Acta Cryst. (1999). C55, 373–377

Two C_3-symmetrical tris(*ortho*-substituted) tribenzylamines

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(*Received 23 July 1998; accepted 23 October 1998*)

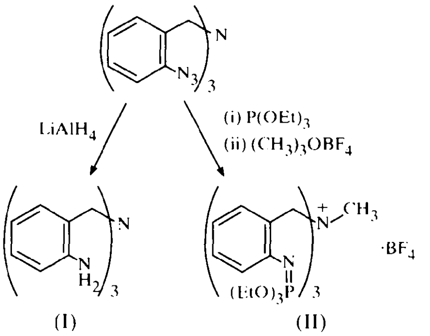
Abstract

The structures of tris(2-aminobenzyl)amine, $C_{21}H_{24}N_4$, (I), and methyltris[2-(triethoxyphosphoranylideneamino)benzyl]ammonium tetrafluoroborate, $C_{40}H_{66}N_4O_9P_3^+\cdot BF_4^-$, (II), have been determined at room temperature and at 150 K, respectively. To our knowledge, this is the first time that a tris(phosphiteimine) compound such as (II) has been described. In (I), all NH_2 groups are involved in weak N—H···N intramolecular hydrogen bonding: two of them act as both donor and acceptor and are responsible for the formation of chains along the *a* axis.

Comment

Polydentate ligands that form cavities around a metal ion are known to influence the structural and functional properties of metal complexes. Extensive interest has recently been devoted to metal complexes of tetradentate tripodal amines such as tren [tris(2-aminoethyl)amine] (Zipp *et al.*, 1974), the most widely used C_3-symmetric tripodal N_4 ligand, as well as the structurally related ligands trpn [tris(3-aminopropyl)amine] (Massoud & Milburn, 1989), tpa [tris(2-pyridylmethyl)amine] (Murthy & Karlin, 1993; Xu *et al.*, 1998) and tepa [tris(2-pyridylethyl)amine] (Che *et al.*, 1990). The construction of new members of this family of ligands is an important direction in the development of modern coordination chemistry (Schrock, 1997). For example, variations in the length and flexibility of the three arms of these tripodal ligands, and in their overall electronic characteristics, could potentially alter their coordinative properties.

Our previous work on tripodal tris(azides) (Alajarín *et al.*, 1997) paved the way for the preparation and characterization herein described of a new C_3-symmetric tripodal tetraamine, tris(2-aminobenzyl)amine, (I), which possesses three N donor atoms forming part of aniline fragments. Compound (I) has been obtained by reduction of tris(2-azidobenzyl)amine with lithium aluminium hydride (see scheme below). Furthermore, we also disclose the crystal structure of the first reported tris(phosphiteimine), (II), which is easily obtainable starting from the same tris(azide) whose reduction yielded compound (I), through its reaction with triethyl phosphite and further methylation of the pivotal N atom with trimethyloxonium tetrafluoroborate. To our knowledge, compounds containing three P^V—N double bonds have rarely been characterized (Johnson, 1993).



The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. In spite of the C_3-symmetric arms of both compounds, only in (II) do the ions sit on crystallographic threefold axes passing through N1, C2, B and F2. The lack of threefold symmetry in (I) is reflected in the bond distances and bond angles but mainly in the conformation of the phenyl rings, which show differences of up to 11° in the N1—C*x*1—C*x*2—C*x*3 (*x* = 1, 2, 3) torsion angles (Table 1).

Several differences regarding the molecular structure of both compounds are noteworthy. The charged central

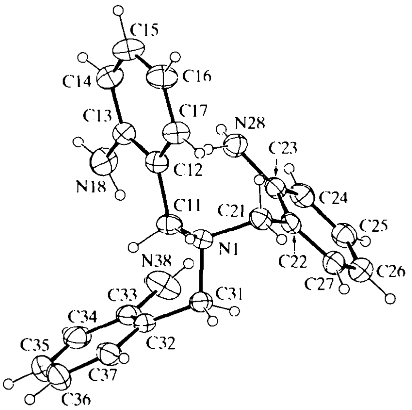


Fig. 1. The molecular structure of (I) showing the numbering scheme. The displacement ellipsoids are drawn at the 30% probability level.

