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Synthesis and structural analysis of Bis(2-hydroxyphenyl) phenylamine, PhN(o-C_6H_4OH)$_2$: Comparison with Tris(2-hydroxyphenyl)amine N(o-C_6H_4OH)$_3$

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The molecular structures of N(o-C_6H_4OH)$_3$, PhN(o-C_6H_4OH)$_2$, and p-TolN(o-C_6H_4OMe)$_2$ have been determined by X-ray diffraction, thereby indicating several structural differences. For example, whereas the nitrogen in N(o-C_6H_4OH)$_3$ is pyramidal with $\Sigma_{C—N—C} = 348.3°$, the nitrogen atoms in PhN(o-C_6H_4OH)$_2$ and p-TolN(o-C_6H_4OMe)$_2$ are trigonal planar with $\Sigma_{C—N—C} = 359.9°$ and $\Sigma_{C—N—C} = 360.0°$, respectively. The phenyl and p-tolyl groups of PhN(o-C_6H_4OH)$_2$ and p-TolN(o-C_6H_4OMe)$_2$ lie close to the trigonal plane, while the o-C_6H_4OH and o-C_6H_4OMe groups are almost orthogonal to this plane. The coplanar and orthogonal orientations of the aryl groups of PhN(o-C_6H_4OH)$_2$ and p-TolN(o-C_6H_4OMe)$_2$ are in marked contrast to those of the phenyl groups within Ph_3N, which exhibit dihedral angles in the range 38–52° and approximate D_3 symmetry. The observed structures of PhN(o-C_6H_4OH)$_2$ and p-TolN(o-C_6H_4OMe)$_2$ may be rationalized in terms of maximizing delocalization of the nitrogen lone pair into the phenyl and p-tolyl groups, while minimizing unfavorable overlap with the o-C_6H_4OH and o-C_6H_4OMe groups due to the presence of π-donating *ortho*-substituents; the orthogonal orientation of the o-C_6H_4OH and o-C_6H_4OMe groups is also one that minimizes unfavorable steric interactions between the *ortho*-substituents.

KEY WORDS: Aryloxide; amine; phenol; tris(2-hydoxyphenyl)amine.

Introduction

Alkoxide (OR) and aryloxide (OAr) ligands feature prominently in the chemistry of the transition and main group elements.[1] While the majority of studies have focused on monodentate alkoxides and arlyoxides, multidentate variants have also found extensive use. For example, tris(2-hydroxyphenyl)amine (also called 2,2′,2″-nitrilotriphenol), N(o-C_6H_4OH)$_3$,[2] is a simple example of a molecule that affords tris(aryloxide) derivatives. An interesting aspect of tripodal ligands of the type [N(–L)$_3$], where "–" represents a spacer and L is a donor atom, is that the nitrogen may either coordinate to the metal or remain uncoordinated. A complex is termed an "atrane" if the nitrogen coordinates and a "proatrane" if there is no interaction.[3] Both coordination modes have been reported for derivatives of N(o-C_6H_4OH)$_3$;[2,4–9] however, despite extensive structural studies on derivatives of N(o-C_6H_4OH)$_3$, the molecular structure of N(o-C_6H_4OH)$_3$ itself has not been reported. In this paper, we report the molecular structure of the

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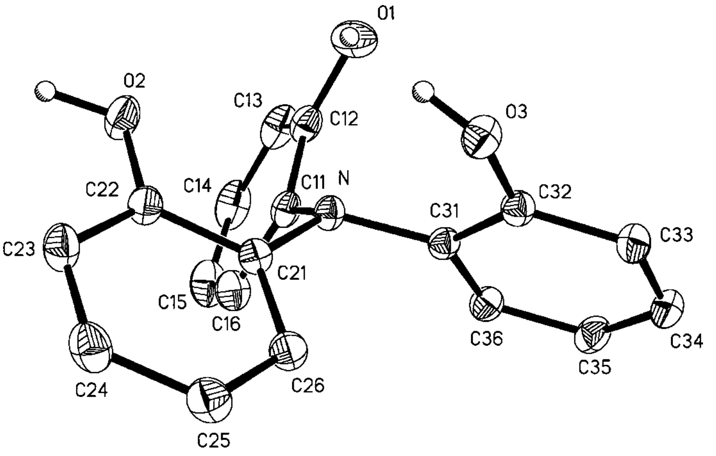


Fig. 1. Molecular structure of $N(o\text{-}C_6H_4OH)_3$ (20% ellipsoids). Selected bond lengths (Å) and angles (°): N−C(11), 1.441(2); N−C(21), 1.432(2); N−C(31), 1.430(2); C(11)−N−C(21), 117.0(1); C(11)−N−C(31), 114.52(9); C(21)−N−C(31), 116.82(9).

tris(phenol) compound $N(o\text{-}C_6H_4OH)_3$ as determined by X-ray diffraction and compare it with that of the analogous bis(phenol) derivative $PhN(o\text{-}C_6H_4OH)_2$.

Results and discussion

Structural characterization of $N(o\text{-}C_6H_4OH)_3$

The molecular structure of $N(o\text{-}C_6H_4OH)_3$[2a] has been determined by single crystal X-ray diffraction studies on crystals obtained from acetone, as illustrated in Figs. 1 and 2, from which there are several noteworthy features. Firstly, it is pertinent to note that $N(o\text{-}C_6H_4OH)_3$ participates in an extensive hydrogen bonding network, as illustrated in Fig. 2. Specifically, two of the OH groups serve as hydrogen bond donors to the oxygen of an acetone molecule [$d_{O\cdots O} = 2.67$ and 2.93 Å], while the other OH serves as a hydrogen bond donor toward the hydroxyl group of another $N(o\text{-}C_6H_4OH)_3$ molecule [$d_{O\cdots O} = 2.76$ Å], thereby forming an infinite strand of $[N(o\text{-}C_6H_4OH)_3(OCMe_2)]$ units. With respect to the structure of the individual $N(o\text{-}C_6H_4OH)_3$ moiety, the three $o\text{-}C_6H_4OH$ groups are arranged in a trigonal pyramid about the nitrogen with an approximate C_3 propeller-like configuration; the magnitude of the displacement of the planes of the phenoxy groups out of the plane defined by the three *ipso* carbon atoms, however, varies

