2)	1.2666 (2)	0.0568 (4)
C18	0.4047 (2)	0.5730 (2)	0.8858 (2)	0.0646 (5)
C19	0.1125 (2)	0.1003 (2)	0.70312 (13)	0.0407 (3)
C20	0.3040 (2)	0.0311 (2)	0.5819 (2)	0.0680 (5)
C21	0.3859 (3)	0.1756 (4)	0.5790 (3)	0.0880 (7)
C22	0.3396 (2)	0.0920 (2)	0.8065 (2)	0.0496 (4)
C23	0.4518 (2)	0.0049 (2)	0.8026 (3)	0.0682 (5)
C24	−0.2968 (2)	−0.6174 (2)	0.4349 (2)	0.0577 (4)
(VIII)				
O1	0.8022 (2)	1.01390 (10)	0.62203 (8)	0.0593 (3)
N1	0.4519 (2)	0.68893 (11)	0.20632 (9)	0.0437 (3)
N2	0.4251 (2)	0.25357 (11)	0.16652 (9)	0.0434 (3)
N3	0.44554 (14)	0.47673 (10)	0.17618 (8)	0.0370 (3)
N4	0.7985 (2)	0.38627 (10)	0.26795 (8)	0.0416 (3)
C1	0.3932 (2)	0.58590 (12)	0.14139 (10)	0.0402 (3)
C2	0.2905 (2)	0.57636 (15)	0.04629 (11)	0.0483 (4)
C3	0.2362 (2)	0.46122 (15)	−0.00813 (11)	0.0491 (4)
C4	0.2768 (2)	0.34640 (13)	0.03005 (10)	0.0430 (3)
C5	0.2134 (2)	0.22255 (15)	−0.02138 (11)	0.0491 (4)
C6	0.2605 (2)	0.12011 (15)	0.02325 (12)	0.0531 (4)
C7	0.3648 (2)	0.13719 (13)	0.11585 (11)	0.0482 (4)
C8	0.3832 (2)	0.35382 (12)	0.12301 (10)	0.0380 (3)
C9	0.5502 (2)	0.51708 (12)	0.26891 (9)	0.0368 (3)
C10	0.5470 (2)	0.64678 (12)	0.28564 (10)	0.0387 (3)
C11	0.6230 (2)	0.74047 (12)	0.37368 (10)	0.0392 (3)
C12	0.6318 (2)	0.71052 (13)	0.47146 (10)	0.0443 (3)
C13	0.6928 (2)	0.80283 (14)	0.55177 (11)	0.0479 (4)
C14	0.7455 (2)	0.92963 (13)	0.53774 (10)	0.0439 (3)
C15	0.7363 (2)	0.96204 (14)	0.44172 (11)	0.0478 (4)
C16	0.6763 (2)	0.86808 (13)	0.36171 (11)	0.0454 (3)
C17	0.0977 (3)	0.2030 (2)	−0.12088 (14)	0.0651 (5)
C18	0.4138 (3)	0.0254 (2)	0.1650 (2)	0.0660 (5)
C19	0.6569 (2)	0.43304 (14)	0.32496 (10)	0.0397 (3)
C20	0.9624 (2)	0.48299 (15)	0.27067 (12)	0.0501 (4)
C21	1.0908 (3)	0.5148 (2)	0.3672 (2)	0.0698 (5)
C22	0.8398 (2)	0.26300 (14)	0.29430 (13)	0.0521 (4)
C23	0.9406 (4)	0.1951 (2)	0.2184 (2)	0.0861 (7)
C24	0.8276 (3)	1.1471 (2)	0.6125 (2)	0.0602 (5)
(IX)				
Br1A	0.06306 (6)	1.06840 (5)	0.36847 (5)	0.0782 (3)
N1A	0.2039 (3)	0.5807 (4)	0.3658 (3)	0.0516 (10)
N2A	0.5847 (4)	0.5907 (4)	0.3860 (3)	0.0510 (10)
N3A	0.3881 (3)	0.5780 (4)	0.3741 (3)	0.0469 (10)
N4A	0.5254 (4)	0.8008 (4)	0.3029 (3)	0.0591 (12)
C1A	0.2719 (4)	0.5159 (5)	0.3661 (3)	0.0505 (13)
C2A	0.2405 (5)	0.3983 (5)	0.3598 (4)	0.0546 (14)
C3A	0.3213 (5)	0.3474 (5)	0.3630 (4)	0.0548 (13)
C4A	0.4405 (4)	0.4074 (4)	0.3716 (3)	0.0479 (12)