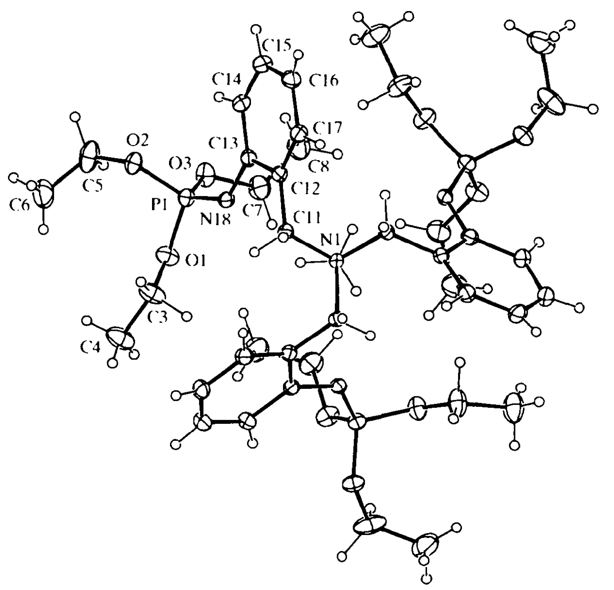


Fig. 2. The molecular structure of (II) along the threefold axis showing the atomic numbering scheme only for the atoms in the asymmetric unit. The displacement ellipsoids are drawn at the 30% probability level.

N atom in (II) shows C—N$^+$ distances greater than in (I) and in the neutral derivatives (see below) retrieved from the Cambridge Structural Database (CSD; Allen *et al.*, 1991). For the latter the mean C—N distance is 1.471 (6) Å, the value in parentheses corresponding to the standard deviation of the sample. In (II), this value agrees with that found in the tripodal tris(phosphazide) [1.519 (11) Å] reported by us (Alajarín *et al.*, 1997). The hybridization of this central N atom in (I) and (II) is sp^3 and the sum of CH_2—N—CH_2 angles $\Sigma\alpha(N1)$ is 329.6 (3) and 325.3 (9)°, respectively.

The influence of the —N═P(OEt)$_3$ substituent is mainly reflected in the external angles at C13. In (I) the two angles are quite alike, while in (II) they are asymmetric, with C14—C13—N18 larger than C12—C13—N18. This situation may be induced by the steric crowding of the —N═P(OEt)$_3$ group, which places the —O3—CH_2—CH_3 chain towards the phenyl ring (C14—C13—N18—P1 and C13—N18—P1—O3, Table 3). This could also be responsible for the differences in the N—P—O angles which follow the trend N18—P1—O1 < N18—P1—O2 < N18—P1—O3, closely related to the conformation of the chain (C13—N18—P1—O1/O2/O3 torsion angles), *trans* for O1 and *gauche* for O2 and O3 (Table 3). The N18 atom lies out the phenyl plane by 0.092 (5) Å.

The internal angles in the phenyl rings at the atoms that carry the substituents (Cx2, Cx3, x = 1, 2, 3) differ slightly from 120° in (I) (Table 1) while in (II) the angle at C13 is smaller than that in (I) by *ca* 2.0° (Table 3). These distortions are ascribable to the electron-donating properties of the substituents (Domenicano & Murray-Rust, 1979). In (II), the P═N and P—O distances, Table 3, are similar to those found in one triethoxyphosphinimide and 12 triphenoxyphosphinimide derivatives retrieved from the CSD [1.524 (12) and 1.561 (12) Å].