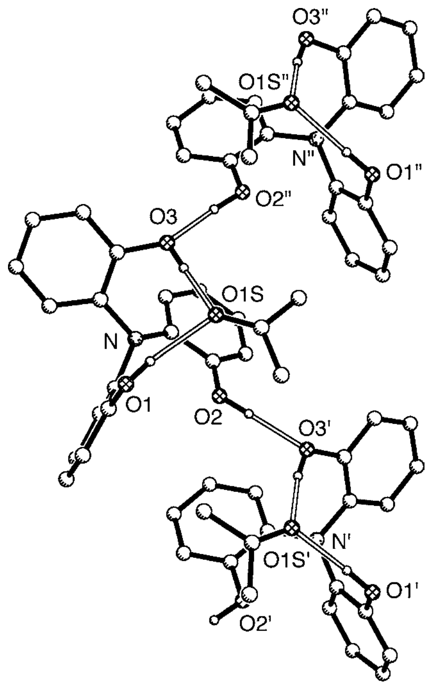


Fig. 2. A portion of the hydrogen bonding network of $[N(o\text{-}C_6H_4OH)_3\cdot(OCMe_2)]$. Hydrogen bonding distances: $d(O1\cdots O1S) = 2.93$ Å, $d(O3\cdots O1S) = 2.67$ Å, and $d(O3\cdots O2'') = 2.76$ Å.

Table 1. Structural Comparison of Some Ar_3N Derivatives

	$\Sigma_{C—N—C}$ (°)[a]	Dihedral range (°)[b]	CCDC#	Reference
$N(C_6Cl_5)_3$	360.0	50–55	CLPHAM	Hayes *et al.*[11]
$N[C_6H_3(o\text{-OMe})_2]_3$	360.0	61–62	YEVVIE	Stoudt *et al.*[12]
$N(C_6H_5)_3$	358.9	38–52	ZZZJLQ01	Sobolev *et al.*[14]
$N(C_6H_4\text{-}p\text{-CHO})(p\text{-Tol})_2$	359.9	28–56	QUTPIE	Xue *et al.*[13]
$N(C_6H_4\text{-}p\text{-Br})(C_6H_3\text{-}o\text{-Br-}p\text{-Me})_2$	355.2	27–57	QUTPOK	Xue *et al.*[13]
$N(o\text{-}C_6H_4OMe)_3$	352.8	40–47	JAPCIM01	Müller and Bürgi[10]
$N(o\text{-}C_6H_4OH)_3$	348.3	36–66		This work
$PhN(o\text{-}C_6H_4OH)_2$	359.9	2–89		This work
$p\text{-TolN}(o\text{-}C_6H_4OMe)_2$	360.0	4–83		This work

[a] $\Sigma_{C—N—C} = 328.5°$ and 360° for idealized "tetrahedral" and trigonal planar geometries, respectively.

[b] Angle between the plane of the aromatic group and the plane of the three *ipso* carbon atoms.

over the substantial range of 36–66°. The extent of pyramidalization at nitrogen may be readily gauged by consideration of the C—N—C bond angles [114.5(1)°, 116.8(1)°, and 117.0(1)°] which total 348.3°, a value that is approximately midway between those for "tetrahedral" ($C—N—C = 109.5°$ and $\Sigma_{C—N—C} = 328.5°$) and trigonal planar ($C—N—C = 120.0°$ and $\Sigma_{C—N—C} = 360.0°$) geometries.

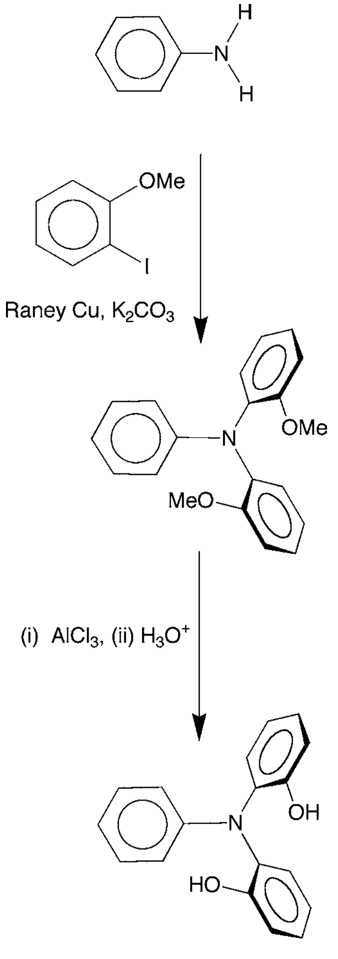
The degree of pyramidalization of $N(o\text{-}C_6H_4OH)_3$ is compared with those of other NAr_3 molecules in Table 1, including the methoxy derivative, $N(o\text{-}C_6H_4OMe)_3$.[10] As expected, the extent of pyramidalization for $N(o\text{-}C_6H_4OH)_3$ [$\Sigma_{C—N—C} = 348.3°$] is comparable to that of the methoxy derivative $N(o\text{-}C_6H_4OMe)_3$ [$\Sigma_{C—N—C} = 352.8°$], but distinctly greater than that of the protonated derivative $[HN(o\text{-}C_6H_4OH)_3]^+$ [$\Sigma_{C—N—C} = 340.5°$]. Of the compounds listed in Table 1, $N(o\text{-}C_6H_4OH)_3$ exhibits the smallest $\Sigma_{C—N—C}$ value (348.3°), thereby indicating that it has the greatest degree of pyramidalization. Indeed, planar geometries are common for NAr_3 derivatives, as illustrated by $N(C_6H_5)_3$ and $N(C_6Cl_5)_3$, with $\Sigma_{C—N—C}$ values of 358.9° and 360.0°, respectively; it should, however, be noted that the planarity of the triarylamines $N(C_6H_5)_3$ and $N(C_6Cl_5)_3$ is in marked contrast to the distinctly nonplanar structures of trialkylamines, e.g. Me_3N [$\Sigma_{C—N—C} = 332.1°$] and $Pr^i{}_3N$ [$\Sigma_{C—N—C} = 348.6°$].[15,16]

