Imidazolium Phenolates

Norbert Kuhn, Eyad Mallah, Cäcilie Maichle-Mößmer, and Manfred Steimann

Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Reprint requests to Prof. Dr. N. Kuhn. E-mail: norbert.kuhn@uni-tuebingen.de

Z. Naturforsch. **2009**, *64b,* 835 – 839; received March 20, 2009

Dedicated to Professor Helmut Werner on the occasion of his 75th birthday

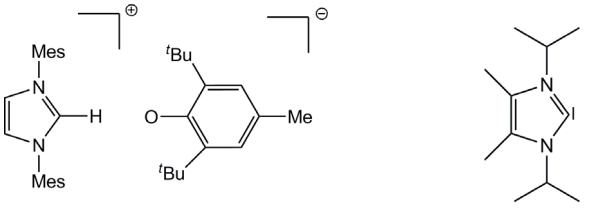
1,3-Diisopropyl-4,5-dimethylimidazolium phenolate (**4a**), pentafluorophenolate (**4b**), and pentachlorophenolate (**4c**) are obtained from 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**2**) and the corresponding phenols **3** as stable crystals in excellent yields. The crystal structure analyses of compounds **4** reveal the presence of ion pairs linked by almost linear C–H···O hydrogen bonds. With 4-hydroxypyridine (**5**), the carbene **2** gives 1,3-diisopropyl-4,5-dimethylimidazolium 4-pyridinolate (**6**) whose crystal structure analysis indicates the ions to be connected by a C–H···N bond.

Key words: Heterocycles, Imidazole, Phenol, Hydrogen Bond, Crystal Structure

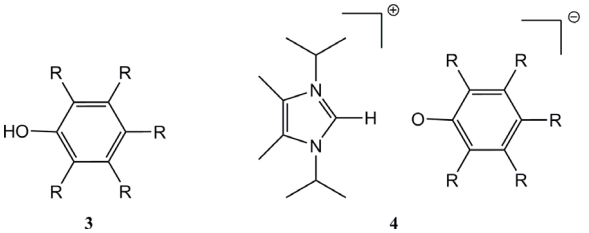
Introduction

Weak hydrogen bonds have attracted considerable interest in structural chemistry [1]. In 2H-imidazolium salts, the ions are commonly linked by hydrogen bonding; these compounds play an important role in the construction of ionic liquids [2].

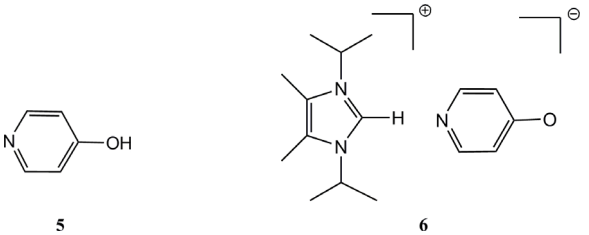
The first synthesis of a stable heterocyclic carbene proceeded *via* deprotonation of the corresponding imidazolium ion with *in situ* generated sodium *tert*-butylate [3]. Some years ago, the structure of 1,3-dimesitylimidazolium 2,4,6-tri-*tert*-butylphenolate (**1**) has been reported, and the results appear to imply the need of sterical hindrance for the stabilization of this salt [4]. Continuing our investigations on the structural chemistry of imidazolium salts [5 – 8] we report on the syntheses and structures of some stable imidazolium phenolates.



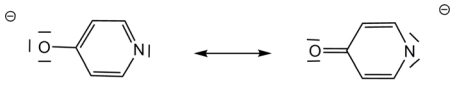
1 **2**



3 **4**



5 **6**



7

Results and Discussion

As expected, the carbene **2** reacts readily with phenols **3** in diethyl ether, and from this mixture the imidazolium salts **4** [R = H (**a**), F (**b**), Cl (**c**)] precipitate as stable colorless salts. The NMR data of their solutions in polar solvents (see Experimental Section) suggest the presence of separated ions. The crystal structure analyses of **4**, however, reveal their ions to be linked by hydrogen bonds in the solid state (Table 1, Figs. 1 – 3).