A CSD search (Allen *et al.*, 1991) revealed that the structure of only three organic compounds related to (I) with C_3-symmetric arms and not forming a macrocyclic cage had been reported: tribenzylamine itself [CSD refcodes: TBENZA, TBENZA01 (Iwasaki & Iwasaki, 1972)] and two derivatives substituted on the phenyl rings {HIFZIF, 1,3,5,7-tetraazatricyclo-[3.3.1.1^{3,7}]decane-4,4′,4″-(nitrilomethylene)tris(2,6-dimethylphenol) (de Bruyn *et al.*, 1996) and TIBHER, *catena*-[bis(lithium {tris[*o*-(diphenylphosphinylmethyloxy)benzyl]amine} thiocyanate) hemihydrate], (Minacheva *et al.*, 1996)}. A comparison of the geometries of these derivatives with compound (I) shows that the significant differences are due to the conformation of the phenyl rings. The N—C—C(Ph)—C(Ph) angles in the reported structures are in the 4.0–55.0° range. To a lesser extent, differences in the N—C—C and C—N—C angles are also observed.

In (I), the N atoms of the amino groups deviate by 0.031 (2), 0.069 (2) and 0.031 (3) Å from the corresponding phenyl rings and they are approximately sp^2 hybridized [$\Sigma\alpha(Nx8)$ = 359, 349 and 356° for (x = 1, 2, 3)]. All groups are involved in weak N—H···N interactions with the N central atom (Table 2) and the molecules form chains along the a axis *via* N18—H18a···N28 interactions (Fig. 3). The crystal is built up of chains related by twofold screw axes parallel to c and connected by C—H···N and C—H/N—H···π interactions (Table 2, C22–27 and C32–37 represent the centroids of the C22,...,C27 and C32,...,C37 phenyl rings). In (II), the molecules are joined only by van der Waals contacts although an intramolecular C—H···π contact is present (Table 4, C12–17 represents the centroid of the C12,...,C17 phenyl ring).

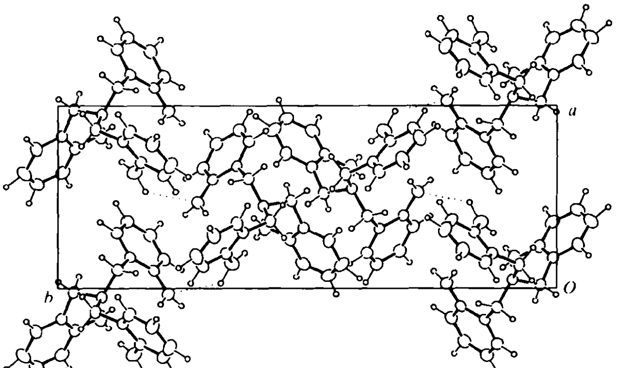


Fig. 3. View of the crystal packing in (I) along the c axis showing two chains of hydrogen-bonded molecules. Dotted lines represent hydrogen bonds.

Experimental

Compound (I). A suspension of lithium aluminium hydride (0.14 g, 3.68 mmol) in dry diethyl ether (15 ml) was added dropwise to a solution of tris(2-azidobenzyl)amine (0.5 g, 1.22 mmol) in the same solvent (15 ml) at room temperature. The resulting mixture was stirred at reflux temperature for 17 h. The reaction flask was then externally cooled to 273 K and an aqueous 10% NaOH solution (50 ml) was added cautiously (Caution: strong H_2 evolution) to destroy the excess of reducing agent. After addition of diethyl ether (60 ml), the organic layer was separated, washed with saturated aqueous NaCl (30 ml), dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude product obtained was purified by column chromatography (SiO_2, hexane/ethyl acetate 6:4), and then crystallized from $CHCl_3$. Yield 82%, m.p. 559–560 K, pale-yellow prisms ($CHCl_3$). Elemental analysis: $C_{21}H_{24}N_4$ (332.45). Calculated (%): C, 75.87, H, 7.27, N, 16.85. Found (%): C, 75.69, H, 7.21, N, 16.79. IR (Nujol) ν: 3435 (*m*), 3358 (*s*), 1624 (*s*), 1580 (*w*), 1495 (*vs*), 1323 (*m*), 1288 (*s*), 1096 (*m*), 1059 (*m*), 961 (*m*), 764 (*vs*) and 756 (*vs*) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.43 (*s*, 2H), 3.86 (*br s*, 2H), 6.53 (*dd*, 1H, J = 1.2, 8.4 Hz), 6.65 (*td*, 1H, J = 0.9, 7.2 Hz), 7.02–7.09 (*m*, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 57.06 (CH_2), 115.55, 117.85, 121.88 (C—CH_2), 128.94, 132.01, 145.60 (C—NH_2). MS (70 eV) *m/z* (%): 332 (M^+, 4), 226 (42), 210 (11), 209 (49), 208 (12), 121 (34), 107 (12), 106 (100), 77 (12).