Synthesis and structural characterization of $ArN(o\text{-}C_6H_4OR)_2$ (Ar = Ph, p-Tol; R = H, Me)

By analogy to the extensive chemistry that has been developed with the tris(phenol) compound $N(o\text{-}C_6H_4OH)_3$, the closely related bis(phenol) $PhN(o\text{-}C_6H_4OH)_2$ also has considerable potential for applications in coordination chemistry. In this regard, much attention has been given to bis(aryloxide) ligands in which the two aryloxide moieties are directly connected,[17] or joined by a linker, such as CH_2 or S.[18–20] Since the chemistry of the system may be modified profoundly by the nature of the linker,[21] we are interested in exploring the application of bis(aryloxide) ligands with different bridges, such as nitrogen. As such, the synthesis of the bis(phenol) $PhN(o\text{-}C_6H_4OH)_2$ was viewed to be a worthwhile objective.[22,23]

$PhN(o\text{-}C_6H_4OH)_2$ may be readily obtained by a sequence which is analogous to that used for the synthesis of $N(o\text{-}C_6H_4OH)_3$.[2] Specifically, $PhN(o\text{-}C_6H_4OH)_2$ is synthesized by a two-step sequence involving (i) a copper-catalyzed Ullmann-type condensation of $PhNH_2$ with 1,2-$C_6H_4(OMe)I$ to give $PhN(o\text{-}C_6H_4OMe)_2$, followed by (ii) ether cleavage using $AlCl_3$ (Scheme 1).

The molecular structure of $PhN(o\text{-}C_6H_4OH)_2$ has been determined by single crystal X-ray diffraction (Figs. 3 and 4) which indicates the presence of both intramolecular and



Scheme 1.

intermolecular hydrogen bonding interactions, resulting in a dimeric structure that exhibits a "square" array of four O—H···O hydrogen bonds (Fig. 4). For each of the independent dimeric units, the intermolecular O···O separation (2.72 Å and 2.76 Å) is slightly shorter than the corresponding intramolecular O···O separation (2.84 Å and 2.81 Å). More interesting than the nature of the hydrogen bonding interactions, however, is the manner in which the replacement of a single OH group in $N(o\text{-}C_6H_4OH)_3$ by a hydrogen atom influences the structure of the molecule. Significantly, there are several noteworthy modifications. Firstly, as illustrated by comparison of Figs. 1 and 3, the nitrogen atom becomes effectively trigonal planar in $PhN(o\text{-}C_6H_4OH)_2$. Thus, the sum of the C—N—C bond angles for $PhN(o\text{-}C_6H_4OH)_2$ is close to 360° for both of the crystallographically independent molecules: i.e. $\Sigma_{C—N—C} = 359.9°$ for N(1) and $\Sigma_{C—N—C} = 359.8°$ for N(2). Secondly, in contrast to $N(o\text{-}C_6H_4OH)_3$ where the aromatic rings are twisted in the range 36–66° relative to the plane defined by the three *ipso* carbon atoms, the aromatic rings in $PhN(o\text{-}C_6H_4OH)_2$ span the much greater range of 7–89° and 2–85° for the two independent molecules. Furthermore, for each of the independent molecules, it is the phenyl group that lies close to the trigonal plane, with the two phenoxy groups being almost orthogonal.

While it is sterically unfavorable for all three aromatic groups to lie in the trigonal plane, it is worthwhile to consider why it is the phenoxy groups and not the phenyl group that rotate out of the plane. Thus, factors that contribute to causing the phenoxy groups to rotate out of the plane include:

1. The hydroxy groups are larger than a hydrogen atom and steric congestion is relieved when the ring with the larger substituent rings rotate out of the trigonal plane.
2. Delocalization of the nitrogen lone pair into the phenyl ring is more favored than delocalization into the $o\text{-}C_6H_4OH$ ring because the π-donating OH groups destabilize a resonance structure that localizes a negative charge on the *ortho* carbon atom (Fig. 5).
3. A hydrogen bonding interaction between the two phenolic groups (Fig. 3) becomes feasible when the phenoxy groups rotate out of the plane, and thereby stabilizes the structure. However, evidence that the hydrogen bonding interaction is not a dominant factor is provided by the fact that a closely related ether derivative $p\text{-}TolN(o\text{-}C_6H_4OMe)_2$ (Fig. 6) exhibits a very similar orthogonal orientation

