DOI: 10.1002/ejoc.200900020

Synthesis and Solid-State Structure of Tetrabutylammonium Imidazolate–Dipyrrole Formed by Self Assembly

Manfred T. Reetz,*[a] H. Martin Herzog,[a] and Richard Goddard[a]

Dedicated to Professor Alain Krief

Keywords: Anions / Heterocycles / Hydrogen bonds / Self-assembly

The reaction of imidazole with an excess of pyrrole in the presence of tetrabutylammonium hydroxide affords, in high yield by a self-assembly process, tetrabutylammonium imidazolate–dipyrrole, as shown by an X-ray structure analysis. The two pyrroles form hydrogen bonds with the two nitrogen atoms of the imidazole anion, and the tetrabutylammonium counterion also forms hydrogen bonds to the same nitrogen atoms, with the formation of a structurally unique supramolecular compound.

Introduction

For many decades metal-free carbanions with tetraalkylammonium counterions, which serve as reagents for a variety of reaction types, were considered to be "naked" anions,[1] in contrast to traditional compounds such as organolithium or Grignard reagents. However, in a series of papers describing the X-ray structure of such reagents, we demonstrated that this is not the case.[2] Rather, the α-methylene units of the tetraalkylammonium cations form strong hydrogen bonds to the negatively charged atoms of the carbanions, and, in most cases, supramolecular dimeric species are involved. Indeed, quantum mechanical calculations of the tetramethylammonium cation, $(CH_3)_4N^+$, clearly indicate that the positive charge is not localized on the N atom as organic chemists usually write, but is in fact delocalized over the four C atoms and the 12 H atoms, and the nitrogen is essentially neutral.[2f] Along these lines, it is interesting to point out that ab initio calculations of a complex between $(CH_3)_4N^+$ and a *neutral* compound, namely benzene, suggest strong binding forces arising from charge-quadruple and charge-polarizibility,[3a] as later postulated in certain peptides,[3b] and that $Ph_3P^+CH_3$ forms hydrogen bonds to furan in clathrates.[3c]

We have reported the solid-state structures of a number of metal-free carbanions, including tetrabutylammonium salts of CH-acidic compounds such as malonic acid diesters,[2a] nitriles,[2a,2b] lactones,[2c] ketones,[2d] 2-nitropropane,[2e] sulfones,[2f] and even 9-ethylfluorene.[2e] The only compound that comes close to being truly "naked" is the tetrabutylammonium salt of cyclopentadiene.[2e] The X-ray structure of a phenyl-stabilized trifluoromethylsulfonyl carbanion with a tetrabutylammonium counterion was reported to involve very weak anion–cation interactions (C–H···O).[4] In recent years, the chemistry of these reagents has been expanded to include new metal-free carbanions and their use in a variety of applications such as Michael additions, alkylations, and aza-Henry reactions,[5] many under the conditions of phase-transfer catalysis.[5f–5h,6,7] Tetraalkylphosphonium salts of such carbanions have also been reported,[5i] although X-ray structural studies appear to be rare.[1k] Tetraalkylammonium halides,[8] sulfides[9] and even complex anions such $[FeCl_4]^-[nBu_4N]^+$[10] constitute ion pairs, which interact with one another through hydrogen bonds. Strong hydrogen-bond networks also exist in the case of nitrogen-centered anions, as in the case of the carbazolide anion, which was shown to interact with the tetrabutylammonium counterion.[11] Structural knowledge of all of these compounds is important in its own right, especially with a focus on different types of hydrogen bonding,[12] but it is also important when attempting to understand asymmetric phase-transfer catalysis[5f–5i,6,7] and various types of metal-free anionic polymerization.[9,13,14]

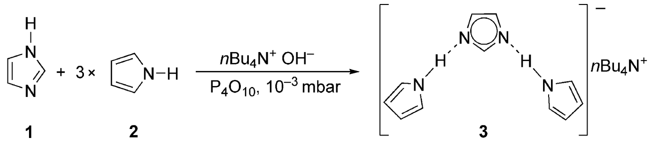
Interestingly, if a potential proton donor is included in the anionic system, which results in the formation of strong H-bonds as in the case of the phenolate/phenol pair, hydrogen bonding still occurs with the tetrabutylammonium counterions.[15] Here we describe the synthesis and crystal structure of tetrabutylammonium imidazolate, which is