Compound (II). A solution of tris(2-azidobenzyl)amine (0.5 g, 1.22 mmol) in dry diethyl ether (15 ml) was added dropwise at room temperature to a stirred solution of triethyl phosphite (0.61 g, 3.67 mmol) in the same solvent (N_2 evolution). The resulting mixture was stirred overnight at that temperature, then the solvent was evaporated under reduced pressure, replaced by dry dichloromethane (35 ml), and trimethyloxonium tetrafluoroborate (0.19 g, 1.28 mmol) was then added. After 3 h stirring at room temperature, diethyl ether (50 ml) was slowly added to the reaction mixture and the precipitated solid was collected by filtration, air-dried and crystallized from a mixture of dichloromethane and diethyl ether. Yield 65%, m.p. 499–501 K, colourless prisms (CH_2Cl_2/Et_2O). Elemental analysis: $C_{40}H_{66}N_4O_9P_3BF_4$ (926.71). Calculated (%): C, 51.83, H, 7.13, N, 6.05. Found (%): C, 51.69, H, 6.99, N, 5.96. IR (Nujol) ν: 1602 (*s*), 1501 (*vs*), 1384 (*vs*), 1363 (*vs*), 1141(*s*), 1093 (*vs*), 1029 (*vs*), 987 (*s*), 907 (*m*), 822 (*m*) and 764 (*s*) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.22 (*dt*, 27H, J = 0.9, 7.2 Hz), 2.77 (*s*, 3H), 3.77 (*m*, 18H), 4.81 (*s*, 6H), 6.78 (*t*, 3H, J = 7.2 Hz), 6.87 (*d*, 3H, J = 8.1 Hz), 7.14 (*dt*, 3H, J = 1.5, 8.1 Hz), 7.51 (*m*, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 16.30 ($^3J_{PC}$ = 6.9 Hz), 42.42, 61.98, 64.12 ($^2J_{PC}$ = 7.5 Hz), 118.69, 120.43 ($^3J_{PC}$ = 27.1 Hz, C—CH_2), 122.80 ($^3J_{PC}$ = 7.0 Hz), 130.85, 135.89 ($^4J_{PC}$ = 2.0 Hz), 149.95 ($^2J_{PC}$ = 6.5 Hz, C—NP). ^{31}P NMR (121 MHz, $CDCl_3$) δ: −2.03. MS (70 eV) *m/z* (%): 300 (7), 299 (46), 271 (26), 242 (9), 186 (7), 135 (5), 134 (6), 106 (7), 49 (22), 47 (100).