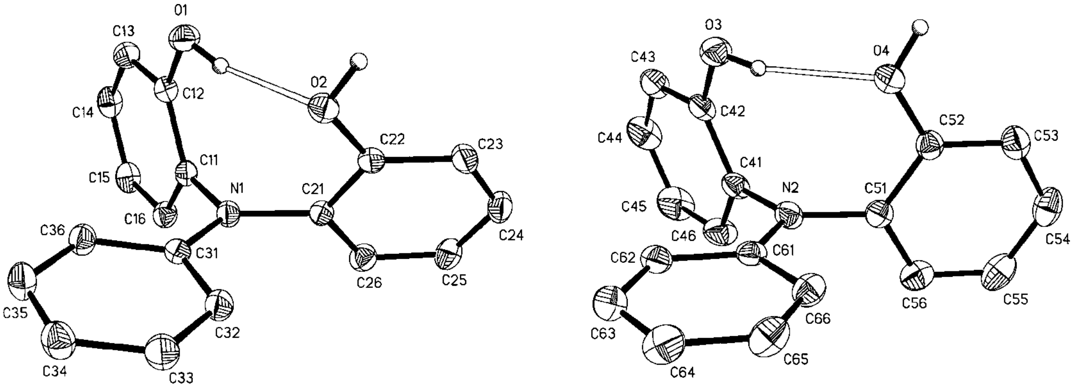


Fig. 3. Structures of the two independent molecules of PhN(o-C_6H_4OH)$_2$ (20% ellipsoids). Selected bond lengths (Å) and angles (°): N(1)—C(11), 1.432(2); N(1)—C(21), 1.433(2); N(1)—C(31), 1.409(2); N(2)—C(41), 1.434(2); N(2)—C(51), 1.434(2); N(2)—C(61), 1.404(2); C(11)—N(1)—C(21), 118.4(1); C(11)—N(1)—C(31), 119.8(1); C(21)—N(1)—C(31), 121.7(1); C(41)—N(2)—C(51), 118.4(1); C(41)—N(2)—C(61), 120.3(1); C(51)—N(2)—C(61), 121.1(1). Dihedral angles (Å) between C11—C21—C31 plane and aromatic rings: C11—C16 89.2, C21—C26 68.0, C31—C36 7.0. Dihedral angles (Å) between C41—C51—C61 plane and aromatic rings: C41—C46 80.4, C51—C56 85.3, C61—C66 1.8.

of the (o-C_6H_4OMe) groups, with the exception that the methoxy groups adopt a "*trans*" disposition such that p-TolN(o-C_6H_4OMe)$_2$ exhibits C_2 symmetry whereas PhN(o-C_6H_4OH)$_2$ exhibits approximate C_s symmetry.

Evidence that delocalization of the nitrogen lone pair into the aryl ring provides a significant contribution to the bonding is provided by the fact that the Ph—N and p-Tol—N bond lengths in PhN(o-C_6H_4OH)$_2$ and p-TolN(o-C_6H_4OMe)$_2$ are consistently shorter than the N—C_6H_4OR bond

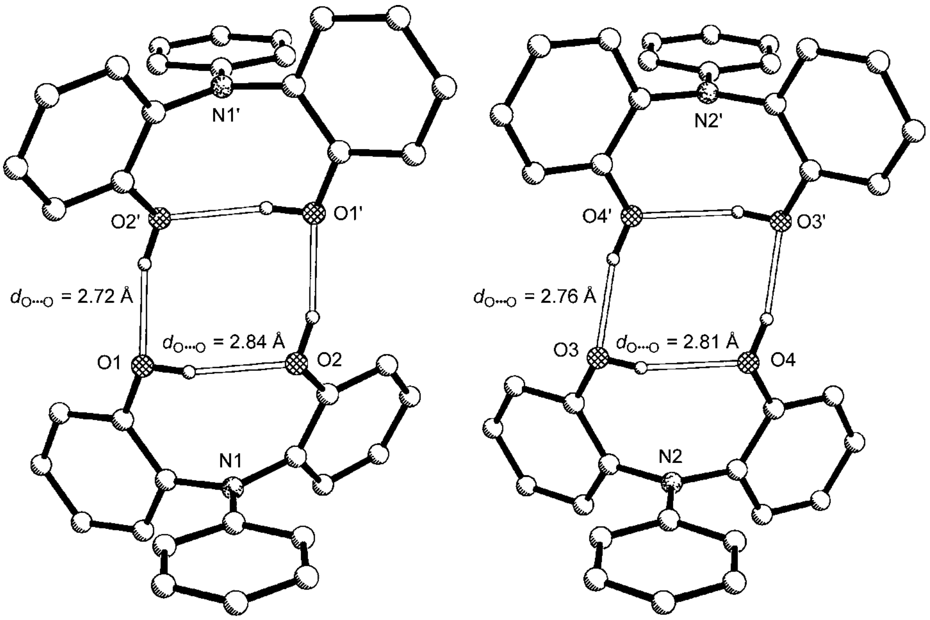


Fig. 4. Hydrogen bonding network for the two independent molecules of PhN(o-C_6H_4OH)$_2$.

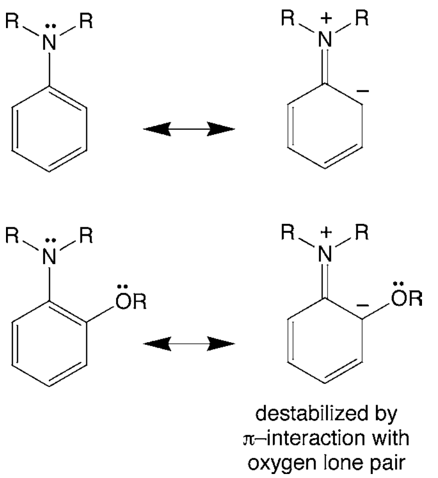


Fig. 5. Resonance structures which illustrate that delocalization of the nitrogen lone pair into the phenyl ring is more favored than that into the C_6H_4OR ring because the negative charge on the *ortho* carbon is destabilized by a π-interaction with the oxygen lone pair.

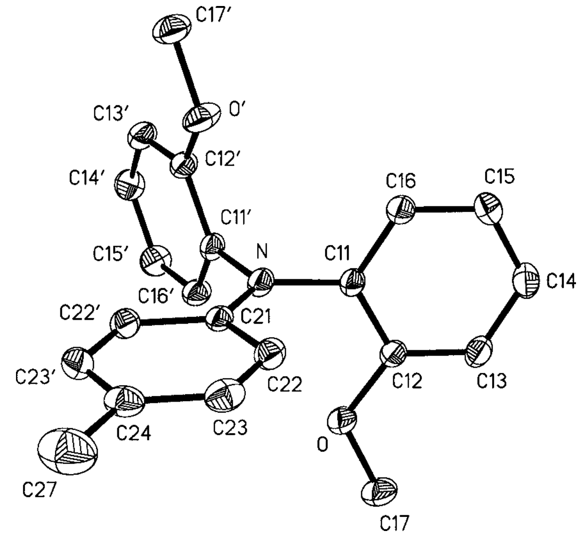


Fig. 6. Molecular structure of p-TolN(o-$C_6H_4OMe)_2$ (20% ellipsoids). Selected bond lengths (Å) and angles (°): N—C(11), 1.433(2); N—C(21), 1.391(3); C(11)—N—C(21), 121.1(1); C(11)—N—C(11′), 117.8(2). Dihedral angles (Å) between C11—C11′—C21 plane and aromatic rings: C11—C16, 82.6; C21—C22′, 3.8.

lengths, as summarized in Table 2. Furthermore, the Ph—N and p-Tol—N bond lengths are also shorter than the N—C_6H_4OH bond length in N(o-$C_6H_4OH)_3$.