---

[a] Max-Planck-Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz 1, 45470 Mülheim/Ruhr, Germany
Fax: +49-208-306-2985
E-mail: Reetz@mpi-muelheim.mpg.de

Supporting information for this article is available on the WWW under http://www.eurjoc.org/ or from the author.

doubly stabilized as a result of two hydrogen bonds originating from two neutral pyrrole molecules by way of self assembly. As will be demonstrated, this complex anionic species is further stabilized by hydrogen bonds with the tetrabutylammonium counterion, which leads to the structurally unusual supramolecular compound **3** (Scheme 1).



Scheme 1. Preparation of tetrabutylammonium imidazolate–dipyrrole **3**.

Results and Discussion

Reaction of a mixture of imidazole (**1**) and excess pyrrole (**2**) in THF with a solution of tetrabutylammonium hydroxide in methanol, followed by removal of the solvent and drying under vacuum in the presence of P_2O_5, resulted in a solid material in essentially quantitative yield. The material was dissolved in DMF and recrystallized at –20 °C, which provided colorless crystals in 73% yield. These proved to be suitable for an X-ray structure analysis. The triclinic unit cell contains two crystallographically independent structures of **3**, which we label here as molecules I and II. The structures are shown in Figures 1 and 2, respectively.

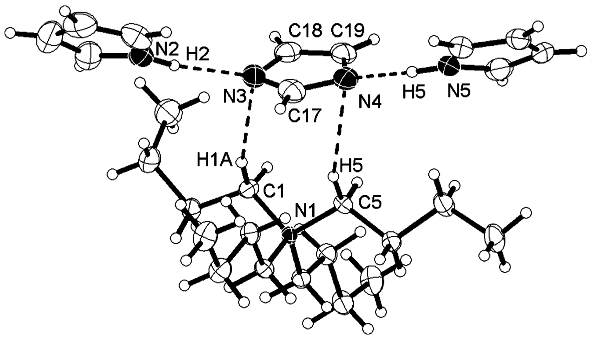


Figure 1. Crystal structure of compound **3** featuring molecule I in the unit cell.

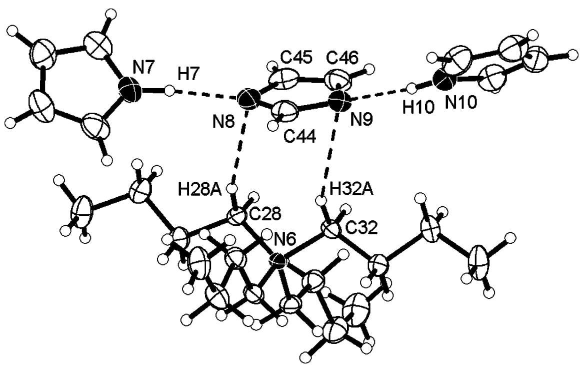


Figure 2. Crystal structure of compound **3** featuring molecule II in the unit cell.

Inspection of Figures 1 and 2 reveals that independent molecules I and II are quite similar because, in both cases, the imidazolate anion is stabilized by two neutral pyrrole units through H-bonds formed with its two N atoms. It is instructive to focus on some of the bond lengths and angles involved in the hydrogen bonding of molecules I and II (Tables 1 and 2, respectively). The N–H···N bond lengths, with a mean value of 2.84(2) Å (N···N), lie at the shorter end of the range observed for hydrogen bonds involving solely nitrogen,[16] and the N–H···N angles are close to the ideal value of 180°. The N–H bonds of the pyrrole rings therefore point towards the nitrogen atoms of the imidazolate anion. The only significant difference between molecules I and II is the orientation of the two stabilizing pyrroles. In molecule I, the two pyrrole units are essentially coplanar (angle between mean planes: 15°), whereas in molecule II they are almost perpendicular to one another (79°). This can be explained in terms of crystal packing forces, which cause the pyrrole rings to rotate about the N–H···N bonds.