0932–0776 / 09 / 0700–0835 $ 06.00 © 2009 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

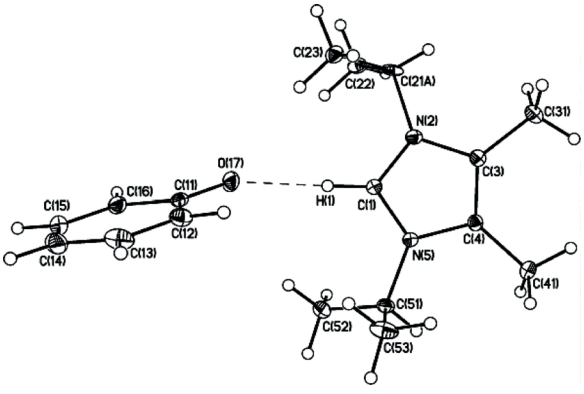


Fig. 1. Molecular structure of the ion pair of $C_{17}H_{26}N_2O$ (**4a**) in the crystal.

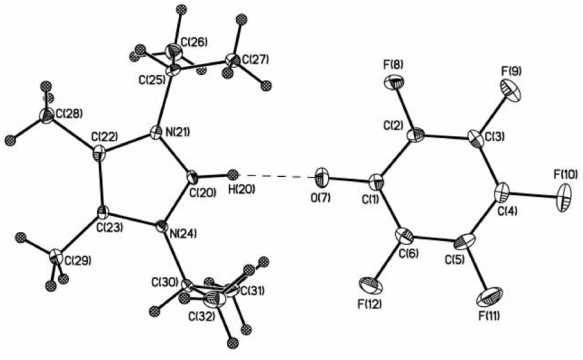


Fig. 2. Molecular structure of the ion pair of $C_{17}H_{21}F_5N_2O$ (**4b**) in the crystal.

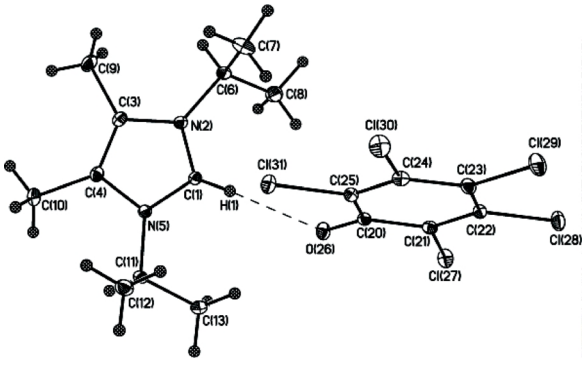


Fig. 3. Molecular structure of the ion pair of $C_{17}H_{21}Cl_5N_2O$ (**4c**) in the crystal.

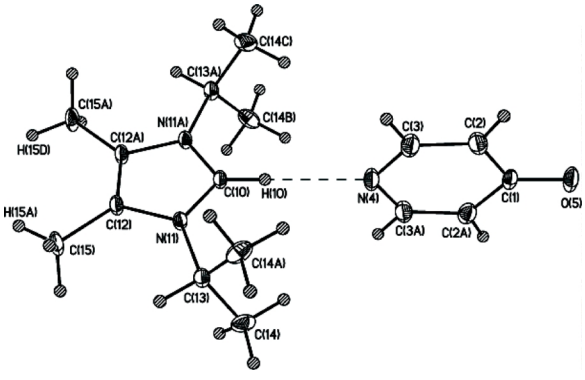


Fig. 4. Molecular structure of the ion pair of $C_{16}H_{25}N_3O$ (**6**) in the crystal.

Table 2 contains the structural details of the interionic hydrogen bonds in **4** which are close to linearity. The structural parameters inside the ions are in the expected range (Tables 3 – 5).