Additional support that there is a definite preference for the phenyl rather than aryloxy group to reside in the trigonal plane is provided by geometry optimization calculations on PhN(o-$C_6H_4OH)_2$. Thus, as illustrated in Fig. 7 and Table 3, the geometry optimized structure of PhN(o-$C_6H_4OH)_2$ corresponds closely to the experimental structure in terms of (i) the planarity of the nitrogen center ($\Sigma_{C—N—C} = 358.9°$), (ii) the orientation of the phenyl and phenoxy groups, (iii) the hydrogen bonding interaction between the two hydroxy groups, and (iv) the shorter Ph—N bond length (1.415 Å) than N—C_6H_4OH bond lengths (1.433 Å).

The calculations also provide evidence for delocalization of the nitrogen lone pair into the aryl ring, as illustrated by the bonding and antibonding molecular orbitals involving the nitrogen p-orbital shown in Fig. 8. Of these orbitals, the antibonding combination is the HOMO of the molecule and has a significant contribution on the *ortho* carbon atoms of the phenyl ring. The HOMO would be destabilized if the *ortho* substituent were to be a π-donor (cf. Fig. 5) and thus it is electronically more favored for the C_6H_5 group, rather than the o-C_6H_4OH group, to reside in the trigonal plane.

For further comparison, geometry optimization calculations on N(o-$C_6H_4OH)_3$ (Fig. 9) are also in accord with the experimental observations with the geometry at nitrogen being nonplanar with $\Sigma_{C—N—C} = 350.8°$ (compared to the experimental value of 348.3°) and a propeller-like configuration of the o-C_6H_4OH groups .[24]

To determine the magnitude of the preference for the phenyl group to reside in the trigonal plane, a geometry optimization was performed in which the phenyl group is constrained to be perpendicular to the plane of the three *ipso* carbon atoms (Fig. 7). The energy of this conformation is 8.0 kcal mol^{-1} higher than that of the fully optimized structure; furthermore, the N—Ph bond length of the perpendicular structure (1.443 Å) is greater than that of the fully optimized structure (1.415 Å).

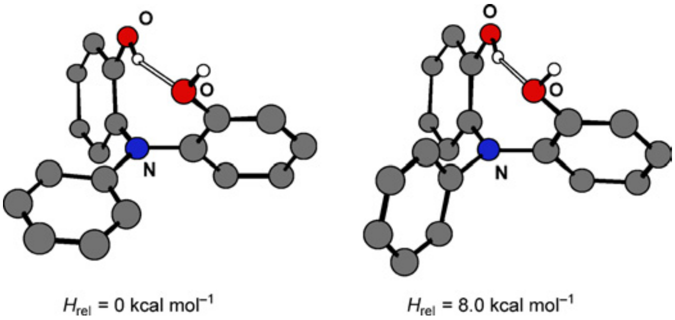
Table 2. Comparison of N−C Bond Lengths

	N(o-C_6H_4OH)$_3$	PhN(o-C_6H_4OH)$_2$	p-TolN-(o-C_6H_4OMe)$_2$
d(N−Ar)/Å	—	1.409(2), 1.404(2)	1.391(3)
d(N−C_6H_4OR)/Å	1.441(2) 1.432(2), 1.430(2)	1.432(2), 1.433(2), 1.434(2), 1.434(2),	1.433(2)

It is interesting to note that the geometries of PhN(o-C_6H_4OH)$_2$ and p-TolN(o-C_6H_4OMe)$_2$ differ considerably from that of Ph_3N which also has an effectively trigonal planar geometry at nitrogen. Specifically, whereas PhN(o-C_6H_4OH)$_2$ and p-TolN(o-C_6H_4OMe)$_2$ have idealized geometries with C_s and C_2 symmetry in which the Ph and p-Tol groups lie in the trigonal plane and the o-C_6H_4OH and o-C_6H_4OMe groups are almost orthogonal, the three phenyl groups of Ph_3N exhibit comparable dihedral angles (38–52°) such that the molecule has approximately D_3 symmetry.[14] The favored structure for Ph_3N is, therefore, one in which all three phenyl groups interact partially with the nitrogen p-orbital, even though the overlap is less efficient since the phenyl groups do not lie in the trigonal plane. Thus, the structure of Ph_3N represents a compromise between electronic and steric factors, i.e. electronic factors favor a planar D_{3h} structure that maximizes delocalization of the nitrogen lone pair, while steric factors favor rotation of the phenyl groups out of the plane.

Previous calculations on Ph_3N not only reproduce the experimentally observed geometry, but also demonstrate that the transition state for rotation about the Ph−N bond is one in which the disposition of the three phenyl groups resemble those of the aryl groups in PhN(o-C_6H_4OH)$_2$ and p-TolN(o-C_6H_4OMe)$_2$, i.e. one in the plane and two orthogonal to the plane (Fig. 10).[25] Thus, the introduction of *ortho*-OH substituents into two of the phenyl rings of Ph_3N causes the stable geometry of the system to resemble that of the transition state for rotation about the Ph−N bond of Ph_3N. Furthermore, the calculations demonstrate that the planar transition state with C_{2v} symmetry (4.73 kcal mol^{-1}) and a single phenyl group in the trigonal plane is considerably more stable than transition states with either pyramidal C_{3v} (12.91 kcal mol^{-1}) or trigonal planar D_{3h} (13.14 kcal mol^{-1}) geometries, as illustrated in Fig. 10.[25] As such, these calculations reinforce the above proposal that, in the absence of steric interactions between *ortho* substituents, the phenyl group electronically prefers to be located in the trigonal plane.

