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4-Phenyl-1*H*-imidazole (a low-temperature redetermination), 1-benzyl-1*H*-imidazole and 1-mesityl-1*H*-imidazole

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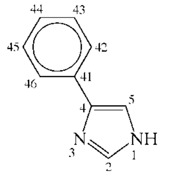
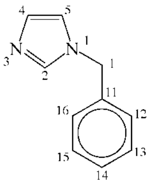
Low-temperature studies of the simple variously substituted imidazole types 4-phenyl-1*H*-imidazole, $C_9H_8N_2$, 1-benzyl-1*H*-imidazole, $C_{10}H_{10}N_2$, and 1-mesityl-1*H*-imidazole, $C_{12}H_{14}N_2$, extend comparisons between parent imidazole species and their derivatives, the pronounced double-bond localization opposite the substituted N atom common to simple neutral species being redistributed aromatically on protonation.

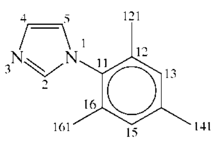
Comment



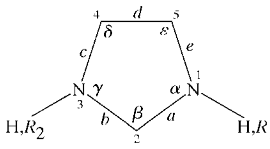
(I)



(II)



(III)



(IV)

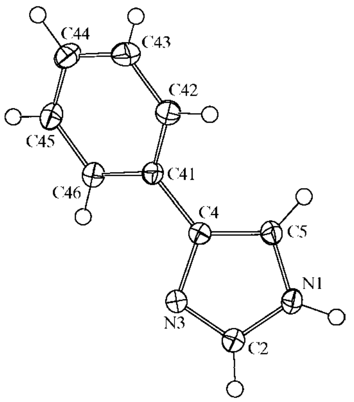


Figure 1
A molecular projection of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius of 0.1 Å.

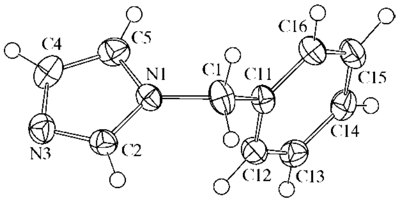


Figure 2
A molecular projection of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius of 0.1 Å.

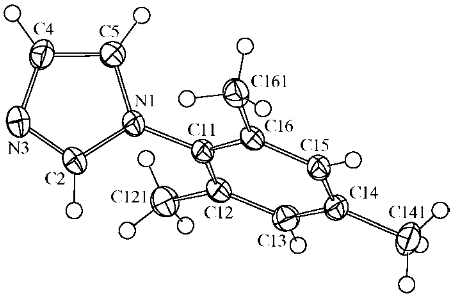


Figure 3
A molecular projection of (III). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with an arbitrary radius of 0.1 Å.

The wide relevance of imidazole (imH) and derivative systems in biological arrays, mono- and oligodentate ligand coordination complexes, and catalytically relevant carbenes has led to experimental and theoretical studies of electron distributions therein (*e.g.* Hsu & Schlemper, 1980; Arduengo *et al.*, 1992). Many structural data are available, some of the more recent being of good precision, but interspecies comparisons and studies of associated structural progressions and evolutions among simple species are relatively sparse. The present study of the title compounds, (I), (II) and (III), comprises additional contributions to the known data; in each case, one molecule, with H-atom positions well defined, comprises the asymmetric unit of the structure. Selected geometric parameters for the non-H atoms are presented in Tables 1–3, and the individual molecules are depicted, normal to their C_3N_2 im planes, in Figs. 1–3.

Recently, an independent study of (I) was published by Claramunt *et al.* (2002); although the temperature of the experiment is not cited in the paper, it would appear from the cell volume and Cambridge Structural Database (Allen, 2002) deposition to have been executed at room temperature. The present determination at a lower temperature offers a more extensive data set, with s.u. values for the bond lengths of the ring reduced generally by a factor of 3. The hydrogen associations and hydrogen bonding, linking successive molecules in a spiral about the major axis, are essentially as described

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and depicted in the earlier report, but the differences in the geometric parameters are substantial and significant.