C5A	0.5312 (5)	0.3597 (5)	0.3762 (3)	0.0544 (13)	C1—N1—C10	105.34 (12)	105.43 (11)	105.3 (4)	105.6 (4)
C6A	0.6426 (6)	0.4288 (6)	0.3863 (4)	0.059 (2)	C7—N2—C8	117.73 (13)	116.95 (12)	117.2 (5)	117.8 (5)
C7A	0.6674 (5)	0.5417 (5)	0.3897 (3)	0.0539 (13)	C1—N3—C8	121.11 (11)	121.29 (11)	120.4 (4)	121.8 (4)
C8A	0.4751 (4)	0.5247 (4)	0.3773 (3)	0.0470 (12)	C1—N3—C9	106.42 (11)	106.61 (11)	106.5 (4)	106.5 (4)
C9A	0.3912 (4)	0.6894 (4)	0.3781 (3)	0.0471 (12)	C8—N3—C9	132.46 (11)	131.95 (11)	133.1 (4)	131.7 (4)
C10A	0.2773 (4)	0.6876 (4)	0.3721 (3)	0.0491 (12)	C20—N4—C19	109.76 (13)	112.72 (11)	108.3 (6)	109.4 (4)
C11A	0.2291 (4)	0.7797 (5)	0.3731 (3)	0.0507 (13)	C22—N4—C19	113.02 (11)	111.83 (11)	114.2 (4)	113.7 (4)
C12A	0.2879 (5)	0.8720 (5)	0.3480 (4)	0.0577 (14)	C22—N4—C20	115.15 (14)	113.99 (12)	118.2 (7)	114.1 (5)
C13A	0.2400 (5)	0.9565 (5)	0.3482 (4)	0.0594 (15)	N1—C1—N3	111.83 (12)	111.59 (12)	111.7 (4)	112.2 (4)
C14A	0.1311 (5)	0.9520 (4)	0.3718 (3)	0.0535 (13)	N1—C1—C2	128.44 (13)	128.48 (13)	128.5 (5)	128.9 (5)
C15A	0.0687 (6)	0.8612 (5)	0.3941 (4)	0.0611 (15)	N3—C1—C2	119.72 (13)	119.93 (13)	119.9 (5)	118.9 (5)
C16A	0.1176 (5)	0.7776 (5)	0.3956 (4)	0.0597 (14)	C1—C2—C3	120.30 (14)	119.96 (14)	120.3 (5)	120.9 (6)
C17A	0.5063 (7)	0.2352 (6)	0.3710 (5)	0.070 (2)	C2—C3—C4	120.88 (13)	120.77 (14)	121.7 (5)	121.3 (5)
C18A	0.7904 (5)	0.6167 (6)	0.3980 (5)	0.074 (2)	C3—C4—C5	123.57 (13)	123.06 (13)	125.0 (5)	124.8 (5)
C19A	0.4993 (5)	0.7883 (5)	0.3919 (4)	0.0507 (13)	C3—C4—C8	119.88 (13)	120.22 (13)	119.6 (5)	119.9 (5)
C20A	0.6201 (8)	0.9147 (12)	0.3297 (9)	0.148 (5)	C5—C4—C8	116.55 (13)	116.71 (13)	115.4 (5)	115.3 (5)
C21A	0.7276 (10)	0.9176 (11)	0.3582 (8)	0.184 (5)	C4—C5—C6	118.43 (13)	117.58 (14)	118.6 (5)	119.2 (5)
C22A	0.5355 (6)	0.6934 (6)	0.2253 (4)	0.065 (2)	C4—C5—C17	121.3 (2)	121.3 (2)	120.9 (5)	121.6 (6)
C23A	0.5380 (9)	0.7013 (10)	0.1286 (6)	0.091 (3)	C6—C5—C17	120.3 (2)	121.1 (2)	120.5 (6)	119.2 (6)
Br1B	0.37938 (6)	-0.07592 (6)	0.10759 (5)	0.0867 (3)	C5—C6—C7	120.54 (14)	121.44 (14)	121.6 (6)	120.7 (6)
N1B	0.2347 (4)	0.4158 (4)	0.1243 (3)	0.0542 (11)	N2—C7—C6	122.17 (14)	122.10 (14)	121.9 (5)	121.7 (6)
N2B	-0.1426 (4)	0.4143 (4)	0.1270 (3)	0.0517 (11)	N2—C7—C18	116.7 (2)	116.5 (2)	116.5 (5)	116.8 (5)
N3B	0.0525 (3)	0.4227 (4)	0.1258 (3)	0.0466 (10)	C6—C7—C18	121.1 (2)	121.39 (14)	121.6 (5)	121.5 (6)
N4B	-0.0750 (4)	0.2066 (4)	0.2089 (3)	0.0524 (10)	N2—C8—N3	117.34 (12)	117.26 (12)	116.6 (4)	117.6 (4)
C1B	0.1669 (5)	0.4802 (5)	0.1257 (3)	0.0513 (13)	N2—C8—C4	124.57 (13)	125.18 (12)	125.2 (5)	125.2 (5)