It is also pertinent to note that the geometry optimized structure of PhN(p-C_6H_4OH)$_2$, in which the OH groups are in *para* positions, is



H_{rel} = 0 kcal mol^{-1} H_{rel} = 8.0 kcal mol^{-1}

Fig. 7. Comparison of the freely geometry optimized structure of PhN(o-C_6H_4OH)$_2$ (*left*) with that in which the phenyl ring is constrained to being orthogonal to the trigonal plane (*right*).

Table 3. Comparsion of Experimental and Geometry Optimized Structures of PhN(o-C_6H_4OH)$_2$ (Average Values Where Appropriate)

	Experimental	Geometry optimized	Geometry optimized with phenyl group orthogonal to trigonal plane
d(N−Ph)/Å	1.407	1.415	1.443
d(N−C_6H_4OH)/Å	1.433	1.433	1.431
d(O···O)/Å	2.83	2.94	2.90
$\Sigma_{C-N-C}/^\circ$	359.9	359.9	360.0

similar to the structure of Ph_3N, with none of the aryl groups lying in the trigonal plane (Fig. 11). This observation provides further evidence that steric interactions and hydrogen bonding play a role in causing the substituted rings of PhN(o-C_6H_4OH)$_2$ and p-TolN(o-C_6H_4OMe)$_2$ to rotate out of the trigonal plane, thereby allowing the Ph and p-Tol rings to become coplanar.

Summary

In conclusion, comparison of the structures of N(o-C_6H_4OH)$_3$ and PhN(o-C_6H_4OH)$_2$ demonstrate that replacing one of the *ortho*-OH groups in N(o-C_6H_4OH)$_3$ with hydrogen causes a significant change in the geometry of the nitrogen atom. Specifically, N(o-C_6H_4OH)$_3$ exhibits a pyramidal geometry [$\Sigma_{C-N-C} = 348.3^\circ$] whereas PhN($o$-$C_6H_4OH$)$_2$ exhibits a trigonal planar geometry [$\Sigma_{C-N-C} = 359.9^\circ$]. While Ph_3N also has an effectively trigonal planar geometry, the structure differs from that of PhN(o-C_6H_4OH)$_2$ with respect to the disposition of the aryl groups. Thus, none of the phenyl groups of Ph_3N lie in the trigonal plane, whereas the phenyl group of PhN(o-C_6H_4OH)$_2$ lies close to this plane with the o-C_6H_4OH groups being almost orthogonal; the ether p-TolN(o-C_6H_4OMe)$_2$ has a very similar structure. The observed structures of PhN(o-C_6H_4OH)$_2$ and p-TolN(o-C_6H_4OMe)$_2$ may be rationalized in terms of maximizing delocalization of the nitrogen lone pair into the phenyl and p-tolyl groups, while minimizing unfavorable overlap with the o-C_6H_4OH and o-C_6H_4OMe groups due to the presence of electron releasing *ortho*-substituents. In addition, the orthogonal orientation of the o-C_6H_4OH and o-C_6H_4OMe groups is also one that minimizes unfavorable steric interactions between the

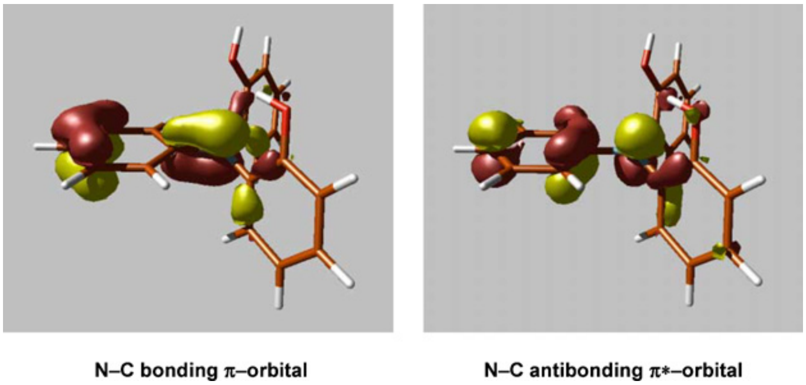


Fig. 8. π Bonding and antibonding molecular orbital involving the nitrogen p-orbital in PhN(o-C_6H_4OH)$_2$.

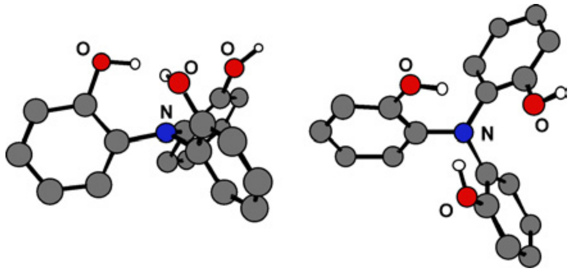


Fig. 9. Two views of the geometry optimized structure of N(o-$C_6H_4OH)_3$.

ortho-substituents and, in the case of the former compound, also maximizes a hydrogen bonding interaction.

Experimental section

General considerations

1,2-C_6H_4(OMe)I, $PhNH_2$, p-$TolNH_2$, K_2CO_3, and Raney copper were obtained from Aldrich, while nitrobenzene was obtained from Fischer Scientific. ^1H and ^{13}C NMR spectra were measured on Bruker 300wb DRX, Bruker Avance 400 DRX, and Bruker Avance 500 DMX spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta = 7.16$ for C_6D_5H) and the ^{13}C resonances ($\delta = 128.0$ for C_6D_6) respectively. All coupling constants are reported in hertz. Mass spectra were measured using a JEOL JMS-HX110HF Tandem Mass Spectrometer (FAB+; ionizing agent: m-nitrobenzylalcohol; direct inlet). IR spectra were recorded as KBr discs on a Nicolet Avatar 370DTGS spectrophotometer.