In Table 4, the geometric parameters of the im rings of (I)–(III) are presented comparatively, together with those of related structures. Although these structure determinations are variable in precision and temperature of execution, a number of useful general comments are possible. The geometric parameters for the im rings of the neutral molecules are generally similar, regardless of replacement of the imine H atom by other substituents or the presence of substituents at other sites in the ring. In respect of the latter, it appears to be widespread that, because of steric and/or electronic and/or lattice force imperatives, the imine H atom tends to lie '*trans*' to any substituent at atoms C4 or C5, so that sites 1 and 4 tend to be occupied, as is the case in (I). Given that disposition, bond *b* is short (see scheme), as is bond *d* (relative to typical aromatic N—C and C—C bonds), with angles β and γ correspondingly enlarged. With protonation of the second ring N atom, the imH_2^+ array becomes more symmetrical, approximating *mm* symmetry, with bonding parameters more evenly aromatic and little altered on passing from imH_2^+ to the imMe_2^+ species that are recorded with comparable precision. A system of particular interest in this context is the 4-(2-$NH_2C_6H_4$)imH array. In this species, the NH_2 substituent of the phenyl ring lies adjacent to the unprotonated imH N atom [N$\cdots$H = 2.11 (4) Å], incipiently protonating it. The torsion angle about the bond between the two rings is −50.3 (6)°, and there is considerable exocyclic asymmetry at the substituted im C atom [121.2 (4)°, *cf*. 129.4 (4)°], the smaller angle being enclosed by the NH_2 substituent. This situation parallels the substituent disposition in (I) (Table 1), where the equivalent torsion angle is −38.6 (2)°. The difference between the pendant N—C(substituent) bond lengths in (II) and (III) is substantial and interesting, reflecting the differences in the electronic characteristics of benzyl and mesityl. The dihedral angle between the two aromatic planes in (III) is 73.7 (1)°.

Experimental

Crystals were obtained by recrystallization from CH_2Cl_2 [for (I) and (II)] and methanol [for (III)].

Compound (I)

Crystal data

$C_9H_8N_2$
M_r = 144.19
Trigonal, *R*3*c*
a = 20.449 (2) Å
c = 9.750 (1) Å
V = 3530.9 (6) Å^3
Z = 18
D_x = 1.221 Mg m^{-3}

Mo *K*α radiation
Cell parameters from 8192 reflections
θ = 2.4–28.6°
μ = 0.08 mm^{-1}
T = 150 (2) K
Slab, colourless
0.40 × 0.35 × 0.14 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.920, $T_{\max}$ = 0.951
13 318 measured reflections

1043 independent reflections
1022 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.026
$\theta_{\max}$ = 29.0°
h = −27 → 27
k = −27 → 27
l = −12 → 12

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.056
S = 1.08
1043 reflections
131 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F^2) + 0.42F^2]$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.16 e Å^{-3}
$\Delta\rho_{\min}$ = −0.16 e Å^{-3}

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

N1—C2	1.351 (2)	N3—C4	1.389 (2)
N1—C5	1.375 (2)	C4—C41	1.473 (3)
C2—N3	1.326 (3)	C4—C5	1.374 (3)
C2—N1—C5	107.32 (13)	N3—C4—C5	109.39 (17)
N1—C2—N3	111.81 (16)	C41—C4—C5	127.85 (17)
C2—N3—C4	105.32 (17)	N1—C5—C4	106.15 (16)
N3—C4—C41	122.67 (19)		

Compound (II)

Crystal data

$C_{10}H_{10}N_2$
M_r = 158.22
Monoclinic, $P2_1/n$
a = 8.222 (2) Å
b = 6.026 (1) Å
c = 16.948 (4) Å
β = 93.283 (3)°
V = 838.3 (3) Å^3
Z = 4

D_x = 1.254 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 3206 reflections
θ = 2.9–29.0°
μ = 0.08 mm^{-1}
T = 150 (2) K
Blade, colourless
0.6 × 0.2 × 0.1 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.94, $T_{\max}$ = 0.96
9721 measured reflections

2124 independent reflections
1533 reflections with $I > 2\,\sigma(I)$
$R_{\rm int}$ = 0.055
$\theta_{\max}$ = 29.0°
h = −11 → 10
k = −8 → 8
l = −22 → 22

Table 2
Selected geometric parameters (Å, °) for (II).

N1—C2	1.352 (2)	N3—C4	1.369 (2)
N1—C5	1.369 (2)	C4—C5	1.358 (3)
N1—C1	1.469 (2)	C1—C11	1.513 (2)
C2—N3	1.316 (2)		
C2—N1—C5	106.67 (13)	C2—N3—C4	104.64 (14)
C2—N1—C1	126.14 (13)	N3—C4—C5	110.77 (15)
C5—N1—C1	127.19 (14)	N1—C5—C4	105.74 (14)
N1—C2—N3	112.19 (13)	N1—C1—C11	112.25 (13)

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

N1—C2	1.368 (4)	C2—N3	1.311 (5)
N1—C5	1.371 (5)	N3—C4	1.383 (5)
N1—C11	1.437 (4)	C4—C5	1.373 (6)
C2—N1—C5	106.7 (3)	C2—N3—C4	105.1 (4)
C2—N1—C11	125.7 (3)	N3—C4—C5	110.1 (3)
C5—N1—C11	127.7 (2)	N1—C5—C4	105.9 (3)
N1—C2—N3	112.2 (3)		

Table 4
Comparative geometries (Å, °).