Similarly, the salt **6** is obtained from the carbene **2** and 4-hydroxypyridine (**5**). In the crystals of **6** (Table 6, Fig. 4), the imidazolium ions are linked by C–H···N bonds. In addition, we observe weak contacts between the phenolate oxygen atoms and methyl protons of a neighboring cation (Table 2).

Apparently, in the resonance structures of the anion **7** the pyridonate form predominates [11]. In fact, the solid state structure of **6** corresponds to the crystal structure of 4-pyridone 6/5 hydrate [12] where also N–H···O hydrogen bonds are present while in its 4-nitrophenyl adduct both N–H···O and O–H···O bonds were detected [13].

The O···H distances of the salts **4** do not correlate with the base strengths of their phenolate ions. Thus, packing effects seem to predominate. In comparison with the structure of **1**, a marked lengthening of the O···H distances is observed.

^{13}C NMR data of a CD_3OD solution reveal the carbene **2** to be protonated also by methanol, as indicated by the strong shift of C^2 (**2**: δ = 205.9 [9]) up to 125 ppm. Interestingly, the carbene **2** may be recovered unchanged on evaporation of the solvent. Thus, dissolving **2** in methanol offers a useful method to store the carbene in an air-stable form.

Over all, solid state structures and stabilities of imidazolium alcoholates are not correlated directly with the basicity of their anions. Apparently, the structures are strongly influenced by packing effects, and the decomposition of the methylate salt *in vacuo* is due to the high volatility of methanol.

Experimental Section

All reactions were performed in purified solvents under argon. 2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidaz-

Table 1. Crystal data and structure refinement for $C_{17}H_{26}N_2O$ (**4a**), $C_{17}H_{21}F_5N_2O$ (**4b**), $C_{17}H_{21}Cl_5N_2O$ (**4c**) and $C_{16}H_{25}N_3O$ (**6**).

	4a	**4b**	**4c**	**6**
Empirical formula	$C_{17}H_{26}N_2O$	$C_{17}H_{21}F_5N_2O$	$C_{17}H_{21}Cl_5N_2O$	$C_{16}H_{25}N_3O$
Formula weight	274.4	364.4	446.6	275.4
Temperature, K	173			
Wavelength; λ, Å	MoK_α; 0.71073			
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	*Cmcm*
a, Å	12.422(1)	8.661(1)	8.678(1)	12.029(1)
b, Å	9.771(1)	13.833(1)	10.060(1)	13.537(1)
c, Å	13.740(2)	14.752(2)	23.425(2)	9.959(2)
β, deg	107.80(1)			
Volume, Å^3	1587.9(3)	1767.4(4)	2045.1(2)	1621.0(4)
Z	4	4	4	4
$D_{calcd.}$, g cm^{-3}	1.148	1.369	1.451	1.128
μ (MoK_α), mm^{-1}	0.071	0.122	0.718	0.072
$F(000)$, e	600	760	920	600
θ, deg	3.06 – 26.37	3.10 – 26.37	3.22 – 26.36	3.39 – 26.37
Refls. coll./indep.	21946/3240	24963/3619	24012/4175	11310/920
Refinement method	Full-matrix least-squares on F^2			
Param. refined	285	307	311	93
Final $R_1/wR2$ [$I \geq 2\sigma(I)$]	0.0613/0.0961	0.0873/0.1147	0.0237/0.0556	0.0578/0.1281
Final $R_1/wR2$ (all data)	0.0675/0.0992	0.1196/0.1233	0.0252/0.0562	0.0634/0.1312
Goodness-of-fit on F^2	1.092	1.219	1.100	1.207
Extinction coefficient	0.000(1)	0.006(1)	0.001(1)	0.007(1)
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	$+0.537/-0.311$	$+0.225/-0.236$	$+0.177/-0.217$	$+0.232/-0.149$

Table 2. Bond lengths (Å) and angles (deg) of the interionic hydrogen bonds C–H$\cdots$E[a,b].