Compound (I)

Crystal data

$C_{21}H_{24}N_4$
M_r = 332.45
Orthorhombic
$Pna2_1$
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 83 reflections
a = 8.4793 (2) Å
b = 22.5318 (10) Å
c = 9.7774 (3) Å
V = 1868.01 (11) Å^3
Z = 4
D_x = 1.182 Mg m^{-3}
D_m not measured
θ = 2–45°
μ = 0.556 mm^{-1}
T = 293 K
Square prism
0.50 × 0.40 × 0.40 mm
Pale yellow

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1792 measured reflections
1792 independent reflections
1736 reflections with $I > 2\sigma(I)$
θ_{max} = 67.46°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 11$
2 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F
R = 0.029
wR = 0.030
S = 0.891
1736 reflections
226 parameters
H-atom parameters not refined
$w = k/[(a + bF_o)^2][c + d(\sin\theta)/\lambda]$
$(\Delta/\sigma)_{max}$ = 0.0001
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 140 (7)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (I)*

N1—C21	1.476 (2)	C13—N18	1.384 (3)
N1—C11	1.479 (2)	C23—N28	1.390 (2)
N1—C31	1.483 (2)	C33—N38	1.381 (3)
C21—N1—C11	110.4 (1)	N28—C23—C24	120.5 (2)
C21—N1—C31	110.4 (1)	N28—C23—C22	120.7 (2)
C11—N1—C31	108.8 (1)	C24—C23—C22	118.8 (2)
C13—C12—C17	119.0 (2)	C37—C32—C33	119.1 (2)
N18—C13—C12	120.7 (2)	N38—C33—C34	120.7 (2)
N18—C13—C14	120.0 (2)	N38—C33—C32	120.2 (2)
C12—C13—C14	119.4 (2)	C34—C33—C32	119.1 (2)
C27—C22—C23	119.2 (2)		
C21—N1—C11—C12	70.2 (2)	C21—N1—C31—C32	163.5 (2)
C31—N1—C11—C12	168.5 (2)	N1—C11—C12—C13	62.3 (2)
C11—N1—C21—C22	168.7 (1)	N1—C21—C22—C23	−69.8 (2)
C31—N1—C21—C22	−71.0 (2)	N1—C31—C32—C33	−73.3 (2)
C11—N1—C31—C32	−75.2 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···A	D—H	H···A	D···A	D—H···A
N18—H18*b*···N1	0.90	2.38	3.035 (3)	130
N28—H28*b*···N1	0.96	2.55	3.173 (2)	123
N38—H38*b*···N1	0.85	2.58	3.177 (3)	135
N18—H18*a*···N28^{i}	0.96	2.59	3.414 (2)	144
C14—H14···N28^{i}	1.04	2.99	3.791 (3)	135
C31—H31*b*···N38^{ii}	1.00	2.98	3.987 (3)	175
C35—H35···N18^{iii}	0.96	2.93	3.769 (4)	146
N28—H28*a*···C22–27^{i}	0.91	2.63	3.478 (2)	156
C21—H21*a*···C32–37^{ii}	0.97	2.99	3.892 (2)	155

Symmetry codes: (i) $\frac{1}{2}+x$, $\frac{1}{2}-y$, z; (ii) $-x$, $-y$, $\frac{1}{2}+z$; (iii) $1-x$, $-y$, $z-\frac{1}{2}$.

Compound (II)

Crystal data

$C_{40}H_{66}N_4O_9P_3^{3+}\cdot BF_4^-$
M_r = 926.71
Cu $K\alpha$ radiation
λ = 1.5418 Å

Trigonal
$R3$
$a = 18.1459\ (6)$ Å
$c = 12.2532\ (5)$ Å
$V = 3494.1\ (3)$ Å^3
$Z = 3$
$D_x = 1.321$ Mg m^{-3}
D_m not measured

Cell parameters from 65 reflections
$\theta = 2\text{–}45°$
$\mu = 1.781$ mm^{-1}
$T = 150$ K
Square prism
$0.50 \times 0.33 \times 0.33$ mm
Colourless

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.483$, $T_{\max} = 0.556$
2886 measured reflections
1307 independent reflections

1298 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 65.12°$
$h = -17 \rightarrow 18$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 14$
2 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F
$R = 0.042$
$wR = 0.048$
$S = 1.517$
1298 reflections
185 parameters
H-atom parameters not refined
$w = k/[(a + bF_o)^2][c + d(\sin\theta)/\lambda]$
$(\Delta/\sigma)_{\max} = 0.047$