	a	*b*	*c*	*d*	*e*	*α*	*β*	*γ*	*δ*	*ε*
Neutral molecules										
imH†	1.340 (3)	1.316 (3)	1.369 (3)	1.353 (3)	1.351 (3)	107.3 (2)	111.7 (2)	104.9 (2)	109.9 (2)	106.3 (2)
imMe‡	1.334	1.288	1.363	1.335	1.347	106.6	112.2	104.9	110.1	106.2
imBn§	1.352 (2)	1.316 (2)	1.369 (2)	1.358 (3)	1.369 (2)	106.7 (1)	112.3 (1)	104.6 (1)	110.8 (2)	105.7 (1)
imMes§	1.368 (4)	1.311 (5)	1.383 (5)	1.373 (6)	1.371 (5)	106.7 (3)	112.2 (3)	105.1 (3)	110.1 (3)	105.8 (3)
4Ph(imH)§	1.351 (2)	1.326 (3)	1.389 (2)	1.374 (3)	1.375 (2)	107.3 (1)	111.8 (2)	105.3 (1)	109.4 (2)	106.2 (2)
¶	1.343 (6)	1.305 (7)	1.384 (5)	1.370 (8)	1.368 (6)	105.8 (3)	113.6 (3)	104.9 (3)	108.9 (4)	106.9 (4)
4-(2-$NH_2C_6H_4$)imH††	1.343 (5)	1.319 (5)	1.362 (6)	1.362 (6)	1.356 (6)	107.3 (3)	111.3 (3)	105.8 (3)	108.8 (4)	106.8 (4)
Cationic species										
imH^{2+}‡‡	1.320 (2)	1.313 (2)	1.372 (2)	1.344 (2)	1.365 (2)	108.5 (1)	108.9 (1)	108.6 (1)	106.8 (1)	107.2 (1)
§§	1.319 (4)	1.324 (4)	1.353 (4)	1.350 (4)	1.374 (4)	108.5 (3)	108.5 (3)	109.1 (3)	107.2 (3)	106.7 (3)
	1.315 (4)	1.323 (4)	1.372 (4)	1.340 (4)	1.372 (4)	108.6 (3)	108.9 (3)	108.3 (3)	107.1 (3)	107.0 (3)
imMe^{2+}¶¶	1.324 (2)	1.335 (3)	1.380 (2)	1.346 (3)	1.376 (3)	109.0 (2)	108.3 (2)	108.5 (2)	107.1 (2)	107.1 (2)

† Bolte & Lemke (1999); 173 K. ‡ Wang & Craven (1979); in its co-crystallized 1:1 barbital adduct, 295 K. § This work; *ca* 150 K. ¶ Claramunt *et al.* (2002); 293 K. †† Ishida *et al.* (1990); 295 K. ‡‡ Hsu & Schlemper (1980); X-ray study, 295 K. §§ Blessing (1986); 293 K, two molecules. ¶¶ Arduengo *et al.* (1992); 203 K.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.085$
$S = 1.01$
2124 reflections
149 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F^2) + 0.092F^2]$
$(\Delta/\sigma)_{\max} = 0.013$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Compound (III)

Crystal data

$C_{12}H_{14}N_2$
$M_r = 186.28$
Orthorhombic, $Pna2_1$
$a = 10.346$ (1) Å
$b = 9.222$ (2) Å
$c = 10.803$ (2) Å
$V = 1030.7$ (3) Å^3
$Z = 4$
$D_x = 1.200$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2807 reflections
$\theta = 2.9$–$28.8°$
$\mu = 0.07$ mm^{-1}
$T = 150$ (2) K
Fragment, colourless
0.35 × 0.22 × 0.16 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
21 713 measured reflections
1503 independent reflections
1281 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.072$
$\theta_{\max} = 29.5°$
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.067$
$S = 1.07$
1503 reflections
126 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F^2) + 0.18F^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

H atoms were located from difference Fourier maps, and were then placed at idealized positions [C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C)]. All H-atom parameters were refined for (I) and (II), and fixed for (III).

For the three title compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *Xtal*3.5 (Hall *et al.*, 1995); program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5; molecular graphics: *Xtal*3.5; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1452). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Arduengo, A. J. III, Dias, H. V. R., Harlow, R. L. & Kline, M. (1992). *J. Am. Chem. Soc.* **114**, 5530–5534.
Blessing, R. H. (1986). *Acta Cryst.* B**42**, 613–621.
Bolte, M. & Lemke, A. (1999). Cambridge Structural Database, private deposition, refcode IMAZOL. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
Claramunt, R. M., Santa Maria, M. D., Infantes, L., Cano, F. H. & Elguero, J. (2002). *J. Chem. Soc. Perkin Trans.* 2, pp. 564–568.
Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). *The Xtal*3.5 *User's Manual.* University of Western Australia: Lamb, Perth.
Hsu, B. & Schlemper, E. O. (1980). *Acta Cryst.* B**36**, 3017–3023.
Ishida, T., In, Y., Inoue, M., Kurihara, T., Moriomoto, K., Morisaka, K. & Shibata, K. (1990). *Chem. Pharm. Bull.* **18**, 1803–1809.
Sheldrick, G. M. (1996). *SADABS.* University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wang, A. & Craven, B. M. (1979). *J. Pharm. Sci.* **68**, 361–363.