	C–H	H$\cdots$E	C–H$\cdots$E
1[c]	–	1.88(3)	169(2)
4a	0.98(1)	2.00(1)	179(1)
4b	0.93(2)	2.07(1)	172(1)
4c	0.84(2)	2.27(2)	177(1)
6[d]	0.93(2)	2.23(1)	180[e]

[a] E = O (**1**, **4a** – **c**), N (**6**); [b] the hydrogen atoms in the structure determinations of **4a** – **c** and **6** were placed in idealized positions and subsequently refined with isotropic displacement parameters; [c] ref. [4]; [d] O(5)$\cdots$H(15A) 2.479; [e] C(10), H(10) and N(4) lie on two perpendicular crystallographic mirror planes.

Table 3. Selected bond lengths (Å) and angles (deg) for $C_{17}H_{26}N_2O$ (**4a**).

N(5)–C(1)	1.320(2)	N(5)–C(4)	1.388(2)
N(2)–C(3)	1.388(2)	C(3)–C(4)	1.338(2)
C(1)–N(2)	1.322(2)	C(11)–C(16)	1.415(2)
C(11)–O(17)	1.288(2)	C(11)–C(12)	1.410(2)
C(12)–C(13)	1.381(2)	C(13)–C(14)	1.374(2)
C(14)–C(15)	1.374(2)	C(15)–C(16)	1.375(2)
C(1)–N(5)–C(4)	109.8(1)	N(5)–C(1)–N(2)	107.2(1)
C(1)–N(2)–C(3)	110.1(1)	C(4)–C(3)–N(2)	106.2(1)
C(3)–C(4)–N(5)	106.8(1)	O(17)–C(11)–C(12)	122.8(1)
O(17)–C(11)–C(16)	122.2(1)	C(12)–C(11)–C(16)	115.0(1)
C(13)–C(12)–C(11)	121.4(1)	C(14)–C(13)–C(12)	121.8(1)
C(13)–C(14)–C(15)	118.4(1)	C(14)–C(15)–C(16)	120.7(1)
C(15)–C(16)–C(11)	122.7(1)		

Table 4. Selected bond lengths (Å) and angles (deg) for $C_{17}H_{21}F_5N_2O$ (**4b**).

C(1)–O(7)	1.276(5)	C(1)–C(2)	1.409(6)
C(1)–C(6)	1.413(7)	C(2)–F(8)	1.364(5)
C(2)–C(3)	1.376(6)	C(3)–F(9)	1.351(5)
C(3)–C(4)	1.376(7)	C(4)–F(10)	1.357(5)
C(4)–C(5)	1.371(7)	C(5)–F(11)	1.349(6)
C(5)–C(6)	1.368(7)	C(6)–F(12)	1.354(5)
C(20)–N(24)	1.324(5)	C(20)–N(21)	1.328(5)
N(21)–C(22)	1.391(5)	C(22)–C(23)	1.356(6)
C(23)–N(24)	1.388(5)		
O(7)–C(1)–C(2)	124.1(4)	O(7)–C(1)–C(6)	123.6(4)
C(2)–C(1)–C(6)	112.3(4)	C(3)–C(2)–C(1)	124.3(4)
C(4)–C(3)–C(2)	120.2(4)	C(5)–C(4)–C(3)	118.2(4)
C(6)–C(5)–C(4)	121.0(4)	C(5)–C(6)–C(1)	123.9(4)

ol-2-ylidene (**2**) was obtained according to a published procedure [9].

*$C_{17}H_{26}N_2O$ (**4a**)*

To a solution containing 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**2**, 0.465 g, 2.58 mmol) in 30 mL of diethyl ether, phenol (**3a**, 0.243 g, 2.58 mmol) was added at −50 °C. After stirring for 12 h at r. t., the precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield after recrystallization from diethyl ether/acetonitrile: 0.670 g (95 %), colorless crystals. – ^{1}H NMR (CD_2Cl_2): δ = 1.58 (d, 12 H, 1,3$_{Im}$-CH*Me*$_2$, ^3J = 6.8 Hz), 2.15 (s, 6 H, 4,5$_{Im}$-Me), 4.41 (sept, 2 H, 1,3$_{Im}$-C*H*Me$_2$),

Table 5. Selected bond lengths (Å) and angles (deg) for $C_{17}H_{21}Cl_5N_2O$ (**4c**).