C2B	0.1956 (6)	0.5950 (5)	0.1254 (4)	0.060 (2)	N3—C8—C4	118.09 (12)	117.53 (12)	118.1 (5)	117.2 (5)
C3B	0.1146 (5)	0.6473 (5)	0.1259 (4)	0.0601 (14)	N3—C9—C10	104.51 (11)	104.69 (11)	105.1 (4)	104.7 (4)
C4B	-0.0030 (5)	0.5906 (4)	0.1265 (3)	0.0517 (13)	N3—C9—C19	125.32 (12)	123.92 (11)	125.1 (5)	126.1 (5)
C5B	-0.0932 (5)	0.6382 (5)	0.1250 (3)	0.0566 (14)	C10—C9—C19	130.06 (12)	130.94 (12)	129.8 (5)	128.9 (5)
C6B	-0.2041 (6)	0.5733 (6)	0.1239 (4)	0.063 (2)	N1—C10—C9	111.90 (12)	111.61 (12)	111.5 (4)	111.2 (4)
C7B	-0.2267 (5)	0.4620 (5)	0.1247 (3)	0.0561 (14)	N1—C10—C11	118.95 (12)	118.37 (11)	119.2 (4)	119.7 (4)
C8B	-0.0359 (5)	0.4758 (4)	0.1271 (3)	0.0471 (12)	C9—C10—C11	129.15 (13)	129.99 (12)	129.2 (4)	129.1 (5)
C9B	0.0498 (4)	0.3130 (4)	0.1255 (3)	0.0463 (12)	N4—C19—C9	113.57 (11)	111.58 (11)	114.1 (4)	113.5 (4)
C10B	0.1636 (4)	0.3117 (4)	0.1239 (3)	0.0495 (13)	N4—C20—C21	117.0 (2)	117.59 (14)	117.1 (12)	118.5 (7)
C11B	0.2119 (4)	0.2179 (4)	0.1196 (3)	0.0484 (12)	N4—C22—C23	112.3 (2)	112.8 (2)	112.7 (6)	112.6 (5)
C12B	0.1543 (5)	0.1244 (5)	0.1439 (4)	0.0564 (14)	C1—N3—C9—C19	176.80 (1)	-170.5 (1)	176.7 (5)	-174.23 (5)
C13B	0.2046 (5)	0.0372 (5)	0.1392 (4)	0.0575 (14)	C8—N3—C9—C19	-2.90 (2)	14.0 (2)	-2.9 (9)	6.57 (9)
C14B	0.3119 (5)	0.0422 (5)	0.1105 (4)	0.0606 (14)	C20—N4—C19—C9	169.86 (1)	77.8 (1)	169.3 (7)	-171.82 (5)
C15B	0.3723 (6)	0.1349 (6)	0.0889 (4)	0.068 (2)	C22—N4—C19—C9	-60.21 (2)	-152.2 (1)	-56.7 (7)	59.45 (8)
C16B	0.3221 (5)	0.2207 (5)	0.0923 (4)	0.0622 (15)	C19—N4—C20—C21	68.62 (2)	72.8 (2)	73.2 (2)	-71.75 (8)
C17B	-0.0713 (7)	0.7622 (6)	0.1262 (6)	0.072 (2)	C19—N4—C22—C23	170.68 (2)	163.4 (2)	168.3 (6)	-170.64 (6)
C18B	-0.3483 (5)	0.3894 (6)	0.1242 (5)	0.070 (2)	C20—N4—C22—C23	-62.28 (2)	-67.3 (2)	-62.5 (9)	63.00 (8)
C19B	-0.0563 (5)	0.2151 (5)	0.1167 (4)	0.0517 (13)	C22—N4—C20—C21	-60.35 (3)	-56.1 (2)	-58.7 (3)	56.94 (9)
C20B	-0.1721 (6)	0.0963 (7)	0.1901 (6)	0.094 (2)	N3—C9—C19—N4	104.26 (2)	60.6 (2)	103.0 (6)	-104.88 (6)
C21B	-0.2851 (7)	0.0937 (8)	0.1653 (6)	0.125 (3)	C10—C9—C19—N4	-80.36 (2)	-110.5 (2)	-81.1 (7)	83.41 (7)
C22B	-0.0870 (5)	0.3155 (6)	0.2852 (4)	0.0553 (14)	C19—C9—C10—N1	-176.48 (1)	170.0 (1)	-175.8 (5)	173.91 (5)
C23B	-0.0865 (7)	0.3121 (9)	0.3838 (5)	0.077 (2)	C19—C9—C10—C11	4.40 (3)	-12.0 (2)	3.2 (9)	-4.59 (9)
					N1—C10—C11—C12	-162.90 (2)	144.9 (1)	-158.9 (5)	162.92 (5)
					N1—C10—C11—C16	14.03 (2)	-29.2 (2)	18.4 (8)	-15.56 (8)
					C9—C10—C11—C12	16.37 (3)	-33.0 (2)	22.2 (9)	-18.89 (9)
					C9—C10—C11—C16	-166.80 (2)	152.2 (2)	-160.5 (6)	162.83 (6)