Table 1. Selected distances and angles in **3** (molecule I) involved in H-bonding.

Atoms	Distance [Å] or angle [°]
N2···N3	2.835(2)
N2–H2	0.91(3)
H2···N3	1.94(3)
N2–H2···N3	166(1)
N4···N5	2.813(2)
N4···H5	1.91(3)
H5–N5	0.93(2)
N4···H5–N5	164(1)

Table 2. Selected distances and angles in **3** (molecule II) involved in H-bonding.

Atoms	Distance [Å] or angle [°]
N7···N8	2.831(3)
N7–H7	0.94(3)
H7···N8	1.90(3)
N7–H7···N8	173(1)
N9···N10	2.866(2)
N9···H10	2.01(3)
H10–N10	0.87(2)
N9···H10–N10	170(1)

The orientation of the anion with respect to the cation is also essentially identical in both cases; hydrogen bonds between two α-methylene units of the tetrabutylammonium counterion and the two N atoms of imidazolate provide further stabilization. The measured N···C distances in the case of molecule I are: N3···C1 3.578(2) Å and N4···C5 3.669(2) Å. In molecule II they are: N8···C28 3.575(2) Å and N9···C32 3.662(2) Å, which in addition to the almost linear N···H–C arrangement [163(1)°, 155(1)°, 162(1)°, and 148(1)°, respectively], clearly indicate the presence of hydrogen bonds between the anion and cation.

As already pointed out, this latter type of interaction is typical of tetraalkylammonium salts of CH- and NH-acidic compounds.[2,11] Thus, N···H–C–N stabilized cation–anion interaction is in operation here, even though the imidazolate anion is already stabilized by two neutral molecules of pyrrole.[17]

Conclusions

Reaction of a THF solution of imidazole (**1**) and excess pyrrole (**2**) with a methanol solution of tetrabutylammonium hydroxide, followed by removal of the solvent, led to a self assembly process that resulted in the formation of the unique compound, tetrabutylammonium imidazolate–dipyrrole **3**, which was analyzed by X-ray structure analysis. It proves to be a supramolecular compound in which the imidazolate anion is stabilized by hydrogen bonds originating from the two other "partners", namely the two pyrrole units. In spite of these interactions, further hydrogen bonds between the α-methylene units of the tetrabutylammonium cations and the two N atoms of imidazolate contribute to the overall stabilization.

Experimental Section

Preparation of Tetrabutylammonium imidazolate–dipyrrole 3: A mixture of imidazole (**1**) (335 mg, 5 mmol) and pyrrole (**2**) (1 g, 15 mmol) in THF (5 mL) was treated with a methanol solution of tetrabutylammonim hydroxide (5 mL of a 1 M solution) (Aldrich). Subsequently, the solvent was removed at 10^{-3} mbar. The solid was placed in a desiccator containing P_2O_5 and kept there under vacuum for 72 h. The solid was taken up in a small amount of DMF and slowly cooled to –20 °C. After 40 h, colorless crystals (1.6 g, 73% yield) were collected and used for the X-ray structure analysis.

Supporting Information (see footnote on the first page of this article): Structural data of compound **3** are presented.

CCDC-715557 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Fonds der Chemischen Industrie (FCI).