C(1)–N(2)	1.334(2)	C(1)–N(5)	1.334(2)
N(2)–C(3)	1.386(2)	C(3)–C(4)	1.354(2)
C(4)–N(5)	1.390(2)	C(20)–O(2)	1.263(2)
C(20)–C(25)	1.434(2)	C(20)–C(21)	1.436(2)
C(21)–C(22)	1.384(2)	C(21)–Cl(27)	1.737(2)
C(22)–C(23)	1.393(2)	C(22)–Cl(28)	1.731(2)
C(23)–C(24)	1.399(2)	C(23)–Cl(29)	1.728(2)
C(24)–C(25)	1.385(2)	C(24)–Cl(30)	1.727(2)
C(25)–Cl(31)	1.731(2)		
N(2)–C(1)–N(5)	108.4(2)	C(1)–N(2)–C(3)	108.8(1)
C(4)–C(3)–N(2)	107.2(1)	C(3)–C(4)–N(5)	106.8(1)
C(1)–N(5)–C(4)	108.8(1)	O(26)–C(20)–C(25)	123.6(2)
O(26)–C(20)–C(21)	123.5(2)	C(25)–C(20)–C(21)	112.9(1)
C(22)–C(21)–C(20)	123.7(2)	C(21)–C(22)–C(23)	120.7(2)
C(22)–C(23)–C(24)	118.3(2)	C(25)–C(24)–C(23)	120.8(2)

Table 6. Selected bond lengths (Å) and angles (deg) for $C_{17}H_{26}N_2O$ (**6**)[a].

C(1)–O(5)	1.268(4)	C(1)–C(2)	1.422(4)
C(2)–C(3)	1.371(4)	C(3)–N(4)	1.341(3)
C(10)–N(11)	1.329(2)	N(11)–C(12)	1.387(3)
C(12)–C(12)$^{\#2}$	1.353(4)		
O(5)–C(1)–C(2)	123.5(2)	C(2)–C(1)–C(2)$^{\#2}$	113.0(3)
C(3)–C(2)–C(1)	120.7(3)	N(4)–C(3)–C(2)	126.0(3)
C(3)–N(4)–C(3)$^{\#1}$	113.4(3)		

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x, y, $-z+1/2$; $^{\#2}$ $-x$, y, z.

7.01 – 7.22 (m, 5 H, Ph), 10.58 (s, 1 H, 2_{Im}-H). – ^{13}C NMR (CD_2Cl_2): δ = 7.7 ($4,5_{Im}$-Me), 21.9 ($1,3_{Im}$-CH*Me*$_2$), 50.2 ($1,3_{Im}$-*C*HMe$_2$), 115.6 (C^4_{Ph}), 121.6 ($C^{2,6}_{Ph}$), 124.8 (C^2_{Im}), 128.8 ($C^{3,5}_{Ph}$), 133.2 ($C^{4,5}_{Im}$), 156.2 (C^1_{Ph}). – MS (FAB neg.): *m/z* (%) = 93 (100) [C_6H_5O]. – Elemental analysis for $C_{17}H_{26}N_2O$ (274.40): calcd. C 74.41, H 9.55, N 10.21; found C 75.25, H 10.07, N 10.21.