Table 2. Selected geometric parameters (Å, °) for (VII)–(IX)

	(VII)	(VIII)	(IXA)	(IXB)
N1—C1	1.316 (2)	1.318 (2)	1.321 (6)	1.310 (6)
N1—C10	1.379 (2)	1.380 (2)	1.383 (6)	1.378 (6)
N2—C7	1.332 (2)	1.340 (2)	1.331 (7)	1.331 (7)
N2—C8	1.336 (2)	1.336 (2)	1.340 (6)	1.322 (6)
N3—C1	1.395 (2)	1.392 (2)	1.394 (6)	1.386 (6)
N3—C8	1.406 (2)	1.412 (2)	1.414 (6)	1.414 (6)
N3—C9	1.403 (2)	1.399 (2)	1.396 (6)	1.398 (6)
N4—C19	1.475 (2)	1.466 (2)	1.462 (6)	1.472 (6)
N4—C20	1.467 (2)	1.465 (2)	1.487 (10)	1.492 (7)
N4—C22	1.464 (2)	1.463 (2)	1.445 (7)	1.457 (7)
C1—C2	1.417 (2)	1.417 (2)	1.415 (7)	1.422 (8)
C2—C3	1.340 (2)	1.343 (2)	1.327 (8)	1.330 (8)
C3—C4	1.434 (2)	1.438 (2)	1.418 (7)	1.418 (8)
C4—C5	1.412 (2)	1.412 (2)	1.409 (7)	1.395 (7)
C4—C8	1.409 (2)	1.407 (2)	1.414 (7)	1.422 (7)
C5—C6	1.374 (2)	1.376 (2)	1.367 (8)	1.374 (8)
C5—C17	1.502 (2)	1.502 (2)	1.513 (8)	1.533 (8)
C6—C7	1.395 (2)	1.387 (2)	1.377 (8)	1.384 (8)
C7—C18	1.499 (2)	1.498 (2)	1.512 (8)	1.515 (8)
C9—C10	1.379 (2)	1.377 (2)	1.376 (7)	1.385 (7)
C9—C19	1.494 (2)	1.494 (2)	1.498 (7)	1.495 (7)
C10—C11	1.478 (2)	1.475 (2)	1.449 (7)	1.454 (7)
C20—C21	1.506 (4)	1.515 (3)	1.351 (14)	1.402 (10)
C22—C23	1.517 (2)	1.506 (3)	1.519 (9)	1.522 (8)

All H atoms except those attached to C21 in (IXA) and (IXB) were located from difference maps and refined isotropically. Those attached to C21A and C21B were geometrically fixed and allowed to ride.