$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: $4.8\ (6) \times 10^2$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute structure: Flack (1983)
Flack parameter = 0.02 (4)

Table 3. *Selected geometric parameters (Å, °) for (II)*

N1—C2	1.488 (8)	P1—O2	1.560 (5)
N1—C11	1.535 (5)	P1—O3	1.566 (7)
C13—N18	1.388 (6)	P1—O1	1.568 (3)
N18—P1	1.538 (7)		
C2—N1—C11	110.5 (2)	C12—C13—C14	118.0 (4)
C11$^{\rm i}$—N1—C11	108.4 (3)	N18—P1—O2	113.8 (4)
C17—C12—C11	119.4 (5)	N18—P1—O3	119.5 (2)
N18—C13—C12	118.0 (4)	N18—P1—O1	109.5 (3)
N18—C13—C14	124.0 (5)		
C2—N1—C11—C12	−61.4 (4)	C14—C13—N18—P1	−6.5 (9)
C11$^{\rm ii}$—N1—C11—C12	59.8 (5)	C13—N18—P1—O1	−171.7 (5)
N1—C11—C12—C13	94.8 (5)	C13—N18—P1—O2	−50.4 (6)
C11—C12—C13—N18	−3.4 (8)	C13—N18—P1—O3	70.7 (7)

Symmetry codes: (i) $1 - y, x - y, z$; (ii) $1 - x + y, 1 - x, z$.

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3a···C12–17$^{\rm i}$	0.94	3.04	3.903 (8)	154

Symmetry code: (i) $1 - y, x - y, z$.

In spite of the different space groups and the analogy of both compounds regarding symmetry, no reduction of the unit cell in (I) could be obtained (Zimmermann & Burzlaff, 1985). Data for both compounds were initially collected at room temperature and the structures were solved by direct methods using *SIR*92 (Altomare *et al.*, 1994). In (II), all atoms displayed very high displacement parameters and a second data collection was carried out at 150 K using an Oxford Cryosystems Cooler (Cosier & Glazer, 1986) and only the structure derived from this data set is retained. The displacement parameters displayed by C5 and C8 are still rather high but no viable disorder model could be developed. In (II), the maximum θ value was limited to 65° due to the presence of the low-temperature equipment. All H atoms were found from a difference synthesis and were kept fixed during refinement. Friedel pairs were collected and the absolute configuration determined according to Flack (1983). The weighting schemes were established in an empirical way so as to give no trends in $\langle w\Delta^2F\rangle$ *versus* $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$: $w = k/[(a + bF_o)^2][c + d(\sin\theta)/\lambda]$ by adjustment of the a, b, c and d parameters (*PESOS*; Martinez-Ripoll & Cano, 1975).

For both compounds, data collection: *Philips PW*1100 *Software* (Hornstra & Vossers, 1973); cell refinement: *LSUCRE* (Appleman, 1971); data reduction: *Xtal DIFDAT SORTRF ADDREF* (Hall *et al.*, 1992); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *Xtal CRYLSQ*; molecular graphics: *Xtal ORTEP*; software used to prepare material for publication: *Xtal BONDLA CIFIO.*

Thanks are given to the DGICYT of Spain for financial support (PB95–1019 and PB96–0001–C03–02).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1283). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 377-381

Three 2,4,6-trimethylpyridine–benzoic acid complexes at 150 K

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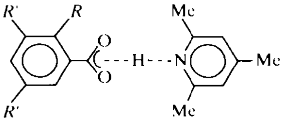
(*Received 5 May 1998; accepted 21 October 1998*)

Abstract

The crystal structures of three 1:1 adducts of 2,4,6-trimethylpyridine with benzoic acid, $C_8H_{11}N{\cdot}C_7H_6O_2$, (I), 2-nitrobenzoic acid, $C_8H_{12}N^+{\cdot}C_7H_4NO_4^-$, (II), and 3,5-dinitrobenzoic acid, $C_8H_{12}N^+{\cdot}C_7H_3N_2O_6^-$, (III), determined at 150 K show that the carboxylic proton has been transferred to the pyridine-N atom only in the nitrobenzoic derivatives, (II) and (III). In all three structures, both moieties are hydrogen bonded to each other *via* their respective OH, (I), and N$^+$H, (II) and (III), groups with N$\cdots$O distances of 2.613 (4), 2.596 (3) and 2.597 (2) Å, respectively.