*$C_{17}H_{21}F_5N_2O$ (**4b**)*

To a solution containing 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**2**, 0.547 g, 3.03 mmol) in 30 mL of diethyl ether, pentafluorophenol (**3b**, 0.560 g, 3.04 mmol) was added at −50 °C. After stirring for 12 h at r. t., the precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield after recrystallization from diethyl ether/acetonitrile: 0.920 g (84 %), colorless crystals. – ^{1}H NMR (CD_3CN): δ = 1.50 (d, 12 H, $1,3_{Im}$-CH*Me*$_2$, ^3J = 6.7 Hz), 2.23 (s, 6 H, $4,5_{Im}$-Me), 4.49 (sept, 2 H, $1,3_{Im}$-C*H*Me$_2$), 9.34 (s, 1 H, 2_{Im}-H). – ^{13}C NMR (CD_3CN): δ = 7.24 ($4,5_{Im}$-Me), 21.4 ($1,3_{Im}$-CH*Me*$_2$), 49.9 ($1,3_{Im}$-*C*HMe$_2$), 137.7 – 142.4 (m, $C^{2,3,4,5,6}_{Ph}$ [10]), 124.8 (C^2_{Im}), 133.2 ($C^{4,5}_{Im}$), 147.6 (t, C^1_{Ph}, ^2J = 14 Hz). – ^{19}F NMR (CD_3CN, CCl_3F ext.): δ = −173.5 (C^4-F), −196.8 ($C^{2,6}$-F), −196.9 ($C^{3,5}$-F). – MS (FAB neg.): *m/z* (%) = 183 (100) [C_6F_5O]. – Elemental analysis for $C_{17}H_{21}F_5N_2O$ (364.35): calcd. C 56.04, H 5.81, N 7.69; found C 55.87, H 5.51, N 7.21.

*$C_{17}H_{21}Cl_5N_2O$ (**4c**)*

To a solution containing 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**2**, 0.560 g, 3.11 mmol) in 30 mL of diethyl ether, pentachlorophenol (**3c**, 0.828 g, 3.10 mmol) was added at −50 °C. After stirring for 12 h at r. t., the precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield after recrystallization from diethyl ether/acetonitrile: 1.27 g (91 %), colorless crystals. – ^{1}H NMR ($CDCl_3$): δ = 1.49 (d, 12 H, $1,3_{Im}$-CH*Me*$_2$, ^3J = 6.8 Hz), 2.15 (s, 6 H, $4,5_{Im}$-Me), 4.41 (sept, 2 H, $1,3_{Im}$-C*H*Me$_2$), 10.37 (s, 1 H, 2_{Im}-H). – ^{13}C NMR ($CDCl_3$): δ = 8.7 ($4,5_{Im}$-Me), 22.4 ($1,3_{Im}$-CH*Me*$_2$), 51.2 ($1,3_{Im}$-*C*HMe$_2$), 115.6 (C^4_{Ph}), 122.1 ($C^{2,6}_{Ph}$), 125.8 (C^2_{Im}), 129.2 ($C^{3,5}_{Ph}$), 134.3 ($C^{4,5}_{Im}$), 161.4 (C^1_{Ph}). – MS (FAB neg.): *m/z* (%) = 265 (100) [C_6Cl_5O]. – Elemental analysis for $C_{17}H_{21}Cl_5N_2O$ (446.62): calcd. C 45.72, H 4.74, N 6.27; found C 45.87, H 4.51, N 6.21.

*$C_{16}H_{25}N_3O$ (**6**)*

To a solution containing 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**2**, 0.680 g, 3.77 mmol) in 30 mL of diethyl ether, 4-hydroxypyridine (**5**, 0.360 g, 3.79 mmol) was added at −50 °C. After stirring for 12 h at r. t., the precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield after recrystallization from diethyl ether/acetonitrile: 0.550 g (55 %), colorless crystals. – ^{1}H NMR (CD_3CN): δ = 1.55 (d, 12 H, $1,3_{Im}$-CH*Me*$_2$, ^3J = 6.7 Hz), 2.22 (s, 6 H, $4,5_{Im}$-Me), 4.48 (sept, 2 H, $1,3_{Im}$-C*H*Me$_2$), 6.00 – 7.64 (m, 4 H, C_6H_4NO), 9.86 (s, 1 H, 2_{Im}-H). – ^{13}C NMR (CD_3CN): δ = 7.3 ($4,5_{Im}$-Me), 21.5 ($1,3_{Im}$-CH*Me*$_2$), 49.8 ($1,3_{Im}$-*C*HMe$_2$), 116.2 ($C^{3,5}_{Py}$), 125.7 (C^2_{Im}), 131.8 ($C^{4,5}_{Im}$), 148.9 ($C^{2,6}_{Py}$), 176.0 (C^4_{Py}). – MS (FAB neg.): *m/z* (%) = 94 (100) [C_5H_4NO]. – Elemental analysis for $C_{16}H_{25}N_3O$ (275.39): calcd. C 69.78, H 9.15, N 15.26; found C 67.77, H 9.63, N 14.77.