---

[1] a) J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed., Wiley, New York, **1992**, p. 464; b) W. Schlenk, J. Holtz, *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 603–608; c) G. Wittig, M. Heintzeler, M.-H. Wetterling, *Justus Liebigs Ann. Chem.* **1949**, *557*, 201–205; d) T. E. Hogen-Esch, J. Smid, *J. Am. Chem. Soc.* **1966**, *88*, 307–318; e) W. J. Middleton, E. L. Little, D. D. Cottman, V. A. Engelhardt, *J. Am. Chem. Soc.* **1958**, *80*, 2795–2806; f) E. B. Troughton, K. E. Molter, E. M. Arnett, *J. Am. Chem. Soc.* **1984**, *106*, 6726–6735; g) M. Makosza, *Tetrahedron Lett.* **1969**, *10*, 673–678; h) S. D. Barker, R. K. Norris, *Aust. J. Chem.* **1983**, *36*, 81–95; i) R. Noyori, I. Nishida, J. Sakata, *J. Am. Chem. Soc.* **1983**, *105*, 1598–1600; j) A. Brändström, U. Junggren, *Acta Chem. Scand.* **1971**, *25*, 1469–1470; k) K. D. Scherfise, F. Weller, K. Dehnicke, *Z. Naturforsch. Teil B: Chem. Sci.* **1985**, *40*, 906–912.

[2] a) M. T. Reetz, S. Hütte, R. Goddard, *J. Am. Chem. Soc.* **1993**, *115*, 9339–9340; b) M. T. Reetz, S. Hütte, R. Goddard, *J. Prakt. Chem.* **1999**, *341*, 297–301; c) R. Goddard, S. Hütte, M. T. Reetz, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *56*, 878–880; d) M. T. Reetz, S. Hütte, R. Goddard, C. Robyr, *Chem. Eur. J.* **1996**, *2*, 382–384; e) M. T. Reetz, S. Hütte, R. Goddard, *Z. Naturforsch. Teil B: Chem. Sci.* **1995**, *50*, 415–422; f) M. T. Reetz, S. Hütte, R. Goddard, *Eur. J. Org. Chem.* **1999**, 2475–2478.

[3] a) K. S. Kim, J. Y. Lee, S. J. Lee, T.-K. Ha, D. H. Kim, *J. Am. Chem. Soc.* **1994**, *116*, 7399–7400; b) D. Barbaras, K. Gademann, *ChemBioChem* **2008**, *9*, 2398–2401; c) R. Hunter, R. H. Haueisen, A. Irving, *Angew. Chem.* **1994**, *106*, 588–591; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 566–568.

[4] H.-J. Gais, G. Hellmann, J. J. Lindner, *Angew. Chem.* **1990**, *102*, 96–99; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 100–103.

[5] Recent examples of the use of metal-free carbanions in synthesis or in mechanistic studies: a) Y. Tanaka, M. Arakawa, Y. Yamaguchi, C. Hori, M. Ueno, T. Tanaka, T. Imahori, Y. Kondo, *Chem. Asian J.* **2006**, *1*, 581–585; b) K. J. Kolonko, H. J. Reich, *J. Am. Chem. Soc.* **2008**, *130*, 9668–9669; c) M. M. Biddle, H. J. Reich, *J. Org. Chem.* **2006**, *71*, 4031–4039; d) T. Murai, S. Hayakawa, S. Kato, *J. Org. Chem.* **2001**, *66*, 8101–8105; e) T. Lemek, H. Mayr, *J. Org. Chem.* **2003**, *68*, 6880–6886; f) K. R. Knudsen, C. E. T. Mitchell, S. V. Ley, *Chem. Commun. (Cambridge, U.K.)* **2006**, 66–68; g) T. Ohshima, T. Shibuguchi, Y. Fukuta, M. Shibasaki, *Tetrahedron* **2004**, *60*, 7743–7754; h) E. Gomez-Bengoa, A. Linden, R. López, I. Múgica-Mendiola, M. Oiarbide, C. Palomo, *J. Am. Chem. Soc.* **2008**, *130*, 7955–7966; i) R. He, X. Wang, T. Hashimoto, K. Maruoka, *Angew. Chem.* **2008**, *120*, 9608–9610; *Angew. Chem. Int. Ed.* **2008**, *47*, 9466–9468.

[6] X-ray structure of a cinchona-based quaternary ammonium *p*-nitrophenolate as a model for an enolate in asymmetric phase-transfer catalysis: a) E. J. Corey, F. Xu, M. C. Noe, *J. Am. Chem. Soc.* **1997**, *119*, 12414–12415; Computational study of key interactions in asymmetric phase-transfer catalyzed Michael additions: b) C. E. Cannizarro, K. N. Houk, *J. Am. Chem. Soc.* **2002**, *124*, 7163–7169.