Comment

As part of our work on proton transfer in heterocyclic compounds, the structure determination of the title compounds (2,4,6-trimethylpyridine carboxylic acid derivatives) was undertaken to establish unambiguously whether the proton of the carboxylic acid is transferred to the 2,4,6-trimethylpyridine molecule. The Cambridge Structural Database (CSD, October 1998 release; Allen *et al.*, 1991) contains three organic 2,4,6-trimethylpyridinium salts, namely 2,4,6-trimethylpyridinium 2,6-dichloro-4-nitrophenolate (CSD refcode REPMUU; Majerz *et al.*, 1995), 2,4,6-trimethylpyridinium pentabromophenolate (GASHAJ; Majerz *et al.*, 1987) and pentachlorophenolate (PARNAX; Majerz *et al.*, 1992), but this is the first time that a neutral complex, (I), has been studied. Of 20 further complexes with other pyridine derivatives, only in bis(benzene-1,3,5-tricarboxylic acid)–tris(4,4′-pyridine) (RAPHAR; Sharme & Zaworotko, 1996) has the proton not been transferred from the carboxylic acid moiety. It is worthy of mention that only in the benzoic acid complex pentakis(4-dimethylaminopyridine)–tris(benzoic acid) decahydrate (ZAPNIN; Biradha *et al.*, 1995) have all three benzoic acid molecules transferred their protons to another three out of the five independent pyridine molecules. The ions, the neutral pyridines and the waters of crystallization are connected as follows: two pyridinium cations form dimers with two neutral pyridines while the remaining pyridinium is hydrogen bonded to a benzoate anion. The other two benzoates and the waters are involved in a complex hydrogen-bonded network.



(I) $R = R' = H$
(II) $R = NO_2$, $R' = H$
(III) $R = H$, $R' = NO_2$

The three title structures differ from each other in the following geometric features. The carboxylic group proton transfers to the pyridine moieties in (II) and (III) (Figs. 1, 2 and 3). This transfer was obvious from the difference Fourier synthesis and is also manifested in the C2—N1—C6 angle of the pyridine ring, in the C10—O17/O18 bonds and in the angles of the carboxylic group around C10 (Tables 1, 3 and 5). The C2—N1—C6 angle is much larger and the C10—O17/O18 bonds and C11—C10—O17/O18 angles are more alike in (II) and (III) than in (I). All these values compare fairly well with those retrieved from the CSD and mentioned above [122.2 (7)°, 1.259 (20), 1.248 (15) Å, 117 (1), 118 (2)° *versus* 117.8 (16)°, 1.307 (12), 1.213 (8) Å, 114 (1), 122 (1)°; the numbers in parentheses represent the standard deviation of the sample for the 17 and three fragments (16 and one structures) of each type found, respectively, among the 20 mentioned above].

The benzene rings are at angles of 47.4 (1), 7.7 (1) and 46.0 (1)° to the pyridine ring in (I), (II) and (III), respectively, and are almost coplanar with their carboxy groups [C12—C11—C10—O17 = −5.9 (5), −24.1 (4) and 10.1 (2)°, respectively]. The large angle in (II) could be due to the *ortho* nitro group attached to C16: it is twisted by −69.4 (3)° to avoid steric hindrance with the neighbouring carboxylate group. The bond angles within the benzene rings show significant differences from ideal values, being affected by the electron-

Acta Crystallographica Section C
ISSN 0108-2701 © 1999