Synthesis of PhN(o-$C_6H_4OMe)_2$

A mixture of 1,2-C_6H_4(OMe)I (102.5 g, 440 mmol), $PhNH_2$ (20 mL, 220 mmol), K_2CO_3 powder (122 g, 880 mmol), and Raney copper (water decanted) (25 g, 393 mmol) in nitrobenzene (100 mL) was refluxed under a nitrogen atmosphere. The liberated water was removed via a Dean–Stark trap and organic layer from the trap was returned to the reaction mixture. After 3 h, the mixture was cooled, the solution phase was decanted, and the residue was extracted with hot chloroform (3 × 100 mL). The extracts were combined with the decanted reaction mixture and filtered through a bed of silica (ca. 8 cm diameter × 4 cm depth) and the volatile components were removed via a rotary-evaporator. The concentrated extract was distilled under vacuum. The first fraction consisted of the nitrobenzene solvent (ca. 74°C, 0.06 mmHg) and was discarded. PhN(o-$C_6H_4OMe)_2$ distilled as a light orange viscous liquid (160°C, 0.06 mmHg), which solidified upon standing for 1 day at room temperature. The solid obtained was dissolved in a minimal quantity of chloroform (ca. 50 mL) and then hexane (ca. 150 mL) was added. Precipitation was

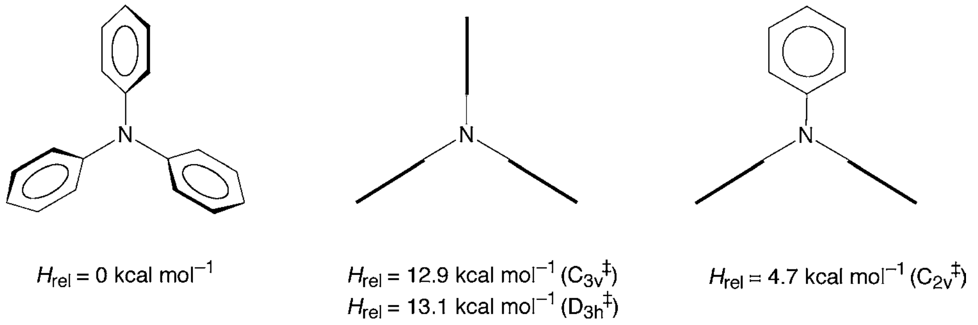


Fig. 10. Energies of various rotamers of Ph_3N (data taken from reference 25).

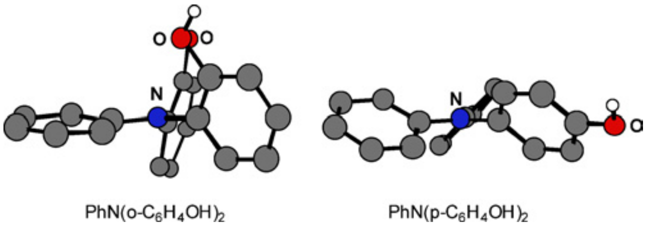


Fig. 11. Comparison of the rotation of the aryl rings from the trigonal planes in PhN(o-$C_6H_4OH)_2$ and PhN(p-$C_6H_4OH)_2$.

induced by reducing the volume of the solution to ca. 50 mL in vacuo. The mixture was filtered and the precipitate obtained was washed with hexane (2 × 20 mL) and dried in vacuo to give PhN(o-$C_6H_4OMe)_2$ as a white powder (16.0 g, 24%). Mass spectrum, $m/z = 305.1$ (M^+). IR data (cm^{-1}): 3061 (w), 3033 (w), 3017 (w), 3002 (w), 2958 (w), 2935 (w), 2834 (w), 1588 (m), 1496 (vs), 1459 (m), 1432 (w), 1334 (s), 1294 (m), 1270 (s), 1238 (s), 1177 (w), 1162 (w), 1114 (m), 1080 (vw), 1045 (m), 1024 (s), 917 (w), 868 (vw), 846 (vw), 796 (w), 778 (vw), 755 (s), 741 (s), 693 (m), 624 (m), 618 (w), 566 (w), 544 (vw), 499 (w), 473 (w). ^1H NMR data (C_6D_6): 3.20 [s, 6H of $(C_6H_5)N(C_6H_4OC\mathit{H}_3)_2$], 6.62 [d, $^3J_{H-H} = 8$, 2H of $(C_6H_5)N(C_6\mathit{H}_4OMe)_2$], 6.76–6.82 [m, 1H of $(C_6\mathit{H}_5)$ and 2H of $(C_6\mathit{H}_4OMe)_2$], 6.88 [d, $^3J_{H-H} = 8$, 2H of $(C_6H_5)N(C_6H_4OMe)_2$], 6.97 [t, $^3J_{H-H} = 8$, 2H of $(C_6H_5)N(C_6\mathit{H}_4OMe)_2$], 7.08 [t, $^3J_{H-H} = 8$, 2H of $(C_6\underline{H}_5)N(C_6H_4OMe)_2$], 7.35 [d, $^3J_{H-H} = 8$, 2H of $(C_6H_5)N(C_6\mathit{H}_4OMe)_2$]. ^{13}C NMR data (C_6D_6): 55.7 [q, $^1J_{H-H} = 143$, CH_3], 113.3 [d, $^1J_{C-H} = 156$, CH], 117.8 [d, $^1J_{C-H} = 160$, CH], 119.5 [d, $^1J_{C-H} = 165$, CH], 121.6 [d, $^1J_{C-H} = 161$, CH], 126.3 [d, $^1J_{C-H} = 160$, CH], 128.8 [d, $^1J_{C-H} = 153$, CH], 129.6 [d, $^1J_{C-H} = 158$, CH], 136.3 [s, quat.], 149.1 [s, quat.], 156.0 [s, quat.]. p-TolN$(C_6H_4OMe)_2$ was obtained in low yield by an analogous procedure. ^1H NMR data ($CDCl_3$): 2.25 [s, 3H of $(C\mathit{H}_3C_6H_4)N(C_6H_4OCH_3)_2$], 3.65 [s, 6H of $(CH_3C_6H_4)N(C_6H_4OC\mathit{H}_3)_2$], 6.61 [d, $^3J_{H-H} = 8.5$, 2H of $(CH_3C_6\mathit{H}_4)N(C_6H_4OMe)_2$], 6.88 [t, $^3J_{H-H} = 7.5$, 2H of $(CH_3C_6H_4)N(C_6\mathit{H}_4OMe)_2$], 6.91–6.94 [m, 2H of $(CH_3C_6\mathit{H}_4)$ and 2H of $(C_6\mathit{H}_4OMe)_2$], 7.10–7.13 [m, 4H of $(CH_3C_6\mathit{H}_4)N(C_6H_4OMe)_2$].