For all compounds, data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXTLPC (Sheldrick, 1990) (direct methods); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: SHELXTLPC; software used to prepare material for publication: SHELXL93, PARST (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1241). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Chua, S. O. & Jackson, W. R. (1995). Unpublished results.  
 Fun, H. K., Sivakumar, K., Chua, S. O., Ooi, M. F., Anwair, M. A. S., Gan, E. E. & Jackson, W. R. (1996). *Acta Cryst.* **C52**, 2231–2236.  
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.  
 Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. University of Göttingen, Germany.  
 Siemens (1994). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Sivakumar, K., Fun, H. K., Chua, S. O., Ooi, M. F., Anwair, M. A. S., Gan, E. E. & Jackson, W. R. (1996). *Acta Cryst.* **C52**, 2236–2239.

*Acta Cryst.* (1996). **C52**, 2243–2245

## Tris(4-chlorophenyl)phosphine and Tris(4-fluorophenyl)phosphine

OMAR BIN SHAWKATALY,<sup>a</sup> JADIVINDRA SINGH,<sup>a</sup>  
 KANDASAMY SIVAKUMAR<sup>b†</sup> AND HOONG-KUN FUN<sup>b</sup>

<sup>a</sup>Chemical Sciences Programme, Centre for Distance Education, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and <sup>b</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: omarsa@usm.my

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## Abstract

The crystal structures  $C_{18}H_{12}Cl_3P$  (1) and  $C_{18}H_{12}F_3P$  (2) have been determined. In (1) the average P—C distance and C—P—C angle are 1.834 (2) Å and 101.9 (1)°, respectively, while in (2) they are 1.825 (5) Å and 102.5 (2)°. Intermolecular C—H...F hydrogen bonds are observed in (2).

## Comment

There have been numerous X-ray structural determinations of tertiary phosphines,  $PR_3$ , which are widely used as ligands in organo-transition-metal chemistry. However, a search of the October 1995 release of the Cam-

bridge Crystallographic Database (Allen, Kennard & Taylor, 1983) revealed only ten entries for organometallic complexes containing the ligand (1), 16 entries for complexes of (2), and no reports on the structures of the free ligands. As part of our study of substitution of metal carbonyls by group 15 ligands, we have previously determined the structures of several tertiary phosphine ligands (Shawkataly, Chong, Fun & Sivakumar, 1996; Shawkataly, Sivakumar & Fun, 1996). We now report the structures of (1) and (2).

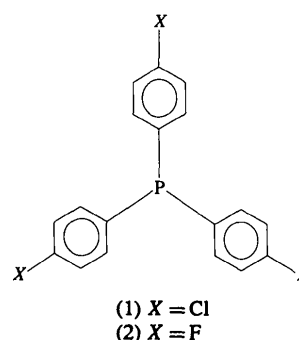


Fig. 1 shows the displacement-ellipsoid plots of the molecules of (1) and (2) with the numbering scheme. Both compounds have the expected geometry whereby the P atom is three coordinate with P—C(Ph) bonds folded back from the lone-pair site, giving a slightly distorted tetrahedral geometry and C—P—C angles less than 109.5°.

In (1) and (2) the mean P—C bond lengths of 1.834 (2) and 1.825 (5) Å are comparable with values of 1.828 (3) and 1.831 (2) Å reported for  $PPh_3$  (Dunne & Orpen, 1991; Daly, 1964) and with the mean value of 1.828 Å for 2239 transition-metal complexes containing  $PPh_3$  (Orpen *et al.*, 1989). The P—C distance in (2), however, is shorter than the corresponding distance of 1.835 (2) Å in *cis*-[Mo(CO)<sub>4</sub>L<sub>2</sub>], L = (2), which has significant Mo—P back bonding (Alyea, Ferguson, Gallagher & Song, 1994). While there are no appreciable differences between the three P—C bond lengths in (1), their variation in (2) may be significant. In (1) and (2) the mean C—P—C bond angles are 101.9 (1) and 102.5 (2)°, respectively. Since both structures were determined at room temperature, a detailed description of the distortion of the phenyl rings (see Domenicano, Vaciago & Coulson, 1975) is not presented. The dihedral angles between the planes of the phenyl rings are 129.40 (7), 92.57 (7) and 66.31 (7)° for (1) and 84.1 (2), 85.0 (2) and 93.6 (2)° for (2). In general, the dihedral angles in  $PPh_3$  and other substituted  $PPh_3$  structures are within 20° of 90° but in (1), an abnormal deviation of 40° is observed.

There are no short contacts observed in (1) but in (2) five possible intermolecular C—H...F hydrogen bonds attributable to the high electronegativity of fluorine have been observed (see Table 5).

† On leave from: Department of Physics, Anna University, Madras-600 025, India.