CCDC 721443 (**4b**), CCDC 721444 (**4c**), CCDC 721445 (**6**), and CCDC 721446 (**4a**) contain the supplementary crystallographic data for his paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[1] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, **1999**.
[2] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772; J. Dupont, R. F. De Souza, P. A. Z. Suarez, *Chem. Rev*. **2002**, *102*, 3667.
[3] A. J. Arduengo, III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc*. **1991**, *113*, 361; A. J. Arduengo, III, H. V. R. Diaz, R. L. Harlow, M. Kline, *J. Am. Chem. Soc*. **1992**, *114*, 5530.
[4] J. A. Cowan, J. A. C. Clyburn, M. G. Davidson, R. L. W. Harris, J. A. K. Howard, P. Küpper, M. A. Leech, S. P. Richards, *Angew. Chem*. **2002**, *114*, 1490; *Angew. Chem. Int. Ed.* **2002**, *41*, 1432.
[5] N. Kuhn, A. Al-Sheikh, *Coord. Chem. Rev*. **2005**, *249*, 829.
[6] N. Kuhn, M. Richter, M. Steimann, M. Ströbele, K. Sweidan, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2054; N. Kuhn, M. Steimann, K. Sweidan, *Z. Naturforsch.* **2005**, *60b*, 123; N. Kuhn, A. Abu-Rayyan, H.-J. Kolb, M. Ströbele, *Z. Anorg. Allg. Chem*. **2005**, *631*, 914.
[7] N. Kuhn, C. Maichle-Mößmer, E. Niquet, M. Steimann, K. Sweidan, *Z. Naturforsch*. **2005**, *60b*, 715; N. Kuhn, C. Maichle-Mößmer, M. Steimann, K. Sweidan, *Z. Naturforsch*. **2007**, *62b*, 101; A. Abu-Rayyan, Q. Abu-Salem, N. Kuhn, C. Maichle-Mößmer, M. Steimann, G. Henkel, *Z. Anorg. Allg. Chem*. **2008**, *634*, 823.
[8] N. Kuhn, A. Abu-Rayyan, Q. Abu-Salem, C. Maichle-Mößmer, E. Mallah, M. Steimann, *Z. Naturforsch*. **2008**, *63b*, 1015; A. Abu-Rayyan, Q. Abu-Salem, E. Mallah, C. Maichle-Mößmer, M. Steimann, N. Kuhn, K.-P. Zeller, *Z. Naturforsch*. **2008**, *63b*, 1438; K. Sweidan, N. Kuhn, C. Maichle-Mößmer, M. Steimann, *Z. Kristallogr., New Crystal Structures*, in print.
[9] N. Kuhn, Th. Kratz, *Synthesis* **1993**, 561.
[10] For a detailed discussion of ^{13}C NMR shifts and ^{13}C,^{19}F coupling constants in pentafluorophenol see V. Wray, *J. Chem. Soc., Perkin 2 Trans*. **1978**, 855.
[11] For a detailed discussion of the hydroxypyridine/pyridone tautomerism see M. Freitag, P. G. Jones, *Acta Crystallogr*. **1999**, *C55*, 1682; K. Wijaya, O. Moers, A. Blaschette, P. G. Jones, *Z. Naturforsch*. **1999**, *54b*, 912.
[12] P. G. Jones, *Acta Crystallogr*. **2001**, *C57*, 880.
[13] C. C. Evans, M. Bagieu-Beucher, R. Masse, J.-F. Nicoud, *Chem. Mater*. **1998**, *10*, 847.