[7] Recent reviews of asymmetric phase-transfer catalysis: a) T. Hashimoto, K. Maruoka, *Chem. Rev.* **2007**, *107*, 5656–5682; b) M. J. O'Donnell, *Acc. Chem. Res.* **2004**, *37*, 506–517; c) M. J. Gaunt, C. C. C. Johansson, *Chem. Rev.* **2007**, *107*, 5596–5605.

[8] The X-ray structure of tetrabutylammonium bromide reveals strong hydrogen bonds between anion and cation: K. Harms, M. T. Reetz, unpublished results, University of Marburg, **1990**.

[9] a) M. T. Reetz, R. Ostarek, *Chem. Commun. (Cambridge, U. K.)* **1988**, 213–215; b) M. T. Reetz, *Angew. Chem.* **1988**, *100*, 1026–1030; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 994–998.

[10] F. Jian, P. Sun, H. Xiao, *Asian J. Chem.* **2007**, *19*, 1137–1140.

[11] M. T. Reetz, S. Hütte, R. Goddard, U. Minet, *J. Chem. Soc., Chem. Commun.* **1995**, 275–277.

[12] a) G. R. Desiraju, *Acc. Chem. Res.* **2002**, *35*, 565–573; b) T. Steiner, *Angew. Chem.* **2002**, *114*, 50–80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76; c) R. K. Castellano, *Curr. Org. Chem.* **2004**, *8*, 845–865.

[13] a) M. T. Reetz, T. Knauf, U. Minet, C. Bingel, *Angew. Chem.* **1988**, *100*, 1422–1424; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1373–1374; b) M. T. Reetz, S. Hütte, R. Goddard, *J. Phys. Org. Chem.* **1995**, *8*, 231–241.

[14] Select examples of metal-free anionic polymerization:[9,13] a) D. J. A. Raj, P. P. Wadgaonkar, S. Sivaram, *Macromolecules* **1992**, *25*, 2774–2776; b) L. C. Kagumba, J. Pnelle, *Macromolecules* **2005**, *38*, 4588–4594; c) N. E. Kamber, W. Jeong, R. M. Waymouth, *Chem. Rev.* **2007**, *107*, 5813–5840.

[15] R. Goddard, H. M. Herzog, M. T. Reetz, *Tetrahedron* **2002**, *58*, 7847–7850.

[16] Typical range: 2.88–3.38 Å. See: G. A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer-Verlag, Berlin Heidelberg, **1991**, p. 29.

[17] *Note added after refereeing (February 4, 2009)*: One of the referees pointed out that one could say that the complex is com-

posed of one imidazolium cation and two pyrrole anions and that recently the imidazolium cation has widely been investigated as a very promising cation for diverse anion recognitions.[18–20] In view of the difference in the pK_a values of imidazole (18.6[21] in DMSO) and pyrrole (23.0[22] in DMSO) and the results of the X-ray analysis, we prefer to think that imidazole is preferentially deprotonated here, but these examples illustrate the amphoteric nature of imidazole.

[18] H. Ihm, S. Yun, H. G. Kim, J. K. Kim, K. S. Kim, *Org. Lett.* **2002**, *4*, 2897–2900.

[19] K. Chellappan, N. J. Singh, I.-C. Hwang, J. W. Lee, K. S. Kim, *Angew. Chem.* **2005**, *117*, 2959–2963; *Angew. Chem. Int. Ed.* **2005**, *44*, 2899–903.

[20] J. Yoon, S. K. Kim, N. J. Singh, K. S. Kim, *Chem. Soc. Rev.* **2006**, *35*, 355–360.

[21] F. G. Bordwell, *Acc. Chem. Res.* **1988**, *21*, 456–463.

[22] F. G. Bordwell, G. E. Drucker, H. E. Fried, *J. Org. Chem.* **1981**, *46*, 632–635.

Received: January 9, 2009