Synthesis of PhN(o-$C_6H_4OH)_2$

A solution of PhN(o-$C_6H_4OMe)_2$ (16.0 g, 52.0 mmol) in dry toluene (100 mL) was treated with $AlCl_3$ (13.9 g, 105 mmol) under a nitrogen atmosphere and refluxed for 90 min giving a purple solution and a white precipitate. After this period, the mixture was cooled to room temperature and the precipitate was isolated. Aqueous HCl (42 mL of 10% w/w) was added to the white precipitate and the mixture was stirred for 30 min. The mixture was filtered and the precipitate obtained was washed with hexanes (3 × 20 mL) and dried in vacuo to give PhN(o-$C_6H_4OH)_2$ as a white solid (11.6 g, 81%). Mass spectrum: $m/z = 277.2$ (M^+). IR data (cm^{-1}): 3390 (m), 3288 (w), 3063 (m), 3037 (w), 1591 (s), 1494 (vs), 1451 (m), 1343 (m), 1315 (s), 1281 (s), 1230 (m), 1205 (m), 1176 (m), 1161 (m), 1146 (m), 1097 (m), 1031 (m), 994 (vw), 945 (vw), 856 (w), 823 (m), 761 (s), 746 (s), 693 (m), 627 (w), 618 (m), 501 (m), 475 (m). ^1H NMR data (C_6D_6): 5.92 [s, $(C_6H_5)N(C_6H_4O\mathit{H})_2$], 6.63–6.75 [m, 3H of $(C_6\mathit{H}_5)$ and 4H of $2(C_6\mathit{H}_4OH)$], 6.86–6.91 [m, 2H of $(C_6H_5)N(C_6\mathit{H}_4OH)_2$], 6.97–7.02 [m, 2H of $(C_6\mathit{H}_5)N(C_6H_4OH)_2$], 7.12–7.14 [m, 2H of $(C_6H_5)N(C_6\mathit{H}_4OH)_2$]. ^{13}C NMR (C_6D_6): 115.6 [d, $^1J_{C-H} = 156$, CH], 117.0 [d, $^1J_{C-H} = 160$, CH], 119.9 [d, $^1J_{C-H} = 160$, CH], 122.1 [d, $^1J_{C-H} = 162$, CH], 128.4 [d, $^1J_{C-H} = 154$, CH], 129.6 [d, $^1J_{C-H} = 160$, CH], 130.4 [d,

Table 4. Crystal, Intensity Collection and Refinement Data

	$N(o\text{-}C_6H_4OH)_3 \cdot Me_2CO$	$PhN(o\text{-}C_6H_4OH)_2$	$p\text{-}TolN\text{-}(o\text{-}C_6H_4OMe)_2$
Lattice	Orthorhombic	Triclinic	Monoclinic
Formula	$C_{21}H_{21}NO_4$	$C_{18}H_{15}NO_2$	$C_{21}H_{21}NO_2$
Formula weight	351.39	277.31	319.39
Space group	*Pbca*	*P-1*	*C2/c*
a (Å)	14.6789(9)	11.236(1)	15.034(1)
b (Å)	11.0975(8)	11.412(1)	14.278(1)
c (Å)	22.730(2)	12.318(1)	10.399(1)
α (°)	90	79.169(2)	90
β (°)	90	82.931(2)	130.325(1)
γ (°)	90	69.533(2)	90
V (Å^3)	3702.7(4)	1450.6(3)	1701.8(2)
Z	8	4	4
Temperature (K)	243	243	243
Radiation (λ, Å)	0.71073	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.261	1.270	1.247
μ (Mo Kα), mm^{-1}	0.087	0.083	0.080
m	0.9576, 0.9334	0.9836, 0.9597	0.9842, 0.9688
θ_{max} (°)	28.3	28.0	28.2
No. of data	4354	6167	1906
No. of parameters	250	396	112
R_1	0.0403	0.0427	0.0463
wR_2	0.1365	0.1148	0.1022
GOF	1.012	1.088	1.065

$^1J_{C-H} = 160$, CH], 132.5 [s, quat.], 148.2 [s, quat.], 153.6 [s, quat.].

X-ray structure determinations

Crystals suitable for X-ray diffraction were obtained by slow evaporation from solutions in the following solvents: $N(o\text{-}C_6H_4OH)_3$, acetone; $PhN(C_6H_4OH)_2$, benzene; and $p\text{-}TolN(C_6H_4OMe)_2$, EtOH/nitrobenzene/pentane. X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector and crystal data, data collection, and refinement parameters are summarized in Table 4. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.03).[26]

Computational details

All calculations were carried out using DFT as implemented in the Jaguar 4.1 suite of ab initio quantum chemistry programs.[27] Geometry optimization was performed with the B3LYP[28] functional employing 6-31G** basis set.[29] The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using the cc-pVTZ(-f) basis sets.[30]

Supplementary material Supplementary crystallographic data for this paper, namely $PhN(o\text{-}C_6H_4OH)_2$ (CCDC #264850), $p\text{-}TolN\text{-}(o\text{-}C_6H_4OMe)_2$ (CCDC #264851), and $N(o\text{-}C_6H_4OH)_3 \cdot Me_2CO$ (CCDC #264852), can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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